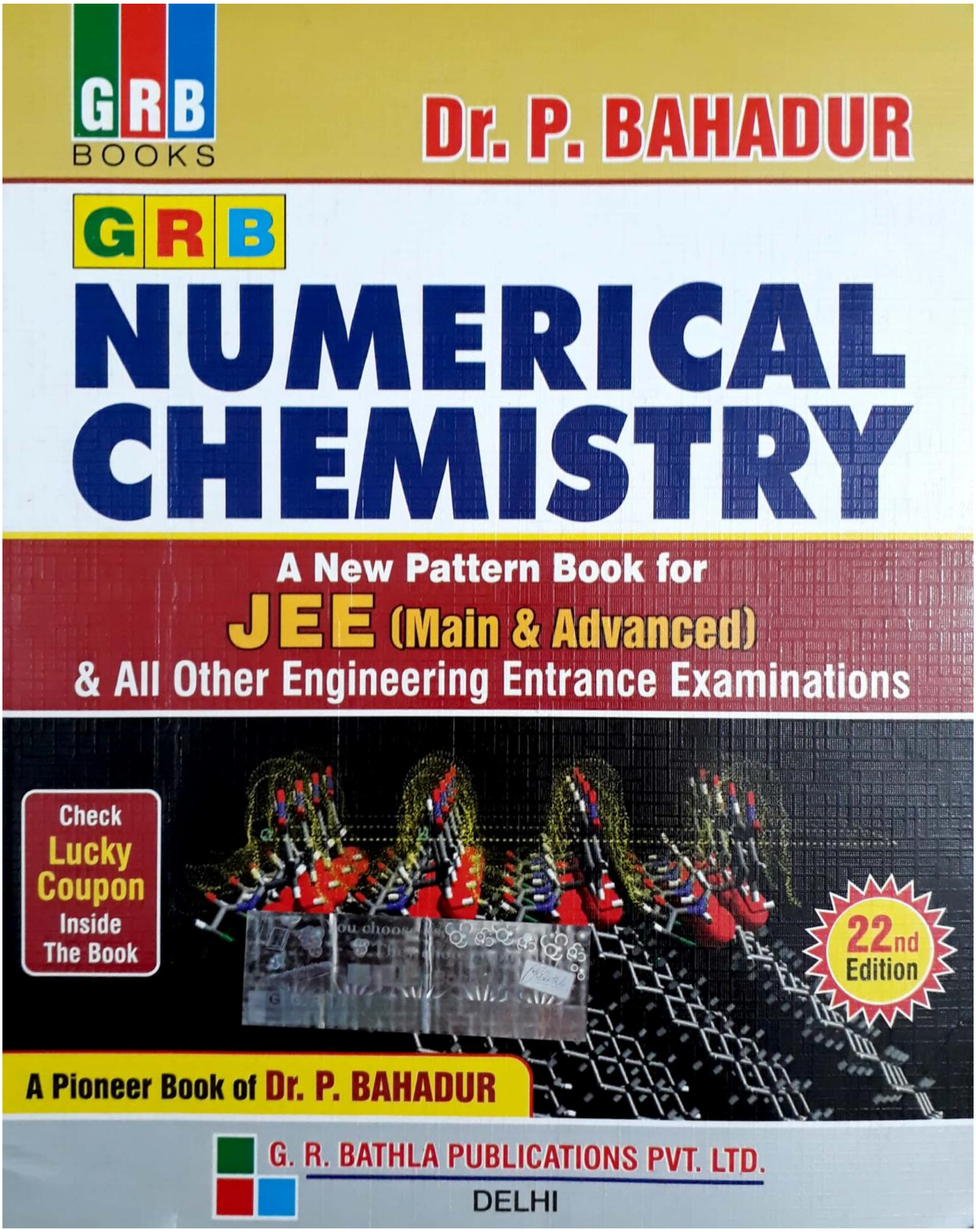

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Dr. P. BAHADUR

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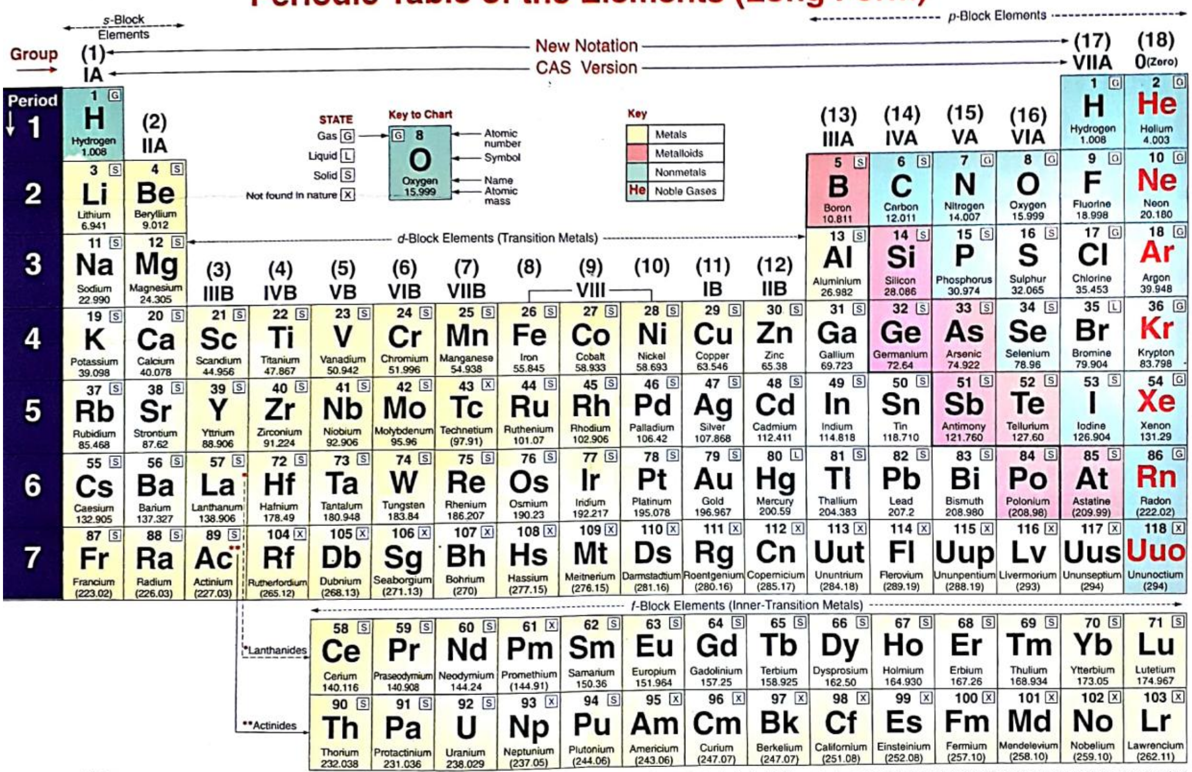
Periodic Table of the Elements (Long Form)



s-Block Elements

p-Block Elements

d-Block Elements (Transition Metals)

f-Block Elements (Inner-Transition Metals)

Group →

New Notation: (1) … (17) (18)

CAS Version: IA … VIIA 0(Zero)

STATE

Gas G

Liquid L

Solid S

Not found in nature X

Key to Chart

G 8 – Atomic number

O – Symbol

Oxygen – Name

15.999 – Atomic mass

Key

🟨	Metals
🟥	Metalloids
🟦	Nonmetals
He	Noble Gases

Period ↓	(1) IA	(2) IIA	(3) IIIB	(4) IVB	(5) VB	(6) VIB	(7) VIIB	(8)	(9) VIII	(10)	(11) IB	(12) IIB	(13) IIIA	(14) IVA	(15) VA	(16) VIA	(17) VIIA	(18) 0(Zero)
1	1 G H Hydrogen 1.008																1 G H Hydrogen 1.008	2 G He Helium 4.003
2	3 S Li Lithium 6.941	4 S Be Beryllium 9.012											5 S B Boron 10.811	6 S C Carbon 12.011	7 G N Nitrogen 14.007	8 G O Oxygen 15.999	9 G F Fluorine 18.998	10 G Ne Neon 20.180
3	11 S Na Sodium 22.990	12 S Mg Magnesium 24.305											13 S Al Aluminium 26.982	14 S Si Silicon 28.086	15 S P Phosphorus 30.974	16 S S Sulphur 32.065	17 G Cl Chlorine 35.453	18 G Ar Argon 39.948
4	19 S K Potassium 39.098	20 S Ca Calcium 40.078	21 S Sc Scandium 44.956	22 S Ti Titanium 47.867	23 S V Vanadium 50.942	24 S Cr Chromium 51.996	25 S Mn Manganese 54.938	26 S Fe Iron 55.845	27 S Co Cobalt 58.933	28 S Ni Nickel 58.693	29 S Cu Copper 63.546	30 S Zn Zinc 65.38	31 S Ga Gallium 69.723	32 S Ge Germanium 72.64	33 S As Arsenic 74.922	34 S Se Selenium 78.96	35 L Br Bromine 79.904	36 G Kr Krypton 83.798
5	37 S Rb Rubidium 85.468	38 S Sr Strontium 87.62	39 S Y Yttrium 88.906	40 S Zr Zirconium 91.224	41 S Nb Niobium 92.906	42 S Mo Molybdenum 95.96	43 X Tc Technetium (97.91)	44 S Ru Ruthenium 101.07	45 S Rh Rhodium 102.906	46 S Pd Palladium 106.42	47 S Ag Silver 107.868	48 S Cd Cadmium 112.411	49 S In Indium 114.818	50 S Sn Tin 118.710	51 S Sb Antimony 121.760	52 S Te Tellurium 127.60	53 S I Iodine 126.904	54 G Xe Xenon 131.29
6	55 S Cs Caesium 132.905	56 S Ba Barium 137.327	57 S La* Lanthanum 138.906	72 S Hf Hafnium 178.49	73 S Ta Tantalum 180.948	74 S W Tungsten 183.84	75 S Re Rhenium 186.207	76 S Os Osmium 190.23	77 S Ir Iridium 192.217	78 S Pt Platinum 195.078	79 S Au Gold 196.967	80 L Hg Mercury 200.59	81 S Tl Thallium 204.383	82 S Pb Lead 207.2	83 S Bi Bismuth 208.980	84 S Po Polonium (208.98)	85 S At Astatine (209.99)	86 G Rn Radon (222.02)
7	87 S Fr Francium (223.02)	88 S Ra Radium (226.03)	89 S Ac** Actinium (227.03)	104 X Rf Rutherfordium (265.12)	105 X Db Dubnium (268.13)	106 X Sg Seaborgium (271.13)	107 X Bh Bohrium (270)	108 X Hs Hassium (277.15)	109 X Mt Meitnerium (276.15)	110 X Ds Darmstadtium (281.16)	111 X Rg Roentgenium (280.16)	112 X Cn Copernicium (285.17)	113 X Uut Ununtrium (284.18)	114 X Fl Flerovium (289.19)	115 X Uup Ununpentium (288.19)	116 X Lv Livermorium (293)	117 X Uus Ununseptium (294)	118 X Uuo Ununoctium (294)

f-Block Elements (Inner-Transition Metals)

*Lanthanides	58 S Ce Cerium 140.116	59 S Pr Praseodymium 140.908	60 S Nd Neodymium 144.24	61 X Pm Promethium (144.91)	62 S Sm Samarium 150.36	63 S Eu Europium 151.964	64 S Gd Gadolinium 157.25	65 S Tb Terbium 158.925	66 S Dy Dysprosium 162.50	67 S Ho Holmium 164.930	68 S Er Erbium 167.26	69 S Tm Thulium 168.934	70 S Yb Ytterbium 173.05	71 S Lu Lutetium 174.967
**Actinides	90 S Th Thorium 232.038	91 S Pa Protactinium 231.036	92 S U Uranium 238.029	93 X Np Neptunium (237.05)	94 S Pu Plutonium (244.06)	95 X Am Americium (243.06)	96 X Cm Curium (247.07)	97 X Bk Berkelium (247.07)	98 X Cf Californium (251.08)	99 X Es Einsteinium (252.08)	100 X Fm Fermium (257.10)	101 X Md Mendelevium (258.10)	102 X No Nobelium (259.10)	103 X Lr Lawrencium (262.11)

Note : (1) The new IUPAC format numbers the groups from 1 to 18. The previous IUPAC numbering system and the system used by Chemical Abstracts Service (CAS) are also shown. For radioactive elements that do not occur in nature, the mass number of the most stable isotope is given in brackets with the longest half-life.

(2) The symbols for elements 104 to 112, 114 and 116 used in this table are those approved and 113, 115, 117 and 118 proposed by IUPAC.

(3) There is no general agreement on the metalloids. Almost every list includes Si, Ge, As, Sb and Te but some also include B, At and Po in the list.

GRB

NUMERICAL CHEMISTRY

For JEE (Main & Advanced)
& All Other Engineering Entrance Examinations

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1

Gaseous State

THE GAS LAWS

Various gas laws were given from time to time to explain the behaviour of gases.

1. Boyle's law : The volume of given mass of a gas is inversely proportional to pressure at constant temperature.

$$V \propto \frac{1}{P} \qquad \text{(at constant mass and } T\text{)}$$

or $$PV = \text{constant} \qquad ...(1)$$

2. Charles' law : The volume of given mass of a gas is directly proportional to absolute temperature at constant pressure.

$$V \propto T \qquad \text{(at constant mass and } P\text{)}$$

or $$\frac{V}{T} = \text{constant} \qquad ...(2)$$

(Gay-Lussac's law)

3. Pressure-temperature law : The pressure of a given mass of a gas is directly proportional to temperature at constant volume.

$$P \propto T \qquad \text{(at constant mass and } V\text{)}$$

or $$\frac{P}{T} = \text{constant} \qquad ...(3)$$

4. The Gas equation :

$$PV = RT \qquad \text{(for one mole gas)} \quad ...(4)$$

and $$PV = nRT \qquad \text{(for } n \text{ mole gas)} \quad ...(5)$$

$\therefore$ $$PV = \frac{w}{M}RT \qquad \left(\because n = \frac{w}{M}\right) \quad ...(6)$$

where, R is molar gas constant, w is mass of gas and M is molar mass of gas.

5. Physical significance of R and its values in different units:

For 1 mole of an ideal gas

$$R = \frac{PV}{T} = \frac{\text{Pressure} \times \text{Volume}}{\text{Temperature}}$$

$$= \frac{(\text{Force / Area}) \times (\text{Area} \times \text{Length})}{\text{Temperature}} = \frac{\text{Force} \times \text{Length}}{\text{Temperature}}$$

Thus, R represents work done per degree per mol. The values of R may be calculated in different units.

Since, 1 mole of any gas at NTP (273 K and 1 atm) occupies 22.4 litre.

$$R = \frac{1 \times 22.4}{273} = 0.0821 \text{ lit-atm per degree per mol}$$

To calculate R in CGS unit,

$n = 1$ mole,

$P = 1 \text{ atm} = 76 \text{cm}$

$\text{Hg} = 76 \times 13.6 \times 981 \text{ dyne /cm}^2$

$V = 22400 \text{ cc}, \quad T = 273 \text{ K}$

$$R = \frac{76 \times 13.6 \times 981 \times 22400}{273}$$

$$= 8.314 \times 10^7 \text{ erg degree}^{-1} \text{mol}^{-1}$$

NOTE : (i) While solving the numericals one should keep in mind proper units.

	Litre atmosphere	**CGS**	**MKS**
P	atm	dyne cm^{-2}	Nm^{-2} or Pa
V	litre	cm^3 or mL	m^3
w	g	g	kg
M	g	g	kg
R	0.821 litre - atm $\text{K}^{-1}\text{mol}^{-1}$	8.314×10^7 erg $\text{K}^{-1}\text{mol}^{-1}$	8.314 J K^{-1} mol^{-1}
T	Kelvin	Kelvin	Kelvin

The other values of $R = 2 \text{ calorie K}^{-1} \text{ mol}^{-1}$

$= 2 \times 10^{-3} \text{ kcal K}^{-1} \text{ mol}^{-1}$

$= 5.18976 \times 10^{19} \text{ eV K}^{-1} \text{ mol}^{-1}$

$= 8.314 \text{ m}^3\text{Pa K}^{-1}\text{mol}^{-1} \text{ or kPa dm}^3\text{K}^{-1}\text{mol}^{-1}$

$= 82.06 \text{ atm cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$

$= 62.36 \text{ litre torr K}^{-1} \text{ mol}^{-1}$

$= 2783 \text{ feet poundal K}^{-1} \text{ mol}^{-1}$

(ii) Standard ambient temperature and pressure (SATP) represents $P = 1$ bar $= 0.987 \text{ atm} = 10^5$ Pa and $T = 25° \text{C}$.

(iii) Volume of 1 mole gas at 1 bar and 0° C is 22.71 litre.

(iv) Volume of 1 mole gas at STP.

(v) Volume of 1 mole gas at SATP is 24.79 litre.

(vi) Isothermal compressibility constant for an ideal gas,

$$\text{'}\beta\text{'} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{n,\,T} = \frac{1}{P}$$

(vii) Thermal expansion coefficient of an ideal gas,

$$\text{'}\alpha\text{'} = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{P,\,n} = \frac{1}{T}$$

6. NTP or STP : NTP is referred as normal temperature and pressure.

STP is referred as standard temperature and pressure.

Both represent the state when

$P = 1$ atm $= 76$ cm, Hg $= 760$ mm, Hg $= 760$ torr

$= 101325$ Pascal $= 0.987$ bar

$T = 0°\text{C} = 273.14\text{ K} \approx 273\text{ K}$

7. Dalton's law of partial pressure : The pressure exerted by a gaseous mixture (P_M) is equal to the sum of partial pressure of each component present in mixture, *i.e.*,

$$P_M = P'_A + P'_B + P'_C + \ldots \qquad \ldots(7)$$

where, $P'_A, P'_B \ldots$ are partial pressures of each component in the mixture, defined as the pressure which it would exert if same amount is filled alone in the same container at same temperature. **The law is valid only for gases which do not combine with each other under normal conditions.**

Let n_A mole of A, n_B mole of B... be filled in a container of volume V at temperature T, then

$$P_M = (n_A + n_B + n_C + \ldots)\frac{RT}{V} \qquad \ldots(8)$$

Also, $$P'_A = n_A\frac{RT}{V} \qquad \ldots(9)$$

$$\therefore \quad \frac{P'_A}{P_M} = \frac{n_A}{n_A + n_B + n_C + \ldots} \qquad \ldots(10)$$

or $\quad P'_A = P_M \times$ mole fraction of A in mixture

or $\quad \boldsymbol{P' = P_M \times}$ **mole fraction of component in mixture** $\quad \ldots(11)$

NOTE : 1. Saturated vapours do not obey gas laws except Dalton's law of partial pressure, *i.e.*,

$$P_{\text{moist gas}} = P_{\text{dry gas}} + P_{\text{water vapour}}$$

$$P_{\text{dry gas}} = P_{\text{moist gas}} - P_{\text{water vapour}}$$

$$= P_{\text{moist gas}} - \text{aqueous tension}$$

2. Aqueous tension remains constant at constant temperature.

3. Relative humidity

$$= \frac{\text{Mass of } H_2O_{(v)} \text{ in air}}{\text{Mass of } H_2O_{(v)} \text{ required to saturate air}}$$

8. Graham's law of diffusion : The rate of diffusion (r) of a gas at constant temperature is directly proportional to its pressure as well as inversely proportional to square root of its vapour density or molar mass.

$$\therefore \quad r \propto P \quad \text{and} \quad r \propto \frac{1}{\sqrt{M}}$$

or $$r \propto \frac{P}{\sqrt{M}} \quad \text{(at constant temperature)}$$

For gas I $\qquad r_1 \propto \dfrac{P_1}{\sqrt{M_1}}$

For gas II $\qquad r_2 \propto \dfrac{P_2}{\sqrt{M_2}}$

$$\therefore \quad \frac{r_1}{r_2} = \frac{P_1}{P_2} \times \sqrt{\left(\frac{M_2}{M_1}\right)} \quad \text{(at constant } T) \qquad \ldots(12)$$

If pressure is also constant

$$\frac{r_1}{r_2} = \sqrt{\left(\frac{M_2}{M_1}\right)} = \sqrt{\left(\frac{d_2}{d_1}\right)} \quad \text{(at constant } P \text{ and } T) \qquad \ldots(13)$$

where, d_1, d_2 are vapour densities of gases and

$$\text{V.D.} = \frac{\text{molar mass}}{2}$$

The rate of diffusion r may also be expressed as

$r = \dfrac{V}{t}$ where V volume of gas diffuses in time t

$r = \dfrac{n}{t}$ where n mole of gas diffuses in time t

$r = \dfrac{d}{t}$ where d distance is travelled by gas molecules in time t

$\therefore$ By Eq. (12) at constant T $\quad$ By Eq. (13) at constant P and T

$$\frac{V_1}{t_1} \times \frac{t_2}{V_2} = \sqrt{\left(\frac{M_2}{M_1}\right)} \times \frac{P_1}{P_2} \qquad \frac{V_1}{t_1} \times \frac{t_2}{V_2} = \sqrt{\left(\frac{M_2}{M_1}\right)} \qquad \ldots(14)$$

$$\frac{n_1}{t_1} \times \frac{t_2}{n_2} = \sqrt{\left(\frac{M_2}{M_1}\right)} \times \frac{P_1}{P_2} \qquad \frac{n_1}{t_1} \times \frac{t_2}{n_2} = \sqrt{\left(\frac{M_2}{M_1}\right)} \qquad \ldots(15)$$

$$\frac{d_1}{t_1} \times \frac{t_2}{d_2} = \sqrt{\left(\frac{M_2}{M_1}\right)} \times \frac{P_1}{P_2} \qquad \frac{d_1}{t_1} \times \frac{t_2}{d_2} = \sqrt{\left(\frac{M_2}{M_1}\right)} \qquad \ldots(16)$$

Also, in terms of mass of gas diffused, Eq. (15) may be written as

$$\therefore \quad \frac{w_1}{M_1 t_1} \times \frac{M_2 t_2}{w_2} = \sqrt{\left(\frac{M_2}{M_1}\right)}$$

$$\therefore \quad \frac{w_1}{t_1} \times \frac{t_2}{w_2} = \sqrt{\left(\frac{M_2}{M_1}\right)} \times \frac{M_1}{M_2}$$

or $$\frac{w_1}{t_1} \times \frac{t_2}{w_2} = \sqrt{\left(\frac{M_1}{M_2}\right)} \qquad \ldots(17)$$

If a mixture of heavier gas B and a lighter gas A is placed in contact with a porous barrier, the gas passing through will be enriched in lighter component by a factor $\sqrt{\dfrac{M_B}{M_A}}$, called enrichment factor because lighter molecules effuse more rapidly than heavier one. The remaining gas will be enriched in the heavier component. Each passage gives an enrichment factor equal to $\sqrt{\dfrac{M_B}{M_A}}$ and so thousands of such barriers in succession are necessary to provide sufficient enrichment of heavier component.

Thus, enrichment factor for first barrier or operation $f_1 = \sqrt{\dfrac{M_B}{M_A}}$

$\therefore$ Overall separation or enrichment factor $f = \dfrac{n'_A/n'_B}{n_A/n_B}$

where, n_A, n_B and n'_A, n'_B are the concentrations of two isotopically different components before and after processing. If the required enrichment of gas A is attained in x-operations then,

$$(f_1)^x = \frac{n'_A/n'_B}{n_A/n_B} = f$$

or
$$x \log f_1 = \log\left[\frac{n'_A/n'_B}{n_A/n_B}\right]$$

or
$$x \log\left[\frac{M_B}{M_A}\right]^{1/2} = \log\left[\frac{n'_A/n'_B}{n_A/n_B}\right]$$

or
$$\frac{x}{2}\log\left[\frac{M_B}{M_A}\right] = \log\left[\frac{n'_A/n'_B}{n_A/n_B}\right]$$

or
$$x = \frac{2\log\left(\dfrac{n'_A/n'_B}{n_A/n_B}\right)}{\log\left(\dfrac{M_B}{M_A}\right)} = \frac{2\log f}{\log\left(\dfrac{M_B}{M_A}\right)} \qquad \ldots(18)$$

Note : 1. Instantaneous rate of diffusion, $-\dfrac{dP}{dt} \propto \dfrac{P}{\sqrt{M}}$.

On integration under limits P_1 to P_2 and from 0 to t, we get

$$P_2 = P_1 \cdot e^{-\frac{Kt}{\sqrt{M}}}$$

2. Rate of diffusion, $\dfrac{\partial V}{\partial t}$ at constant P and T, through a pin hole of area A

$$\frac{\partial V}{\partial T} = \frac{A}{3}\sqrt{\frac{2}{\pi}} \cdot u_{\text{rms}}$$

9. The kinetic equation : For a gas,

$$PV = \frac{1}{3} mnu^2_{\text{rms}} \qquad \ldots(19)$$

where, P is its pressure, V is its volume, m is mass of one molecule, n is no. of molecules of gas

u_{rms} is root mean square speed

$$= \sqrt{\left(\frac{u_1^2 + u_2^2 + u_3^2 + \ldots}{n}\right)} = \sqrt{\frac{\Sigma u^2}{n}} \qquad \ldots(20)$$

Also, if n_1 molecules are moving with speed u_1, n_2 molecules with speed u_2 and so on, then,

$$u_{\text{rms}} = \sqrt{\frac{n_1 u_1^2 + n_2 u_2^2 + n_3 u_3^2 + \ldots}{n_1 + n_2 + n_3}} = \sqrt{\frac{\Sigma n u^2}{\Sigma n}} \qquad \ldots(21)$$

If there is 1 mole of gas then $m \times N$ = molar mass ($\because n = N$ = Av. No.)

$$\therefore \quad PV = \frac{1}{3} Mu^2_{\text{rms}} \quad \text{or} \quad u^2_{\text{rms}} = \frac{3PV}{M}$$

or
$$u = \sqrt{\left(\frac{3PV}{M}\right)} = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3P}{d}\right)} \qquad \ldots(22)$$

$$\left(\because \frac{M}{V} = \text{density}\right)$$

NOTE : White calculating u one should keep in mind,

(a) The proper units of terms

	CGS	MKS
u	cm/sec	m/sec
P	dyne/cm^2	N/m^2
V	cm^3	m^3
M	g	kg
R	erg	joule
d	g/cm^3	kg /m^3

If temperature is mentioned, always use $u = \sqrt{\left(\dfrac{3RT}{M}\right)}$, since, u_{rms} depends only on temperature and in independent of P, V and d.

$$\text{Average speed, } u_{\text{AV}} = \frac{u_1 + u_2 + u_3 + \ldots}{n} \qquad \ldots(23)$$

or
$$u_{\text{AV}} = \frac{n_1 u_1 + n_2 u_2 + n_3 u_3 + \ldots}{n_1 + n_2 + n_3} \qquad \ldots(24)$$

$$\text{Average speed, } u_{\text{AV}} = \sqrt{\left(\frac{8RT}{\pi M}\right)} \qquad \ldots(25)$$

$$\text{and most probable speed, } u_{\text{MP}} = \sqrt{\left(\frac{2RT}{M}\right)} \qquad \ldots(26)$$

$$\therefore \quad u_{\text{MP}} : u_{\text{AV}} : u_{\text{rms}} :: 1 : \sqrt{\left(\frac{4}{\pi}\right)} : \sqrt{\left(\frac{3}{2}\right)}$$

$$u_{\text{MP}} : u_{\text{AV}} : u_{\text{rms}} :: 1 : 1.128 : 1.224 \qquad \ldots(27)$$

10. Kinetic energy : (for 1 mole gas)

$$PV = \frac{1}{3} Mu^2_{\text{rms}} = \frac{2}{3} \times \frac{1}{2} Mu^2_{\text{rms}} = \frac{2}{3} \times \text{KE /mol}$$

$$\therefore \quad \text{Translational KE/mol} = \frac{3}{2} PV = \frac{3}{2} RT \qquad \ldots(28)$$

$$\therefore \quad \text{Translational KE/molecule} = \frac{3}{2}\frac{R}{N} T = \frac{3}{2} kT \qquad \ldots(29)$$

where, k is Boltzmann's constant and $k = \dfrac{R}{N}$ ...(30)

$$\text{For } n \text{ mole of a gas, } \text{KE} = \frac{3}{2} nRT \qquad \ldots(31)$$

11. Mean free path : The distance travelled in between two successive collisions of a molecule is free path. The average of all such free paths is mean free path.

$$\therefore \quad \text{Mean free path, } \lambda = \frac{d_1 + d_2 + \ldots d_n}{n} \qquad \ldots(32)$$

where, $d_1, d_2, \ldots, d_n$ are free paths travelled by a molecule.

12. Collision frequency (c.f.) : No. of collisions taking place in unit time

$$c.f. = \frac{\text{No. of collisions}}{\text{Time}} = \frac{u_{\text{rms}}}{\lambda} \qquad \ldots(33)$$

13. Limitations of gas equation and van der Waals' equation for gases : Gases show deviations from ideal gas behaviour (*i.e.*, $PV = RT$) preferably more at high P and low T. The deviations are expressed in terms of compressibility factor (Z) expressed as

$$Z = \frac{PV}{nRT} \quad \text{(for } n \text{ mole gas)} \qquad ...(34)$$

or

$$Z = \frac{PV}{RT} \quad \text{(for 1 mole gas)} \qquad ...(35)$$

NOTE :
1. $Z = 1$ for ideal gas.
2. $Z > 1$ means for positive deviation from ideal gas behaviour; usually at high $P : Z > 1$, which means $PV > RT$ and attractive forces predominate.
3. $Z > 1$ means negative deviation from ideal gas behaviour; usually at low $P : Z < 1$, which means $PV < RT$ and repulsive forces predominate.
4. $Z = 1$ for real gases at normal P.
5. $Z > 1$ for H_2 and He at all pressure.

van der Waals' pointed out another equation to express behaviour of gases as,

$$\left[P + \frac{a}{V^2}\right][V - b] = RT \quad \text{(for 1 mole gas)} \qquad ...(36)$$

$$\left[P + \frac{n^2a}{V^2}\right][V - nb] = nRT \quad \text{(for } n \text{ mole gas)} \qquad ...(37)$$

where, a = van der Waals' constant for attraction
b = van der Waals' constant for volume

NOTE : (i) Since 'b' is four times of the actual volume of gaseous molecules

$\therefore \quad b = 4N \times v = 4 \times$ Avogadro's no. $\times \frac{4}{3}\pi r^3$

where, r is radius of one gaseous molecule and v is volume of one molecule of gas in rest.

(ii) Units of a = atm litre^2 mol^{-2} = atm dm^3 mol^{-2}
= dyne cm^4 mol^{-2} (In CGS)
= N m^4 mol^{-2} (In MKS)

Units of b = litre mol^{-1} = dm^3 mol^{-1}
= cm^3 mol^{-1} (In CGS)
= m^3 mol^{-1} (In MKS)

14. Molar heat capacity of ideal gases : Specific heat c, of a substance is defined as the amount of heat required to raise the temperature of 1 g of substance through 1°C, the unit of specific heat is calorie g^{-1} K^{-1}. (1 cal is defined as the amount of heat required to raise the temperature of 1 g of water through 1°C).

Molar heat capacity C, is defined as the amount of heat required to raise the temperature of 1 mole of a gas through 1°C. Thus,

Molar heat capacity = Sp. heat × Molar mass of the gas

$$C_P = c_p \times M \qquad ...(38)$$

$$C_v = c_v \times M \qquad ...(39)$$

For gases there are two values of molar heats, *i.e.*, molar heat at constant pressure and molar heat at constant volume respectively denoted by C_p and C_v. C_p is greater than C_v.

and

$$C_p - C_v = R \qquad ...(40)$$

$$c_p - c_v = \frac{R}{M} \qquad ...(41)$$

For a monoatomic gas $C_p = 5$ cal and $C_v = 3$ cal

Poisson's ratio (γ): $$\gamma = \frac{C_p}{C_v} \qquad ...(42)$$

$$\therefore \quad \gamma = \frac{5}{3} = 1.67$$

For diatomic gas $C_p = 7$ cal and $C_v = 5$ cal

$$\gamma = \frac{7}{5} = 1.40$$

For polyatomic gas $C_p = 8$ cal and $C_v = 6$ cal

$$\gamma = \frac{8}{6} = 1.33$$

where, c_p and c_v are specific heats and M is molar mass.

15. Critical constants :

Critical volume, $$V_c = 3b \qquad ...(43)$$

Critical pressure, $$P_c = \frac{a}{27b^2} \qquad ...(44)$$

Critical temperature, $$T_c = \frac{8a}{27Rb} \qquad ...(45)$$

Note : 1. Liquefaction of a gas is a continous process.
2. Ideal gas can not be liquefied.

16. Boyle's temperature : The temperature range at which real gases obey gas laws is called Boyle's temperature (T_b)

$$T_b = \frac{a}{Rb} \qquad ...(46)$$

17. Inversion temperature : The temperature below which a gas on subjecting to Joule-Thomson effect shows cooling effect ($\mu_{\text{J.T.}}$ = +ve) and above which it shows heating effect ($\mu_{\text{J.T.}}$ = −ve) is called inversion temperature (T_i)

$$T_i = \frac{2a}{Rb} \qquad ...(47)$$

$\mu_{\text{J.T.}}$ is Joule-Thomson coefficient expressed as

$$\left(\frac{\delta T}{\delta P}\right)_H = \mu_{\text{J.T.}} \qquad ...(48)$$

$\mu_{\text{J.T.}} = 0$ for an ideal gas.

18. Equation for law of corresponding state :

$$\left[P_r + \frac{3}{V_r{}^2}\right][3V_r - 1] = 8T_r \qquad ...(49)$$

where $P_r = \frac{P}{P_c}$; $V_r = \frac{V}{V_c}$ and $T_r = \frac{T}{T_c}$

Note : At corresponding state; $Z = \frac{3}{8}\frac{P_r \cdot V_r}{T_r}$

NUMERICAL PROBLEMS

1. A gas occupies 300 mL at 27°C and 730 mm pressure. What would be its volume at STP?
2. A gas at 0°C and 1 atm pressure occupies 2.5 litre. What change in temperature would be necessary if the pressure is to be adjusted to 1.5 atm and the gas has been transferred to a 2.0 litre container?
3. Calculate the volume occupied by 7 g N_2 at 27°C and 750 mm of Hg.
4. A container having 3 mole of gas occupies 60 litre at pressure P and T. If 0.01 mole of gas are introduced at same P and T, what will be the change in volume?
5. Calculate the mass of CH_4 in a 9 litre cylinder at 16 atm and 27°C. ($R = 0.08$ L atm K^{-1})
6. 3.7 g of a gas at 25°C occupy the same volume as 0.184 g H_2 at 17°C at same pressure. What is the molar mass of gas?
7. 5 g of ethane are confined in a bulb of 1 litre capacity. The bulb is so weak that it will burst if the pressure exceeds 10 atm. At what temperature will the pressure of gas reach the bursting value?
8. In Victor Meyer's experiment, 0.23 g of a volatile solute displaced air which measures 112 mL at NTP. Calculate the vapour density and molar mass of substance.
9. What should be the percentage increase in pressure for a 5% decrease in volume of a gas at constant temperature?
10. O_2 is present in one litre flask at a pressure of 7.6×10^{-10} mm of Hg. Calculate no. of O_2 molecules at 0°C.
11. The pressure of the atmosphere is 2×10^{-6} mm at about 100 mile above the earth and temperature is -180°C. How many mole are there in 1 mL gas at this altitude?
12. A 1.5 litre sample of a gas having density 1.25 kg/m^3 at 1.0 atm and 0°C was compressed to 575 atm resulting in a gas volume of 3.92 cm^3 in violation of Boyle's law. What is the final density of this gas?
13. The pressure exerted by 12 g of an ideal gas at temperature t°C in a vessel of volume V litre is one atm. When the temperature is increased by 10 degree at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V. (Molar mass of the gas $= 120$). **(IIT 1999)**
14. An iron cylinder contains helium at a pressure of 250 kPa at 300 K. The cylinder can withstand a pressure of 1×10^6 Pa. The room in which cylinder is placed catches fire. Predict whether the cylinder will blow up before it melts or not, melting point of cylinder $= 1800$ K.
15. A volume of 95 mL N_2O at 27°C is collected in a graduated tube over mercury, the level of Hg inside the tube being 60 mm above the outside mercury level when barometer reads 750 mm.
    (a) Calculate the volume of the same mass at STP.
    (b) What volume would the same mass of gas occupy at 40°C when the barometric pressure is 745 mm and the level of Hg inside the tube 25 mm below the outside level?
16. An LPG (liquefied petroleum gas) cylinder weighs 14.8 kg when empty, when full, it masses 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27°C, the mass of full cylinder is reduced to 23.2 kg. Find out the volume of the gas in cubic metres used up at the normal usage conditions and the final pressure inside the cylinder. Assume LPG to be *n*-butane with normal boiling point of 0°C. **(IIT 1994)**
17. A balloon blown up with 1 mole of gas has a volume of 480 mL at 5°C. The balloon is filled to (7/8)*th* of its maximum capacity. Suggest,
    (a) Will the balloon burst at 30°C?
    (b) The minimum temperature at which it will burst.
    (c) The pressure of gas inside the balloon at 5°C.
    (d) The pressure of gas when balloon bursts.
18. 0.553 g of a boron-hydrogen compound created a pressure of 0.658 atm in a bulb of 407 mL at 100°C. Analysis showed it to be 85.7% boron. Calculate its molecular formula.
19. 1.47 litre of a gas is collected over water at 30°C and 744 mm of Hg. If the gas weighs 1.98 g and vapour pressure of water at 30°C is 32 mm, what is the molar mass of gas?
20. Calculate the density of CO_2 at 100°C and 800 mm Hg pressure.
21. A mixture of CO and CO_2 is found to have a density of 1.50 g/litre at 30°C and 730 mm. What is composition of mixture?
22. A spherical balloon of 21 cm diameter is to be filled up with H_2 at NTP from a cylinder containing the gas at 20 atm at 27°C. The cylinder can hold 2.82 litre of water at NTP. Calculate the number of balloons that can be filled up.
23. A balloon of diameter 20 metre weighs 100 kg. Calculate its payload, if it is filled with He at 1.0 atm and 27°C. Density of air is 1.2 kg m^{-3}.
    [$R = 0.082$ dm^3 atm K^{-1} mol^{-1}] **(Roorkee 1994)**
24. The mass of 350 mL of a diatomic gas at 0°C and 2 atm is 1 g. Calculate the mass in g of one atom.
25. A flask is of a capacity of one litre. What volume of air will escape from the flask if it is heated from 27°C to 37°C? Assume pressure is constant.

26. A student forgot to add the reaction mixture to the round bottomed flask at 27° C but put it on the flame. After a lapse of time, he realised his mistake. Using a pyrometer he found that the temperature of the flask was 477° C. What fraction of air would have expelled out?

27. An open flask contains air at 27° C. Calculate the temperature at which it should be heated so that,

(a) $\frac{1}{3}$rd of air measured at 27° C escapes out.

(b) $\frac{1}{3}$rd of air measured at final temperature escapes out.

28. 20% N_2O_4 molecules are dissociated in a sample of gas at 27° C and 760 torr. Calculate the density of the equilibrium mixture. **[Roorkee 1996]**

29. Two flasks of equal volume connected by a narrow tube (of negligible volume) are at 27° C and contain 0.70 mole of H_2 at 0.5 atm. One of the flask is then immersed into a bath kept at 127° C, while the other remains at 27° C. Calculate the final pressure and the number of mole of H_2 in each flask.

30. A vessel contains 7.1g chlorine gas at pressure P and temperature T K. On heating the vessel to 30° higher temperature, 246 mL of chlorine at 1 atm and 27° C is taken out to maintain same pressure in vessel. Calculate:

(a) the original temperature,

(b) if the gas is not allowed to escape out, the pressure increases by 0.11 atm. Calculate the volume of vessel and initial pressure.

31. A car tyre has a volume of 10 litre when inflated. The tyre is inflated to a pressure of 3 atm at 17° C with air. Due to driving the temperature of tyre increases to 47° C.

(a) What would be the pressure at this temperature?

(b) How many litre of air measured at 47° C and pressure of 1 atm should be let out to restore the tyre to 3 atm at 47° C?

32. A gas filled freely collapsible balloon is pushed from the surface level of lake to a depth of 100 meter. Calculate what per cent of its original volume, the balloon finally has. Assume ideal gas nature.

33. Two glass bulbs of equal volumes are connected by a narrow tube and filled with a gas at 0° C and pressure of 76 cm of Hg. One of the bulb is then placed in a water bath maintained at 62° C. What is the new value of the pressure inside the bulbs? The volume of the connecting tube is negligible.

34. Two glass bulbs of internal volumes 0.5 and 0.2 litre respectively are connected by a narrow tube of negligible volume. The pressure of air in the vessel is 75 cm at 17° C. The smaller bulb is immersed in melting ice and the larger bulb in boiling water. Calculate final pressure in the bulbs neglecting the expansion of glass.

35. The volume of the average adult lung when expanded is about 6 litre at 98.4° F, if the pressure of oxygen in inhaled air is 168 mm of Hg, calculate the mass of O_2 required to occupy the lung at 98.4° F.

36. Two gas containers with volumes 0.1 L and 1 L respectively are connected by a tube of negligible volume and contains air at a pressure of 1000 mm of Hg at 0° C. If the temperature of smaller container is raised to 100° C, what volume of air measured at 0° C and 760 mm of Hg will pass from it to a larger container.

37. A 2 litre flask of N_2 at 20° C and 70 cm P is connected with a 3 litre of another flask of O_2 at the same temperature and 100 cm P. What will be the final pressure after the gases have throughly mixed at the same temperature as before? Also calculate the mole % of each gas in the resulting mixture. The volume of stop cock may be neglected.

38. Calculate the total pressure in a 10 litre cylinder which contains 0.4 g of helium, 1.6 g of oxygen and 1.4 g of nitrogen at 27° C. Also calculate the partial pressure of helium gas in the cylinder. Assume ideal behaviour of gases. Given, $R = 0.082$ litre - atm $K^{-1} mol^{-1}$.

(Roorkee 1997)

39. Equal masses of CH_4 and O_2 are mixed in an empty container of one litre at 27° C. Calculate the:

(a) fraction of total pressure exerted by O_2.

(b) total pressure if the masses of gases are 32 g each.

40. Two gases A and B having molar mass 60 and 45 respectively are enclosed in a vessel. The mass of A is 0.50 g and that of B is 0.2 g. The total pressure of the mixture is 750 mm. Calculate partial pressure of the two gases.

41. A 20 g chunk of dry ice is placed in an empty 0.75 litre wine bottle tightly closed. What would be the final pressure in the bottle after all CO_2 has been evaporated and temperature reaches to 25° C?

42. A gaseous mixture of O_2 and N_2 are in the ratio of 1 : 4 by mass. Calculate their ratio of molecules.

43. 50 litre of dry N_2 is passed through 36 g H_2O at 27° C. After passage of gas, there is a loss of 1.20 g in water. Calculate vapour pressure of water.

44. O_2 is collected over water at 20° C. The pressure inside shown by the gas is 740 mm of Hg. What is the pressure due to O_2 alone if V.P. of H_2O is 18 mm at 20° C?

45. The density of a mixture of O_2 and N_2 at NTP is 1.3 g litre^{-1}. Calculate partial pressure of O_2.

46. An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98 g mL^{-1} and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molar mass of the gas.

(IIT 1998)

47. A jar contains a gas and a few drops of water at T K. The pressure in the jar is 830 mm of Hg. The temperature of the jar is reduced by 1%. The vapour pressures of water at two temperatures are 30 and 25 mm of Hg. Calculate the new pressure in the jar.

48. 2 g of a gas A are introduced into an evacuated flask kept at 25°C. The pressure is found to be 1 atm. If 3 g of another gas B are added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate :

(a) the ratio of molar masses of M_A and M_B.

(b) the volume of the vessel, if A is O_2.

49. A long rectangular box is filled with Cl_2 (at. mass 35.45) which is known to contain only Cl^{35} and Cl^{37}. If the box could be divided by a partition and the two types of chlorine molecules put into the two compartments respectively, calculate, where should the partition be made if the pressure on both sides is to be equal. Is this pressure the same as the original pressure?

50. A narrow tube of uniform base, closed at one end has some air entrapped by a small quantity of water. If the pressure of the atmosphere is 760 mm of Hg and vapour pressure of H_2O at 12°C and 35°C are 10.5 mm Hg and 42 mm Hg respectively and the length of the air column is 10 cm at 12°C, what will be its length at 35°C?

51. Mercury diffusion pumps may be used in the laboratory to produce a high vacuum. Cold traps are generally placed between the pump and the system to be evacuated. These cause condensation of mercury vapours and prevent mercury from diffusing back into the system. The minimum pressure of mercury that can exist in the system is the vapour pressure of mercury at the temperature of cold trap. Calculate the number of mercury atom per unit volume in a cold trap at -120°C. The vapour pressure of mercury at this temperature is 10^{-16} torr.

52. Helium is contained at 30.2°C in the system as shown in the figure. The levelling bulb (L) can be raised so as to fill the lower bulb with mercury and force the gas into the upper part of the device. The volume of bulb (A) to the mark 'a' is 100.5 cm^3 and the volume of bulb (B) between the marks 'a' and 'b' is 110 cm^3. The pressure exerted by the He is measured by the difference between the mercury levels in the device and in the evacuated arm of the manometer when mercury level is at 'b', the pressure is 20.14 mm of Hg. What is the mass of the helium in container?

53. A glass capillary tube sealed at both ends is 100 cm long. It lies horizontally with the middle 10 cm containing Hg. The two ends of the tube which are equal in length contain air at 27°C and pressure of 76 cm of Hg. The tube is kept in a horizontal position such that the air column at one end is at 0°C, the other end is maintained at 127°C. Calculate the length of the air column and its pressure which is at 0°C. Neglect the change in volume of Hg and glass.

54. A column of Hg of 10 cm in length is contained in the middle of a narrow 1 m long tube which is closed at both ends. Both the halves of the tube contained air at a pressure 76 cm of Hg. By what distance will the column of Hg be displaced if the tube is held vertical?
(Roorkee Phy. 1989)

55. A vertical cylinder closed at both ends, is divided into two parts by a frictionless piston, each part containing one mole of air. At temperature 300 K, the volume of upper part is 4 times than that of the lower part. At what temperature will the volume of upper part be three times than that of lower part?

56. A thin tube of uniform cross-section is sealed at both ends. It lies horizontally. The middle 5 cm containing Hg and the two equal ends containing air at the same pressure P_0. When the tube is held at an angle 60° with the vertical, the length of the air column above and below the mercury are 46 and 44.5 cm respectively. Calculate the pressure P_0 in cm of Hg. (The temperature of the system is kept at 30°C) **[IIT Phy. 1986]**

57. An under water bubble with a radius of 0.5 cm at the bottom of tank, where the temperature is 5°C and pressure is 3 atm rises to the surface, where temperature is 25°C and pressure is 1 atm. What will be the radius of bubble when it reaches to surface?

58. A mixture of N_2 and water vapours is admitted to a flask which contains a solid drying agent. Immediately after admission, the pressure of the flask is 760 mm. After standing some hours, the pressure reached a steady value of 745 mm,

(a) Calculate the composition in mole % of original mixture.

(b) If the experiment is done at 20°C and the drying agent increases in mass by 0.15 g, what is the volume of flask?

(neglect volume occupied by drying agent)

59. A vessel of volume 5 litre contains 1.4 g of nitrogen at a temperature 1800 K. Find the pressure of the gas if 30% of its molecules are dissociated into atom at this temperature.

60. A vertical hollow cylinder of height 1.52 m is fitted with a movable piston of negligible mass and thickness. The lower half of the cylinder contains an ideal gas and the upper half is filled with mercury. The cylinder is initially at 300 K. When the temperature is raised half of the mercury comes out of the cylinder. Find the temperature assuming the thermal expansion of mercury to be negligible. **(Roorkee Phy. 1993)**

61. Two closed vessels of equal volumes contain air at 105 kPa and 300 K are connected through a narrow tube of negligible volume. If one of the vessel is maintained at 300 K and other at 400 K, what will be the new pressure in vessel? Also calculate the ratio of number of mole in each vessel.

62. One litre flask contains air, water vapour and a small amount of liquid water at a pressure of 200 mm Hg. If this is connected to another one litre evacuated flask, what will be the final pressure of the gas mixture at equilibrium? Assume the temperature to be 50°C. Aqueous tension at $50°C = 93$ mm Hg.

63. A closed vessel contains air, saturated water vapours and excess of water. The total pressure in the vessel is 760 mm Hg at 25°C. The temperature is raised to 100°C. Calculate the total pressure in vessel at 100°C. Aqueous tension of H_2O at 25°C and 100°C are 24 mm and 760 mm Hg.

64. Find out the mass of water vapour per litre of air at 300 K when relative humidity is 50%. The saturation vapour pressure at 300 K is 3.6 kPa.

65. Assume that dry air contains 79% N_2 and 21% O_2 by volume. Calculate the density of dry air and moist air at 25°C and 1 atmospheric pressure when relative humidity is 60%. The vapour pressure of water at 25°C is 23.76 mm.

[Relative humidity is given by percentage relative humidity

$$= \frac{100 \times \text{partial pressure of water}}{\text{vapour pressure of water at that temperature}}\Bigg]$$

66. A mixture of H_2O_v, CO_2 and N_2 was trapped in a glass apparatus with a volume of 0.731 mL. The pressure of total mixture was 1.74 mm of Hg at 23°C. The sample was transferred to a bulb in contact with dry ice (−75°C) so that H_2O_v are frozen out. When the sample returned to normal value of temperature, pressure was 1.32 mm of Hg. The sample was then transferred to a bulb in contact with liquid N_2 (−95°C) to freeze out CO_2. In the measured volume, pressure was 0.53 mm of Hg at original temperature. How many mole of each constituent are in mixture?

67. What would be the final pressure of O_2 in following experiment? A collapsed polyethylene bag of 30 litre capacity is partially blown up by the addition of 10 litre of N_2 at 0.965 atm at 298 K. Subsequently enough O_2 is pumped into bag so that at 298 K and external pressure of 0.990 atm, the bag contains full 30 litre.

68. A mixture of N_2, NO and NO_2 in a closed container was analysed by selective absorption of the oxides of nitrogen. The initial pressure was 3.0 cm. After treatment with water, which absorbs NO_2, the pressure left was 2.42 cm. A ferrous sulphate solution was then shaken with residual gas mixture to absorb NO after which the pressure was 1.24 cm. If vapour pressure of H_2O, in gaseous mixture after shaking with H_2O and in $FeSO_4$ solution were 0.2 cm and 0.18 cm respectively calculate the mole % of gases in initial mixture. Assume all measurements are made at same *P* and *T*.

69. Calculate the change in pressure when 1.04 mole of NO and 20.0 g O_2 in a 20 litre vessel originally at 27°C react to produce the maximum quantity of NO_2 possible according to the equation.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

70. A 40 mL of a mixture of H_2 and O_2 was placed in a gas burette at 18°C and 1 atm *P*. A spark was applied so that the formation of water was complete. The remaining pure gas had a volume of 10 mL at 18°C and 1 atm *P*. If the remaining gas was H_2, what was the initial mole % of H_2 in mixture?

71. A flask of capacity one litre containing NH_3 at 1 atm and 25°C. A spark is passed through until all the NH_3 is decomposed into N_2 and H_2. Calculate:

(a) the pressure of gases left at 25°C.

(b) the mole of N_2 and H_2 formed.

72. At room temperature following reaction goes to completion:

$$2NO + O_2 \longrightarrow 2NO_2 \longrightarrow N_2O_4$$

Dimer N_2O_4 at 262 K is solid. A 250 mL flask and a 100 mL flask are separated by a stop cock. At 300 K, the nitric oxide in the larger flask exerts a pressure of 1.053 atm and the smaller one contains O_2 at 0.789 atm. The gases are mixed by opening the stop cock and after the end of the reaction, the flasks are cooled to 220 K. Neglecting the vapour pressure of dimer, find out the pressure and composition of gas remaining at 220 K. (Assume gases behave ideally) **(IIT 1992)**

73. A compound exists in the gaseous phase both as monomer (*A*) and dimer (A_2). The molar mass of *A* is 48. In an experiment 96 g of the compound was confined in a vessel of volume 33.6 litre and heated to Calculate the pressure developed if the compound exists as dimer to the extent of 50% by mass under these conditions.

74. 60 mL of a mixture of equal volumes of Cl_2 and an oxide of chlorine was heated and then cooled back to the original temperature. The resulting gas mixture was found to have volume of 75 mL. On treatment with caustic soda solution, the volume contracted to 15 mL. Assume that all measurements are made at the same *T* and *P*. Deduce the simplest formula for oxide of Cl_2. The oxide of Cl_2 on heating decomposes quantitatively to O_2 and Cl_2.

75. One litre of O_2 and one litre of H_2 are taken in a vessel of 2 litre capacity at NTP. The gases are made to combine to form water. Calculate:

(a) the mole and mass of water formed.

(b) the amount of gas left in vessel.
(c) the total pressure if the vessel is heated to 100°C.
(d) mole of O_2 used for formation of water.

76. A space capsule is filled with neon at 1 atm and 290 K. The gas effuses through a pin hole into outer space at the rate that pressure drops by 0.3 torr/sec. If the capsule is filled with 30 mole % of He, 20 mole % of O_2 and 50 mole % of N_2. What is the pressure drop under same condition?

77. 20 dm^3 of SO_2 diffuses through a porous partition in 60 second. What volume be O_2 will diffuse under similar conditions in 30 second? **(Roorkee 1996)**

78. Pure O_2 diffuses through an aperature in 224 second, whereas mixture of O_2 and another gas containing 80% O_2 diffuses from the same in 234 sec. What is molar mass of gas?

79. One mole of nitrogen gas at 0.8 atm takes 38 second to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 second to diffuse through the same hole. Calculate the molecular formula of the compound. **(IIT 1999)**

80. For 10 minute each, at 27°C, from two identical holes nitrogen and an unknown gas are leaked into a common vessel of 3 litre capacity. The resulting pressure is 4.18 bar and the mixture contains 0.4 mole of nitrogen. What is the molar mass of unknown gas?

81. The rates of diffusion of two gases A and B are in the ratio 1 : 4. If the ratio of their masses present in the mixture is 2 : 3, calculate the ratio of their mole fraction.

82. The composition of the equilibrium mixture ($Cl_2 \rightleftharpoons 2Cl$), which is attained at 1200°C, is determined by measuring the rate of effusion through a pinhole. It is observed that at 1.80 mm Hg pressure, the mixture effuses 1.16 times as fast as krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms. (Atomic mass of Kr = 84) **(IIT 1995)**

83. A mixture containing 1.12 litre D_2 and 2.24 litre of H_2 at NTP is taken inside a bulb connected to another bulb through a stop cock with a small opening. The second bulb is fully evacuated. The stop cock is opened for a certain time and then closed. The first bulb is now found to contain 0.10 g of D_2. Determine the % by mass of the gases in second bulb. **(Roorkee 1998)**

84. Calculate the relative rates of diffusion for $^{235}UF_6$ and $^{238}UF_6$ in gaseous form. Also if naturally occurring uranium ore having U^{235} and U^{238} in the ratio 0.72 and 99.28%, and if it is desired to enrich the U^{235} to 10% of the sample, making use of relative rates of diffusion of UF_6 having U^{235} and U^{238} isotopes, how many diffusion stages are required?

85. Naturally occurring hydrogen gas has abundance of $_1^1H_1^1H$ (molar mass 2) and $_1^1H_1^2H$ (molar mass 3). The % of $^1H^1H = 90.0\%$. In how much operations during diffusion of natural hydrogen gas will be enriched to 99.8% $^1H^1H$.

86. At 20°C, two balloons of equal volume and porosity are filled to a pressure of 2 atm, one with 14 kg N_2 and other with 1 kg of H_2 balloon leaks to a pressure of 1 / 2 atm in 1 hr. How long will it take for H_2 balloon to reach a pressure of 1 / 2 atm?

87. At 27°C, H_2 is leaked through a tiny hole into a vessel for 20 minute. Another unknown gas at the same T and P as that of H_2 is leaked through the same hole for 20 minute. After the effusion of the gases, the mixture exerts a pressure of 6 atm. The H_2 content of the mixture is 0.7 mole. If volume of container is 3 litre, what is molar mass of unknown gas? **(IIT 1992)**

88. A mixture of 0.5 mole of CO and 0.5 mole of CO_2 is taken in a vessel and allowed to effuse out through a pinhole into another vessel which has vacuum. If a total of A mole has effused out in time t, show that $M_1A + M_2(1 - A) = 36$, where M_1 and M_2 are mean molar masses of the mixture that has effused out and the mixture still remaining in vessel respectively.

89. A straight glass tube has two inlets X and Y at the two ends of 200 cm long tube. HCl gas through inlet X and NH_3 gas through inlet Y are allowed to enter in the tube at the same time and same pressure. White fumes first appears at a point P inside the tube. Calculate distance of P from X.

90. At room temperature, NH_3 gas at 1 atm and HCl gas at P atm are allowed to effuse through identical pinholes from opposite ends of a glass tube of 1 metre length and of uniform cross-section. NH_4Cl is first formed at a distance of 60 cm from the end through which HCl gas is sent in. What is the value of P?

91. The pressure in bulb dropped from 2000 to 1500 mm of Hg in 47 minute when the contained O_2 leaked through a small hole. The bulb was then completely evacuated. A mixture of O_2 and another gas of molar mass 79 in the molar ratio 1 : 1 at a total pressure of 4000 mm of Hg was introduced. Find the mole ratio of two gases remaining in the bulb after a period of 74 minute.

92. A 4 : 1 molar mixture of He and CH_4 is contained in a vessel at 20 bar pressure. Due to a hole in the vessel, the gas mixture leaks out. What is the composition of the mixture effusing out initially? **(IIT 1994)**

93. Calculate the root mean square speed and average speed for a sample of gas having 5, 10 and 15 molecules each one in a set is moving with a speed of 15×10^2, 5×10^2 and 10×10^2 m s^{-1} respectively.

94. Calculate root mean square speed, average speed and most probable speed of :

(a) O_2 at STP.

(b) Ethane at 27°C and 720 mm of Hg.

(c) O_2 at 17°C.

(d) O_2 if its density is 0.0081 g mL^{-1} at 1 atm.

(e) O_2 if 6.431 g of it occupies 5 litre at 750 mm.

(f) O_3 at 20°C and 82 cm Hg. **(IIT 1985)**

95. The average speed at T_1 K and the most probable speed at T_2 K of CO_2 gas is $9 \times 10^4 \text{ cm sec}^{-1}$. Calculate the value of T_1 and T_2. **(IIT 1990)**

96. The average speed of an ideal gas molecule at 27°C is 0.3 m sec^{-1}. Calculate average speed at 927°C.

97. Relate the three speeds with each other, *i.e.*, u_{rms}, u_{AV} and u_{MP}.

98. The average velocity of gas molecules is 400 m/sec. Calculate its rms velocity at the same temperature. **(IIT 2003)**

99. The mass of molecule A is twice the mass of molecule B. The rms speed of A is twice the rms speed of B. If two samples of A and B contain same no. of molecules, what will be the ratio of P of two samples in separate containers of equal volume?

100. Under 3 atm, 12.5 litre of a certain gas weigh 15 g, calculate the average speed of gaseous molecules.

101. Calculate the pressure exerted by 10^{23} gas molecules, each of mass 10^{-22} g in a container of volume one litre. The rms speed is 10^5 cm sec^{-1}.

102. Calculate the root mean square speed, total and average translational kinetic energy in joule of the molecules in 8 g methane at 27°C.

103. The mean kinetic energy of a molecule at 0°C is 5.621×10^{-14} erg. Calculate Boltzmann's constant. If the value of $R = 8.314 \times 10^7$ erg, then also calculate the no. of molecules present in one mole of gas.

104. A glass bulb of 1 litre capacity contains 2×10^{21} molecules of nitrogen exerting pressure of $7.57 \times 10^3 \text{ Nm}^{-2}$. Calculate the root mean square speed and the temperature of gas molecules. If the ratio of u_{MP} to u_{rms} is 0.82, calculate u_{MP} for these molecules at this temperature. **(IIT 1993)**

105. Two bulbs A and B of equal capacity are filled with He and SO_2 respectively, at the same temperature.

(i) If the pressure in two bulbs is same, calculate ratio of u_{rms} for them.

(ii) At what temperature velocity of SO_2 becomes half of the speed of He molecules at 27°C?

(iii) How will the speeds be effected if volume of B becomes four times?

(iv) How will the speeds be effected if half of the molecules of SO_2 are removed from B?

106. The kinetic molecular theory attributes an average translational kinetic energy of $\frac{3}{2}\frac{RT}{N}$ to each particle. What rms speed would a mist particle of mass 10^{-12} g have at room temperature (27°C) according to kinetic theory of gases?

107. Two flasks A and B have equal volumes. Flask A contains H_2 at 27°C while B contains equal mass of C_2H_6 at 627°C. In which flask and by how many times are molecules moving faster? Assume ideal gas nature for both.

108. Assuming O_2 molecule spherical in shape and occupying the radius 150 pm, calculate:

(a) the volume of single molecule of gas.

(b) the percentage of empty space in one mole of O_2 at NTP.

(c) comment on the percentage of empty space.

109. During an experiment, an ideal gas is found to obey an additional law $PV^2 = \text{constant}$. The gas is initially at temperature T and volume V. Calculate the temperature when it expands to a volume $2V$.

110. For one mole of a gas if $P = \dfrac{P_0}{1 + \left(\dfrac{V}{V_0}\right)^2}$, where P_0 and V_0 are constant. Find the temperature of gas when $V = V_0$.

111. Calculate the volume correction and pressure correction for 4.4 g CO_2 kept in 1 litre flask. Given $a = 3.6 \text{ atm L}^2 \text{ mol}^{-2}$ and $b = 0.04 \text{ L mol}^{-1}$ for CO_2.

112. The value of 'b' for steam is $0.0305 \text{ litre mol}^{-1}$. The density of liquid water is 0.958 g/mL at 100°C. What % of volume of water molecules occupy in gaseous phase of water in liquid phase?

113. Calculate the percentage of free volume available in 1 mole gaseous water at 1.0 atm and 100°C. Density of liquid H_2O at 100°C is 0.958 g/mL. Assume ideal gas behaviour.

114. Calculate the average volume available to a molecule in a sample of nitrogen gas at STP. What is the average distance between neighbouring molecules if nitrogen molecules are spherical in nature?

115. Calculate molecular diameter of He from its van der Waals' constant $b = 24 \text{ mL mol}^{-1}$.

116. Atomic and molecular sizes are of the order of a few angstrom ($1 \text{ Å} = 10^{-10}$ m). Assuming that N_2 molecule is spherical in shape with radius 2×10^{-10} m, calculate:

(i) the volume of single N_2 molecule.

(ii) the percentage of empty space in one mole of N_2 gas at STP.

117. Calculate the pressure exerted by 5 mole of CO_2 in one litre vessel at 47°C using van der Waals' equation. Also report the pressure of gas if it behaves ideally in nature. Given that $a = 3.592$ atm litre^2 mol^{-2},
$b = 0.0427$ litre mol^{-1}.

118. If volume occupied by CO_2 molecules is negligible, then calculate the pressure exerted by one mole of CO_2 gas at 273 K. $a = 3.592$ atm litre^2 mol^{-2}. **(IIT 2000)**

119. The compression factor (compressibility factor) for 1 mole of a van der Waals' gas at 0°C and 100 atmosphere pressure is found to be 0.5. Assuming that the volume of gas molecule is negligible, calculate the van der Waals' constant. **(IIT 2001)**

120. Calculate the compressibility factor for CO_2, if one mole of it occupies 0.4 litre at 300 K and 40 atm. Comment on the result.

121. The compressibility factor for a given real gas is 0.927 at 273 K and 100 atm. Calcualte the mass of gas required to fill a gas cylinder of 100 litre capacity under given conditions. [Molar mass of gas = 30]

122. The density of the vapours of a substance at 1 atm pressure and 500 K is 0.36 kg m^{-3}. The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition.

(a) Determine (i) molar mass, (ii) molar volume, (iii) compression factor (Z) of the vapours and (iv) which forces among the gas molecules are dominating, the attractive or the repulsive?

(b) If the vapours behaves ideally at 1000 K, determine the average translational kinetic energy of molecules. **(IIT 2002)**

123. Using van der Waals' equation, calculate the constant, 'a' when two mole of a gas confined in a four litre flask exerts a pressure of 11.0 atmospheres at a temperature of 300 K. The value of 'b' is 0.05 litre mol^{-1}. **(IIT 1998)**

124. 5.6 litre of an unknown gas at NTP requires 12.5 calorie to raise its temperature by 10°C at constant volume. Calculate:

(a) C_v of gas, (b) atomicity of gas.

125. Calculate the temperature of gas if it obeys van der Waals' equation from the following data. A flask of 25 litre contains 10 mole of a gas under 50 atm. Given $a = 5.46$ atm litre^2 mol^{-2} and $b = 0.031$ litre mol^{-1}.

126. Compressibility factor (Z) for N_2 at −50°C and 800 atm pressure is 1.95. Calculate mole of N_2 gas required to fill a gas cylinder of 100 mL capacity under the given conditions.

127. The critical constant for water are 374°C, 218 atm and 0.0566 litre mol^{-1}. Calculate a, b and R.

128. One way of writing the equation of state for real gases is:

$$PV = RT\left[1 + \frac{B}{V} + ...\right]$$

where B is a constant. Derive an approximate expression for B in terms of van der Waals' constants a and b. **(IIT May 1997)**

129. A certain gas 'A' polymerises to a small extent at a given P and T as $nA \rightleftharpoons [A]_n$. Show that the gas obeys the approximate equation $\frac{PV}{RT}\left[1 - \frac{(n-1)K_C}{V^{n-1}}\right]$ where $K_C = \frac{[A_n]}{[A]^n}$ and V is the volume of container. Initially 1 mole of 'A' was taken in container.

130. The molar volume of He at 10.1325 MPa and 273 K is 0.011075 of its molar volume at 101.325 kPa at 273 K. Calculate the radius of helium atom. The gas is assumed to show real gas nature. Neglect the value of a for He.

131. A real gas is supposed to obey the gas equation $P(V - b) = nRT$ at STP. If one mole of a gas occupies, 25 dm^3 volume at STP, calculate:

(a) diameter of each gas molecule.

(b) compressibility factor for gas.

132. Calculate van der Waals' constants a and b if critical temperature and critical pressure are 30°C and 72 atm respectively.

133. The critical temperature of O_2 and N_2 are 155 K and 126 K respectively. Calculate the ratio of reduced temperature of O_2 and N_2 at 300 K.

134. Reduced temperature and reduced volume of benzene are 0.7277 and 0.40 respectively. Calculate reduced pressure of benzene.

135. van der Waals' constant a and b for hydrogen are 0.246 L^2 atm mol^{-2} and 0.0267 L mol^{-1} respectively. Calculate inversion temperature and Boyle's temperature of H_2 gas.

136. A vacuum pump has a cylinder of volume v and is connected to a vessel of volume V to pump out air from the vessel. The initial pressure of gas in vessel is P. Show that after n strokes, the pressure in vessel is reduced to $P_n = P\left[\frac{V}{V + v}\right]^n$.

137. A graph is plotted between PV_m along y-axis and P along x-axis, where V_m is the molar volume of a real gas. Find the intercept along y-axis. **(IIT 2004)**

138. 1 g of He having rms speed 1000 m/s and 4 g of oxygen having rms speed 1000 m/s are introduced in a thermally isolated vessel. Find the rms speed of He and O_2 molecules when thermal equilibrium is attained.

139. The number of molecules in a gas sample that have the range of most probable speed (u_{mp}) at a temperature T is one half the number of same type of molecules that have the most probable speed at 300 K. What is T?

140. A bottle contains 1.0 mol He(g) and a second bottle contains 1.0 mol Ar(g) at the same temperature. At this temperature, the root mean square speed of He is 1477 m s^{-1} and that of Ar is 467 m s^{-1}. What is the ratio of the number of He atoms in the first bottle to the number of Ar atoms in the second bottle having these speeds? Assume that both gases behave ideally.

SOLUTIONS (Numerical Problems)

1. Given, initially $V_2 = \frac{300}{1000}$ litre, $P_2 = \frac{730}{760}$ atm,

$T_2 = 300\,\text{K}$

At STP $V_1 = ?$, $P_1 = 1\,\text{atm}$, $T_1 = 273\,\text{K}$

Now use, $\frac{P_2V_2}{T_2} = \frac{P_1V_1}{T_1}$

$V_1 = 0.2622$ litre

$\therefore$ Volume (V) at STP $= \mathbf{262.2\ mL}$

2. Given, $P_1 = 1\,\text{atm}$, $V_1 = 2.5$ litre, $T_1 = 273\,\text{K}$,

$P_2 = 1.5\,\text{atm}$, $V_2 = 2.0$ litre, $T_2 = ?$

Now use, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$\therefore$ $T_2 = \mathbf{327.6\ K}$ or $\mathbf{54.6°C}$

3. Given, $w = 7\,\text{g}$, $T = 300\,\text{K}$, $P = \frac{750}{760}$ atm and $M = 28\,\text{g mol}^{-1}$

Now use, $PV = \frac{w}{M}RT$ ($R = 0.0821$ litre atm K^{-1} mol^{-1})

$\therefore$ $V = \mathbf{6.239\ litre}$

4. $V \propto n$ also $V = kn$

$\therefore$ $60 = k \times 3$ or $k = 20.0$

$\Delta V = k \cdot \Delta n$

$\Delta V = 20 \times 0.1 = \mathbf{2\ litre}$

5. $P = 16\,\text{atm}$, $V = 9$ litre, $T = 300\,\text{K}$, $M = 16$

Now use, $PV = \frac{w}{M}RT$

$\therefore$ $w = \mathbf{96\ g}$

6. For H_2,

$w = 0.184\,\text{g}$, $T = 290\,\text{K}$ at pressure P and volume V.

$\therefore$ $PV = \frac{0.184}{2} \times R \times 290$ ...(1)

For the gas,

$w = 3.7\,\text{g}$, $T = 298\,\text{K}$ at pressure P and volume V

$\therefore$ $PV = \frac{3.7}{M} \times R \times 298$ ...(2)

By Eqs. (1) and (2), $M = \mathbf{41.326\ g\ mol^{-1}}$

7. $w = 5\,\text{g}$, $M = 30$ for C_2H_6, $V = 1$ litre

Let the bulb bursts at T kelvin, *i.e.*, when pressure becomes 10 atm.

$\because$ $PV = \frac{w}{M}RT$ so $10 \times 1 = \frac{5}{30} \times 0.0821 \times T$

$\therefore$ $T = 730.81\,\text{K} = \mathbf{457.81°C}$

8. Volume occupied by solute at NTP

= Volume of air displaced at NTP = 112 mL

$\because$ For volatile solute, $PV = \frac{w}{M}RT$

at NTP $P = 1\,\text{atm}$, $T = 273\,\text{K}$

$\therefore$ $1 \times \frac{112}{1000} = \frac{0.23}{M} \times 0.0821 \times 273$

$\therefore$ $M = \mathbf{46.02\ g\ mol^{-1}}$ and V.D. $= \mathbf{23.01}$

9. Given, $P_1 = P$, $V_1 = V$, $T_1 = T$

$P_2 = P_2$, $V_2 = V - \frac{5V}{100}$, $T_2 = T$

$\therefore$ $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ or $P \times V = P_2 \times \left(V - \frac{5V}{100}\right)$

or $P_2 = \frac{100}{95}P$

$\therefore$ $P_2 = 1.0526P$

$\therefore$ Increase in $P = 0.0526$

$\therefore$ % increase in $P = 0.0526 \times 100 = \mathbf{5.26}$

10. $P = 7.6 \times 10^{-10}\,\text{mm} = \frac{7.6 \times 10^{-10}}{760}$ atm

$V = 1$ litre, $T = 273\,\text{K}$

$\because$ $PV = nRT$

$\frac{7.6 \times 10^{-10}}{760} \times 1 = n \times 0.0821 \times 273$

$\therefore$ $n = 4.46 \times 10^{-14}$ mole of O_2

$\therefore$ No. of molecule of

$O_2 = 4.46 \times 10^{-14} \times 6.023 \times 10^{23} = \mathbf{2.68 \times 10^{10}}$

11. Given, $P = \frac{2 \times 10^{-6}}{760}$ atm, $T = -180 + 273 = 93\,\text{K}$,

$V = 1\,\text{mL} = \frac{1}{1000}$ litre

$\because$ $PV = nRT$

$\frac{2 \times 10^{-6}}{760} \times 10^{-3} = n \times 0.0821 \times 93$

$\therefore$ $n = \mathbf{3.45 \times 10^{-13}\ mol}$

12. Mass of gas in 1.5 litre

or $1.5 \times 10^{-3}\,\text{m}^3 = 1.25 \times 1.5 \times 10^{-3}\,\text{kg}$

New density $= \frac{\text{Mass}}{\text{New volume}} = \frac{1.25 \times 1.5 \times 10^{-3}}{3.92 \times 10^{-6}}\,\text{kg/m}^3$

$= \mathbf{478.3\ kg/m^3}$

13. **Case I** Given, $P = 1\,\text{atm}$, $w = 12\,\text{g}$, $T = (t + 273)\,\text{K}$, $V = V$ litre

Case II $T = (t + 283)$; $P = 1 + \frac{10}{100} = 1.1\,\text{atm}$, $w = 12\,\text{g}$, $V = V$ litre

Using gas equation :

Case I $1 \times V = \frac{12}{M} \times R\,(t + 273)$

Case II $1.1 \times V = \frac{12}{M} \times R\,(t + 283)$

By Eqs. (1) and (2), $\frac{1.1}{1} = \frac{t + 283}{t + 273}$

$\therefore$ $1.1t + 300.3 = t + 283$

$\therefore$ $0.1t = -17.3$

$\therefore$ $t = -173°\text{C} = \mathbf{100\ K}$

Also, from **Case I** $1 \times V = \frac{12}{120} \times 0.082 \times 100$ ($\because M = 120$)

$V = \mathbf{0.82\ litre}$

14. Given, $P_1 = 250\,\text{kPa}$, $T_1 = 300\,\text{K}$

$P_2 = 1\times10^6\ \text{Pa}$, $T_2 = ?$

Since, volume of cylinder remains constant.

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

$$\frac{250\times10^3}{300} = \frac{1\times10^6}{T_2}$$

$\therefore$ $T_2 = \mathbf{1200\ K}$

The cylinder will blow up at 1200 K before its melting (m.pt. 1800 K).

15. (a)

	At STP
$V_1 = 95\,\text{mL} = \frac{95}{1000}$ litre	$V_2 = ?$
$T_1 = 300\,\text{K}$	$T_2 = 273\,\text{K}$
$P_1 = 750 - 60 = 690\,\text{mm} = \frac{690}{760}\,\text{atm}$	$P_2 = \frac{760}{760}\,\text{atm} = 1\,\text{atm}$

$\because$ $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{690\times95}{760\times1000\times300} = \frac{1\times V_2}{273}$$

$\therefore$ $V_2 = 0.07848\ \text{litre} = \mathbf{78.48\ mL}$

(b) $V_2 = ?$, $T_2 = 313\,\text{K}$

$P_2 = 745 + 25 = 770\,\text{mm} = \frac{770}{760}\,\text{atm}$

Again using $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{690\times95}{760\times300\times1000} = \frac{770\times V_2}{760\times313}$$

$\therefore$ $V_2 = 0.0888\ \text{litre} = \mathbf{88.8\ mL}$

16. Mass of butane in cylinder

$= 29.0 - 14.8 = 14.2\,\text{kg} = 14.2\times10^3\ \text{g}$

$P = 2.5\,\text{atm}$, $T = 300\,\text{K}$, Molar mass of butane = 58

$\because$ $$PV = \frac{w}{M}RT$$

$$2.5\times V = \frac{14.2\times10^3}{58}\times0.0821\times300$$

$\therefore$ $V = 2.4\times10^3\ \text{litre} = 2.4\ \text{m}^3$

This is volume of cylinder or volume of gas.

Now the mass of gas left after use

$= 23.2 - 14.8 = 8.4\,\text{kg} = 8.4\times10^3\ \text{g}$

The volume remains constant.

Again usin $$PV = \frac{w}{M}RT$$

$$P\times2.412\times10^3 = \frac{8.4\times10^3}{58}\times0.0821\times300$$

$\therefore$ Pressure (P) of the gas left in cylinder = **1.50 atm**

Now, pressure of gas given out = 1

Mass of gas given out = 29.0 − 23.2

$= 5.8\,\text{kg} = 5.8\times10^3\ \text{g}$

Thus, volume of gas given out under these conditions is

$\therefore$ $$1\times V = \frac{5.8\times10^3}{58}\times0.0821\times300$$

$\therefore$ $V = 2.4\times10^3\ \text{litre} = \mathbf{2.4\ m^3}$

17. Maximum capacity or volume of balloon

$= \frac{8}{7}\times480 = 548.57\,\text{mL}$

Also, $V_1 = 480\,\text{mL}$, $T_1 = 278\,\text{K}$, $n = 1\,\text{mole}$

(a) The balloon will burst at the temperature say T_2 when volume becomes 548.57 mL,

$\because$ $$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{480}{278} = \frac{548.57}{T_2}$$

$\therefore$ $T_2 = 317.71\,\text{K} = \mathbf{44.71^\circ C}$

Thus, balloon will not burst at **30° C**.

(b) The minimum temperature at which balloon bursts is **44.71° C**.

(c) Pressure of gas at 5° C having 1 mole and $V = 480\,\text{mL}$

$$P\times\frac{480}{1000} = 1\times0.0821\times278$$

$P = \mathbf{47.5\ atm}$

(d) Since, V increases with temperature rise from 5° C to 44.71° C at which the balloon bursts and therefore pressure remains constant. Thus presssure of gas in balloon when it bursts is **47.5 atm**.

18. For B-H compound,

$P = 0.658\,\text{atm}$, $V = \frac{407}{1000}$ litre, $T = 373\,\text{K}$, $w = 0.553\,\text{g}$

$\because$ $$PV = \frac{w}{M}RT$$

$$0.658\times\frac{407}{1000} = \frac{0.553}{M}\times0.0821\times373$$

$M = \mathbf{63.23\ g\ mol^{-1}}$

$\because$ 100 g compound has 85.7 g B

$\therefore$ 63.23 g compound has $= \frac{85.7\times63.23}{100}$ g B = 54.19 g B

$= \frac{54.19}{10.8}$ g -atom of B = 5 g -atom of B

$\therefore$ Formula becomes B_5H_x

$\therefore$ $5\times10.8 + x = 63.25$

$x = 9.25 = 9$ (an integer)

$\therefore$ Formula of compound is $\mathbf{B_5H_9}$.

19. $w = 1.98\,\text{g}$, $V = 1.47$ litre, $T = 303\,\text{K}$

$$P = 744 - 32 = 712\,\text{mm} = \frac{712}{760}\,\text{atm}$$

$\because$ For dry gas, $$PV = \frac{w}{M}RT$$

$$\frac{712}{760}\times1.47 = \frac{1.98}{M}\times0.0821\times303$$

$\therefore$ $M = \mathbf{35.76\ g\ mol^{-1}}$

20. $P = \frac{800}{760}\,\text{atm}$, $T = 273 + 100 = 373\,\text{K}$

Let density be d for CO_2.

For CO_2, $$PV = \frac{w}{M}RT$$

$\therefore$ $$P = \frac{d}{M}RT \qquad \left(\because \frac{w}{V} = d\right)$$

$$\frac{800}{760}=\frac{d}{44}\times 0.0821\times 373$$

$\therefore$ $d = \mathbf{1.5124\ g\ litre^{-1}}$

21. For mixture of CO and CO_2, $d = 1.50\,\text{g litre}^{-1}$

$$P=\frac{730}{760}\,\text{atm}, \qquad T = 303\,\text{K}$$

$\because$ $PV=\frac{w}{M}RT$

$$P=\frac{w}{VM}RT$$

$$\frac{730}{760}=\frac{1.50}{M}\times 0.0821\times 303 \qquad \left(\because \frac{w}{V}=d\right)$$

$\therefore$ $M = \mathbf{38.85\ g\ mol^{-1}}$

i.e., Molar mass of mixture of CO and $CO_2 = 38.85$

Let % of mole of CO be a in mixture, then

$$\text{Average mol. mass}=\frac{a\times 28+(100-a)\times 44}{100}$$

$$38.85=\frac{28a+4400-44a}{100}$$

$\therefore$ $a = 32.19$

$\therefore$ Mole % of CO $= \mathbf{32.19}$

Mole % of $CO_2 = \mathbf{67.81}$

22. Volume of one balloon which is to be filled

$$=\frac{4}{3}\pi\left(\frac{21}{2}\right)^3 = 4851\,\text{mL} = 4.851\,\text{litre}$$

Let n balloons are filled, then volume of H_2 occupied by balloons

$= 4.851\times n$

Also, cylinder will not be empty and it will occupy volume of

$H_2 = 2.82$ litre

$\therefore$ Total volume occupied by H_2 at NTP

$= 4.851\times n + 2.82$ litre

Therefore, at STP available H_2

$P_1 = 1\,\text{atm}$ $\qquad P_2 = 20\,\text{atm}$

$V_1 = 4.851\times n + 2.82$ $\qquad V_2 = 2.82$ litre

$T_1 = 273\,\text{K}$ $\qquad T_2 = 300\,\text{K}$

$\because$ $\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$

or $\frac{1\times(4.851n+2.82)}{273}=\frac{20\times 2.82}{300}$

$\therefore$ $\mathbf{n = 10}$

23. Mass of balloon = 100 kg = 10×10^4 g

$$\text{Volume of balloon}=\frac{4}{3}\pi r^3=\frac{4}{3}\times\frac{22}{7}\times\left(\frac{20}{2}\times 100\right)^3$$

$$= 4190\times 10^6\ \text{cm}^3 = 4190\times 10^3\ \text{litre}$$

$$\text{Mass of gas (He) in balloon}=\frac{PVM}{RT} \qquad \left(\because PV=\frac{w}{M}RT\right)$$

$$=\frac{1\times 4190\times 10^3\times 4}{0.082\times 300}=68.13\times 10^4\ \text{g}$$

$\therefore$ Total mass of gas and balloon

$= 68.13\times 10^4 + 10\times 10^4 = 78.13\times 10^4$ g

$$\text{Mass of air displaced}=\frac{1.2\times 4190\times 10^6}{10^3}=502.8\times 10^4\ \text{g}$$

$\therefore$ Pay load = mass of air displaced − (mass of balloon + mass of gas)

$\therefore$ Pay load $= 502.8\times 10^4 - 78.13\times 10^4 = \mathbf{424.67\times 10^4\ g}$

24. For diatomic gas

$V = 350\,\text{mL}$, $\quad P = 2\,\text{atm}$, $\quad T = 273\,\text{K}$, $\quad w = 1\,\text{g}$

$\because$ $PV=\frac{w}{m}RT$

$$2\times\frac{350}{1000}=\frac{1}{m}\times 0.0821\times 273$$

$\therefore$ Molar mass 'M' of gas = 32.02

$\therefore$ Atomic mass of gas $=\frac{\text{molar mass}}{2}=\frac{32.02}{2}=16.01$

$\therefore$ Mass of 1 atm of gas $=\frac{16.01}{6.023\times 10^{23}}=\mathbf{2.66\times 10^{-23}\ g}$

25. Suppose at $T = 27^\circ\text{C} = 300\,\text{K}$, $T_1 = 37^\circ\text{C} = 310\,\text{K}$, $V = 1$ litre, $V_1 = ?$

At constant pressure $\frac{V}{T}=\frac{V_1}{T_1}$

$$\frac{1}{300}=\frac{V_1}{310} \quad \therefore V_1=\frac{310}{300}=1.0333\ \text{litre}$$

Since, capacity of flask is 1 litre.

$\therefore$ Volume of air escaped out

$= 1.0333 - 1 = 0.0333$ litre $= \mathbf{33.3\ mL}$

26. At $T_1 = 300$ K, mole of air $= n_1$

At $T_2 = 750$ K, mole of air $= n_2$

$\because$ At constant P, V, $n_1T_1 = n_2T_2$

$\therefore$ $n_1\times 300 = n_2\times 750$ or $n_2=\frac{300}{750}\times n_1$

or $n_2 = 0.4\,n_1$

$\therefore$ Mole of air escaped out $= n_1 - n_2 = n_1 - 0.4\,n_1 = 0.6n_1$

or fraction of air escaped out $= \mathbf{0.6}$

27. (a) Initial temperature = 300 K

Let no. of mole at 300 K = n

New temperature be = T K

$\therefore$ Mole coming out at T K $=\frac{1}{3}n$

$\therefore$ Mole left at T K $= n-\frac{1}{3}n=\frac{2}{3}n$

Under constant P and V, $\quad n_1T_1 = n_2T_2$

$\therefore$ $n\times 300=\frac{2}{3}n\times T$

$\therefore$ $T = 450\,\text{K} = \mathbf{177^\circ C}$

(b) Initial temperature = 300 K

New temperature becomes = T K

Let no. of mole present at T K = n

Mole coming out at T K $=\frac{1}{3}n$

$\therefore$ No. of mole at 300 K should be $= n+\frac{1}{3}n=\frac{4n}{3}$

$\therefore$ $\frac{4n}{3}\times 300 = n\times T$

$\therefore$ $T = 400\,\text{K} = \mathbf{127^\circ C}$

28.

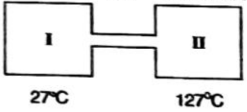
	$N_2O_4 \rightleftharpoons$	$2NO_2$
Mole present initially	1	0
Mole at eq.	$(1-0.2)$	0.4

$\therefore$ Molar mass of mixture $= \frac{0.8\times 92+0.4\times 46}{1.2} = 76.66$

Now, $PV = \frac{w}{M}RT$

or $\frac{w}{V} = \frac{PM}{RT} = \frac{76.66\times 1}{0.082\times 300} = \mathbf{3.116\ g\ litre^{-1}}$

29.



Two flasks initially at 27° C and 0.5 atm, have same volume and 0.7 mole; thus each flask has 0.35 mol.

Let n mole of gas are diffused from II to I on heating the II flask at 127° C.

$\therefore$ Mole in I flask $= (0.35+n)$

and Mole in II flask $= (0.35-n)$

Thus, if new pressure of flask is P, then

For I, $P_{new} \times V = (0.35+n)\times R\times 300$

For II, $P_{new} \times V = (0.35-n)\times R\times 400$

$\therefore$ $n = 0.05$

$\therefore$ Mole in flask I $= 0.35+0.05 = 0.40$

and Mole in flask II $= 0.35-0.05 = 0.30$

Also, $0.5\times 2V = 0.7\times 0.0821\times 300$ (initial condition)

$\therefore$ $V = 17.241$ litre

Thus, $P_{new} \times 17.241 = 0.30\times 0.0821\times 400$

$\therefore$ $P = \mathbf{0.5714\ atm}$

30. (a) Mole of gas coming out on heating

$$n = \frac{PV}{RT} = \frac{1\times 0.246}{0.0821\times 300} = 0.009987$$

Thus, mole of gas left $= \frac{7.1}{71} - 0.009987$

$= 0.1 - 0.009987 = 0.09$

Also, for 0.1 mole of gas $PV = 0.1RT$ ...(1)

for 0.09 mole of gas $PV = 0.09R(T+30)$ ...(2)

By Eqs. (1) and (2), $T = \mathbf{270\ K}$

(b) Also, if gas is not allowed to escape, then for 0.1 mole of gas

$P\times V = 0.10\times R\times 270$ ...(3)

$(P+0.11)V = 0.10\times R\times 303$ ...(4)

By Eqs. (3) and (4), $P = \mathbf{0.99\ atm}$

By Eq. (3), $0.99\times V = 0.10\times R\times 270$

$\therefore$ $V = \mathbf{2.239\ litre}$

31. Given, $V = 10$ litre, $P = 3$ atm, $T = 290$ K

(a) After driving $V = 10$ litre, $P = ?$, $T = 320$ K

$\because$ $\frac{P_1}{P_2} = \frac{T_1}{T_2}$, (at constant V of tyre)

$\frac{3}{P} = \frac{290}{320}$

$\therefore$ $P = \mathbf{3.31\ atm}$

(b) At 47° C

Now volume is to be taken out so that tyre is left at a pressure of 3 atm, *i.e.*, decrease in pressure as a result of it,

$= 3.31 - 3.0 = 0.31$ atm

At 0.31 atm volume of air is 10 litre and therefore, at 1 atm this air will occupy V litre

$\because$ $P_1V_1 = P_2V_2$ (temperature is 47° C)

$\therefore$ $0.31\times 10 = 1\times V_2$

$\therefore$ $V_2 = \mathbf{3.1\ litre}$

32. Pressure at 100 meter depth

= Atmospheric pressure + Pressure of water

$= 76\times 13.6\times 981 + 100\times 100\times 1\times 981$

$= 1013961.6 + 9810000 = 10823961.6$ dyne cm^{-2}

Let volume of balloon at the surface level be V_i cm^3 and the volume of balloon at the depth of 100 meter is V_f, then

$P_1V_1 = P_2V_2$

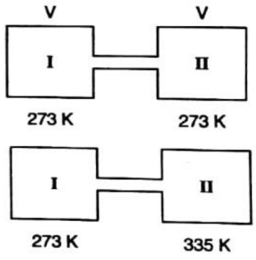
$\therefore$ $76\times 13.6\times 981\times V_i = 10823961.6\times V_f$

$\therefore$ $V_f = \frac{76\times 13.6\times 981}{10823961.6}\times V_i$

$V_f = 0.0937V_i$

$\therefore$ $V_f = \mathbf{9.37\%\ of}\ V_i$

33.



Initially when both bulbs are at 273 K, the mole in each bulb

$$= \frac{\text{Total mole}}{2} = \frac{P\cdot 2V}{2RT} = \frac{PV}{RT} = \frac{76\times V}{R\times 273} \quad ...(1)$$

On heating II bulb, some mole of gas are transferred to bulb I till the pressure in two bulbs becomes same

For bulb I, $n_1 = \frac{P_1\times V}{R\times 273}$

For bulb II, $n_2 = \frac{P_2\times V}{R\times 335}$

Since, $n = n_1 + n_2$

$\therefore$ $\frac{76\times V}{R\times 273}\times 2 = \frac{P_1\times V}{R\times 273} + \frac{P_2\times V}{R\times 335}$ Also, $P_1 = P_2$

$\therefore$ $P_1 = \mathbf{83.75\ cm\ of\ Hg}$

34. Initial mole of air present $= \frac{PV}{RT}$

$= \frac{75\times 0.7}{76\times 0.0821\times 290}$

($V = 0.2+0.5 = 0.7$ litre)

$= 0.029$

Now, let n_2 mole are present in boiling water vessel and n_1 mole in melting ice vessel

$$\therefore \quad n = 0.029 = n_1 + n_2$$

$$0.029 = \frac{P \times 0.2}{0.0821 \times 273} + \frac{P \times 0.5}{0.0821 \times 373}$$

(P remains same at equilibrium)

$$\therefore \quad P = \frac{0.029}{8.92 \times 10^{-3} + 16.33 \times 10^{-3}}$$

$$= 1.15\,\text{atm} = \mathbf{87.4\ cm\ of\ Hg}$$

35. 98.4° F can be converted to ° C as

$$\frac{F-32}{9} = \frac{C}{5}$$

$$\frac{98.4-32}{9} = \frac{C}{5}$$

$$\therefore \quad C = 36.88°\,\text{C} \quad \text{or} \quad 309.88\,\text{K}$$

Thus using, $PV = \frac{w}{M}RT$

$$\frac{168}{760} \times 6 = \frac{w}{32} \times 0.0821 \times 309.88$$

$$\therefore \quad w = \mathbf{1.67\ g}$$

36. Mole present initially in 1 L container

$$(n_1) = \frac{PV}{RT} = \frac{1000 \times 1}{760 \times 0.0821 \times 273} = 5.87 \times 10^{-2}$$

Mole present initially in 0.1 L container

$$(n_2) = \frac{PV}{RT} = \frac{1000 \times 0.1}{760 \times 0.0821 \times 273} = 5.87 \times 10^{-3}$$

$$\therefore \quad n_1 + n_2 = 5.87 \times 10^{-2} + 5.87 \times 10^{-3} = 6.46 \times 10^{-2}$$

Also, on heating the vessel of 0.1 L to 373K, let 'n' mole remain in it, then since, pressure will remain the same, then $\frac{nRT}{V}$ is constant in both

$$\frac{n \times 373}{0.1} = \frac{(6.46 \times 10^{-2} - n) \times 273}{1}$$

$$\therefore \quad n = 4.40 \times 10^{-3}$$

i.e., mole left in 0.1 litre container after heating $= 4.40 \times 10^{-3}$

$\therefore$ Mole moved from 0.1 L to 1 L vessel

$$= 5.87 \times 10^{-3} - 4.40 \times 10^{-3}$$

$$= 1.47 \times 10^{-3}$$

$\therefore$ Volume of air moved at 0° C and 760 mm

$$V = \frac{nRT}{P} = \frac{1.47 \times 10^{-3} \times 0.0821 \times 273}{1}$$

$$= \mathbf{32.9\ mL}$$

37. I flask : Volume = 2 litre, $P_{N_2} = 70\,\text{cm}, T = 293\,\text{K}$

II flask : Volume = 3 litre, $P_{O_2} = 100\,\text{cm}, T = 293\,\text{K}$

Before mixing

$$\text{Mole of } N_2 = \frac{PV}{RT} = \frac{70 \times 2}{76 \times 0.0821 \times 293} = 7.658 \times 10^{-2}$$

$$\text{Mole of } O_2 = \frac{PV}{RT} = \frac{100 \times 3}{76 \times 0.0821 \times 293} = 16.41 \times 10^{-2}$$

After mixing total volume becomes 5 litre.

$$\therefore P'_{N_2} = \frac{nRT}{V} = \frac{7.658 \times 10^{-2} \times 0.0821 \times 293}{5} = 0.368\,\text{atm}$$

$$P'_{O_2} = \frac{nRT}{V} = \frac{16.41 \times 10^{-2} \times 0.0821 \times 293}{5} = 0.79\,\text{atm}$$

$$\therefore \quad P_M = P'_{N_2} + P'_{O_2} = 0.368 + 0.79 = \mathbf{1.158\ atm}$$

$$\text{Mole \% of } N_2 = \frac{7.658 \times 10^{-2}}{(7.658 + 16.41) \times 10^{-2}} \times 100 = \mathbf{31.8\%}$$

$$\therefore \quad \text{Mole \% of } O_2 = \mathbf{68.2\%}$$

38. Given, $V = 10$ litre, $T = 27 + 273 = 300\,\text{K}$

$$\text{Mole of He} = \frac{0.4}{4} = 0.10$$

$$\text{Mole of } O_2 = \frac{1.6}{32} = 0.05$$

$$\text{Mole of } N_2 = \frac{1.4}{28} = 0.05$$

$$\therefore \quad \text{Total mole} = 0.10 + 0.05 + 0.05 = 0.20$$

$$P_M = \frac{nRT}{V} = \frac{0.20 \times 0.082 \times 300}{10} = 0.492\,\text{atm}$$

$$P'_{He} = P_M \times \text{mole fraction of He} = 0.492 \times \frac{0.10}{0.20}$$

$$= \mathbf{0.246\ atm}$$

$$P'_{O_2} = P_M \times \text{mole fraction of } O_2 = 0.492 \times \frac{0.05}{0.20}$$

$$= \mathbf{0.123\ atm}$$

$$P'_{N_2} = P_M \times \text{mole fraction of } N_2 = 0.492 \times \frac{0.05}{0.20}$$

$$= \mathbf{0.123\ atm}$$

39. Given, mass of CH_4 = mass of $O_2 = w\,\text{g}$, $V = 1$ litre, $T = 300\,\text{K}$

(a) $\text{Mole fraction of } CH_4 = \frac{w/16}{w/16 + w/32} = \frac{2}{3}$

$$\text{Mole fraction of } O_2 = \frac{w/32}{w/16 + w/32} = \frac{1}{3}$$

$$\because \quad P'_{O_2} = P_M \times \text{mole fraction of } O_2$$

(Dalton's law of partial pressure)

$$\therefore \quad \frac{P'_{O_2}}{P_M} = \text{mole fraction of } O_2 = \frac{1}{3}$$

(b) $P'_{CH_4} \times 1 = (32/16) \times 0.0821 \times 300 = 49.26\,\text{atm}$

$$P'_{O_2} \times 1 = (32/32) \times 0.0821 \times 300 = 24.63\,\text{atm}$$

$$\therefore \quad P_M = P'_{CH_4} + P'_{O_2} = 49.26 + 24.63 = \mathbf{73.89\ atm}$$

40. Given, mass of gas $A = 0.50\,\text{g}$, Molar mass of gas $A = 60$ mass of gas $B = 0.2\,\text{g}$, Molar mass of gas $B = 45$

$$P_M = 750\,\text{mm}$$

From Dalton's law of partial pressure

$$P'_A = P_M \times \text{mole fraction of } A$$

$$= 750 \times \frac{0.5/60}{\left(\frac{0.5}{60}\right) + \left(\frac{0.2}{45}\right)} = \mathbf{489.23\ mm}$$

Now, $P_M = P'_A + P'_B$

$$\therefore \quad P'_B = P_M - P'_A = 750 - 489.23 = \mathbf{260.77\ mm}$$

41. $w = 20\,\text{g}$ dry CO_2 which will evaporate to develop P.

$M = 44\,\text{g mol}^{-1}$, $V = 0.75$ litre, $P = ?$, $T = 298\,\text{K}$

$$\because \quad PV = \frac{w}{M}RT$$

$$P \times 0.75 = \frac{20}{44} \times 0.0821 \times 298$$

$$\therefore \quad P = \mathbf{14.828\ atm}$$

NOTE : Pressure inside the bottle $= P + \text{atm. pressure}$

$= 14.828 + 1 = \mathbf{15.828\ atm}$

42. Let mass of $O_2 = w_1$

mass of $N_2 = w_2$

$\because$ Given, $\frac{w_1}{w_2} = \frac{1}{4}$

Also, Mole of $O_2 = \frac{w_1}{32}$

Mole of $N_2 = \frac{w_2}{28}$

$$\therefore \quad \frac{\text{Mole of } O_2}{\text{Mole of } N_2} = \frac{w_1}{32} \times \frac{28}{w_2} = \frac{28}{32} \times \frac{1}{4} = \mathbf{\frac{7}{32}} \quad \left(\because \frac{w_1}{w_2} = \frac{1}{4}\right)$$

43. The water vapours occupy the volume of N_2 gas, *i.e.*, 50 litre.

$\therefore$ For H_2O vapour $V = 50$ litre, $w = 1.20$g, $T = 300$K, $m = 18$

$$\because \quad PV = \frac{w}{M}RT$$

$$P \times 50 = \frac{1.2}{18} \times 0.0821 \times 300$$

$$P = 0.03284 \text{ atm}$$

$$= \mathbf{24.95\ mm}$$

44. According to Dalton's law of partial pressure,

Given, $P_M = 740$ mm, $P_{H_2O} = 18$ mm

$$P_M \text{ or } P_{\text{wet } O_2} = P_{O_2} + P_{H_2O}$$

$$740 = P_{O_2} + 18$$

$$\therefore \quad P_{O_2} = \mathbf{722\ mm}$$

45. Partial pressure of O_2, $P'_{O_2} = P_m \times$ mole fraction

Since, $P_m = 1$ atm (given, NTP condition)

$\therefore \quad P'_{O_2} = 1 \times$ mole fraction ...(1)

For mixture $PV = \frac{w}{M}RT$

$$\therefore \quad M = \frac{w}{VP}RT$$

$$M = \frac{1.3 \times 0.0821 \times 273}{1} \quad \left(\because \frac{w}{V} = 1.3 \text{ g L}^{-1}\right)$$

$\therefore$ Molar mass of mixture $= 29.137 \text{ g mol}^{-1}$

If n_1 and n_2 are mole of O_2 and N_2 respectively,

Now,
$$\frac{32 \times n_1 + 28 \times n_2}{(n_1 + n_2)} = 29.137$$

$$\frac{28n_1 + 28n_2}{n_1 + n_2} + \frac{4n_1}{n_1 + n_2} = 29.137$$

$$\therefore \quad \frac{n_1}{n_1 + n_2} = \frac{29.137 - 28}{4} = 0.28$$

$\therefore$ Mole fraction of $O_2 = 0.28$

$\therefore$ By Eq. (1), $P'_{O_2} = \mathbf{0.28\ atm}$

46. Mass of liquid $= 148 - 50 = 98$ g

Volume of liquid $= \frac{98}{0.98} = 100$ mL = volume of vessel

Thus, a vessel of 100 mL contains ideal gas at 760 mm of Hg at 300 K.

Mass of gas $= 50.5 - 50 = 0.5$ g

Using, $PV = nRT$

$$\frac{760}{760} \times \frac{100}{1000} = \frac{0.5}{m} \times 0.0821 \times 300$$

$\therefore$ Molar mass of gas $(m) = \mathbf{123}$

47. At T K, $P_{\text{gas}} = P_{\text{dry gas}} + P_{\text{moisture}}$

$$\therefore \quad P_{\text{dry gas}} = 830 - 30 = 800 \text{ mm}$$

Now at new temperature $T_1 = T - \frac{T}{100} = 0.99T$

Since, $V_1 = V_2$; $\frac{P}{T} = \text{constt.}$

$$\therefore \quad P_{\text{dry gas}} = \frac{800 \times 0.99T}{T} = 792 \text{ mm}$$

$\therefore \quad P_{\text{gas}} = P_{\text{dry gas}} + P_{\text{moisture}} = 792 + 25 = \mathbf{817\ mm\ of\ Hg}$

48. Given, mass of gas $A = 2$ g

Pressure of $A = 1$ atm, $T = 298$ K

Now another gas is introduced

mass of gas $B = 3$ g

Pressure of mixture $= 1.5$ atm

From Dalton's law of partial pressure

$$P_M = P'_A + P'_B$$

$$1.5 = 1.0 + P'_B$$

$$P'_B = 0.5 \text{ atm}$$

(a) For gas A, $P'_A \times V = \frac{2}{M_A} \times RT$

For gas B, $P'_B \times V = \frac{3}{M_B} \times RT$

$$\therefore \quad \frac{P'_A}{P'_B} = \frac{2}{3} \times \frac{M_B}{M_A}$$

$$\therefore \quad \frac{M_A}{M_B} = \frac{2}{3} \times \frac{P'_B}{P'_A} = \frac{2}{3} \times \frac{0.5}{1.0} = \mathbf{\frac{1}{3}}$$

(b) If A is O_2, molar mass of $O_2 = 32$

$$\therefore \quad P'_A \times V = \frac{2}{32} \times 0.0821 \times 298$$

$$1 \times V = \frac{2}{32} \times 0.0821 \times 298$$

$$V = \mathbf{1.529\ litre}$$

49. Average molar mass $= \frac{35n_1 + 37n_2}{n_1 + n_2} = 35.45$

where, n_1 and n_2 are mole of Cl^{35} and Cl^{37} isotopes.

$$\therefore \quad \frac{n_1}{n_2} = \mathbf{3.44}$$

$$\because \quad P \times V_1 = n_1RT$$

$$P \times V_2 = n_2RT$$

$$\therefore \quad \frac{V_1}{V_2} = \frac{n_1}{n_2}$$

Now volume ∝ mole, when other things being equal and thus partition should be made at the point where mole ratio is 3.44 : 1. Pressure at this condition is **same** as the original pressure ($\because V, T, n$ are constant).

50. $P_{w\,air} = 760$ mm at 285 K,

$\therefore \quad P_{air} = 760 - 10.5 = 749.5$ mm Hg

$P_{w\,air} = 760$ mm at 308 K, $\therefore P_{air} = 760 - 42 = 718$ mm Hg

Length of the air = 10 cm at 285 K

$\therefore$ Volume of the air $= 10 \times a$ (where, a is area of tube)

Let h be the length of air column at 308 K

$$\therefore \quad 718 \times h \times a = n \times R \times 308$$

$$749.5 \times 10 \times a = n \times R \times 285$$

$$\therefore \quad h = \frac{308}{285} \times \frac{749.5 \times 10}{718}$$

$$= \mathbf{11.28\ cm}$$

51. Given, $P = 10^{-16}$ mm, $V = 1$ litre, $T = 273 - 120 = 153$

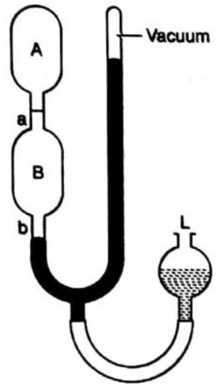
$$\because \quad PV = nRT$$

$$\therefore \quad n = \frac{PV}{RT} = \frac{10^{-16} \times 1}{760 \times 0.0821 \times 153} = 1.05 \times 10^{-20}$$

$\therefore$ Number of Hg-atom $= 6.023 \times 10^{23} \times 1.05 \times 10^{-20}$

$= \mathbf{6324}$ **atom per litre**

52.



Pressure of He = 20.14 mm

Temperature of He = 273 + 30.2 = 303.2 K

Volume of He $= 110 + 100.5 = 210.5\,\text{cm}^3$

$$\because \quad PV = nRT = \frac{w}{M}RT$$

$$\therefore \quad w = \frac{PVM}{RT}$$

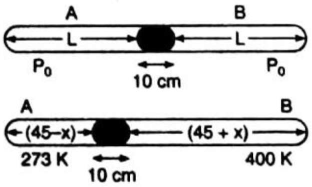
$$= \frac{20.14 \times 210.5 \times 4}{760 \times 0.0821 \times 303.2 \times 1000}$$

$$w_{He} = \mathbf{8.96 \times 10^{-4}\ g}$$

53. According to problem

Initially $2L + 10 = 100$

$$\therefore \quad L = 45\,\text{cm}$$



Let initial pressure be P_0 atm on each side. When one end is cooled and other is heated, expansion of gas occurs at hoter end till the pressure on two sides becomes same. Let Hg column is displaced by x cm to cooler end,

i.e., $P_1 = P_2 = P$

Now **for end** A: $\dfrac{P_0 \times 45 \times a}{300} = \dfrac{P_1\,(45 - x) \times a}{273}$ ...(1)

because mole of gas remains same at 273 and 300 K; a is area of cross-section of tube.

For end B: $\dfrac{P_0 \times 45 \times a}{300} = \dfrac{P_2\,(45 + x) \times a}{400}$ ...(2)

Evaluating P_1 and P_2 from Eqs. (1) and (2) and since

$$P_1 = P_2$$

$$\therefore \quad \frac{273 \times 45 \times P_0}{300 \times (45 - x)} = \frac{400 \times 45 \times P_0}{300 \times (45 + x)}$$

$$\therefore \quad x = \mathbf{8.49\ cm}$$

Thus, length of air column at 0°C

$= 45 - 8.49 = \mathbf{36.51\ cm}$

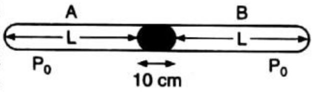
Length of air column at $127°\,\text{C} = 45 + 8.49 = \mathbf{53.49\ cm}$

Also, pressure $(P) = P_1 = \dfrac{273 \times 45 \times 76}{300 \times 36.51} = \mathbf{85.25\ cm\ of\ Hg}$

54. Let initially the length of air column on each side be L, then

$$2L + 10 = 100$$

$$\therefore \quad L = 45\,\text{cm}$$



If the tube is held vertically, let the Hg column be displaced downwards by y to attain same pressure above and below the column of Hg. Then,

$$P_B + 10 = P_A \qquad ...(1)$$

Pressure are taken in terms of length of Hg.

For end A: Since mole remains same on two sides

$$\frac{P_0 \times L \times a}{RT} = \frac{P_A \times (L - y) \times a}{RT} \qquad ...(2)$$

$$\therefore \quad P_A = \frac{LP_0}{(L - y)} \qquad ...(3)$$

For end B:

$$\frac{P_0 \times L \times a}{RT} = \frac{P_B \times (L + y) \times a}{RT} \qquad ...(4)$$

$$\therefore \quad P_B = \frac{LP_0}{(L + y)} \qquad ...(5)$$

By Eqs. (1), (3) and (5)

$$\left[\frac{LP_0}{L + y}\right] + 10 = \frac{LP_0}{(L - y)}$$

Putting $L = 45$ cm and $P_0 = 76$ cm

$$y^2 + 684y - (45)^2 = 0$$

$$\therefore \quad y = \mathbf{3\ cm}$$

55. Case I, at 300 K :

Let pressure in upper half be P_1 and lower half be P_2. Also P_0 is pressure of piston

At equilibrium $\quad P_2 = P_0 + P_1 \qquad ...(1)$

Let volume of cylinder be V litre

$\therefore$ Volume of upper half $= \frac{4V}{5}$

and Volume of lower half $= \frac{V}{5}$

Also in the two parts of cylinder, each part contains 1 mole at 300 K and thus,

$$P_1 \times \frac{4V}{5} = P_2 \times \frac{V}{5}$$

$$\therefore \quad \frac{P_2}{P_1} = 4 \qquad \text{...(2)}$$

By Eqs. (1) and (2), $\quad P_1 = \frac{P_0}{3} \qquad$ ...(3)

Case II, at T K :

Now the temperature becomes T at which volume of upper half is $\frac{3V}{4}$ and lower half is $\frac{V}{4}$.

Again $\quad P_1' \times \frac{3V}{4} = P_2' \times \frac{V}{4}$

$$\therefore \quad \frac{P_2'}{P_1'} = 3 \qquad \text{...(4)}$$

By Eqs. (1) and (4), $\quad P_1' = \frac{P_0}{2} \qquad$ ...(5)

Now using $PV = nRT$ for upper parts of cylinder at 300 K and T K

$$P_1 \times \frac{4V}{5} = 1 \times R \times 300$$

Case I upper part

$$P_1' \times \frac{3V}{4} = 1 \times R \times T$$

Case II upper part

$$\therefore \quad \frac{P_1}{P_1'} \times \frac{16}{15} = \frac{300}{T} \qquad \text{...(6)}$$

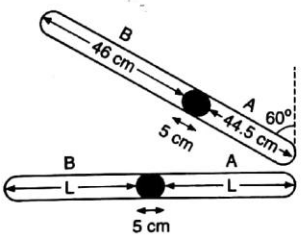
Using Eqs. (3) and (5) in Eq. (6), $\frac{2}{3} \times \frac{16}{15} = \frac{300}{T}$

$$\therefore \quad T = \frac{300 \times 3 \times 15}{2 \times 16} = \mathbf{421.875\ K}$$

56. Let initially the length of air column in tube be L cm, then

$$2L + 5 = 46 + 5 + 44.5$$

$$\therefore \quad L = 45.25\,\text{cm}$$



When the tube is held vertically at 60°, the Hg will be displaced to lower end, so that

$$P_B + 5\cos 60^\circ = P_A$$

or $\quad P_A - P_B = 5 \times \frac{1}{2} = \frac{5}{2} = 2.5\,\text{cm of Hg} \qquad$ ...(1)

For end A : $\frac{P_0 \times a \times 45.25}{RT} = \frac{P_A \times 44.5 \times a}{RT}$

$$\therefore \quad P_A = \frac{45.25}{44.5} \times P_0 \qquad \text{...(2)}$$

For end B : $\frac{P_0 \times a \times 45.25}{RT} = \frac{P_B \times a \times 46}{RT}$

$$\therefore \quad P_B = \frac{45.25}{46} \times P_0 \qquad \text{...(3)}$$

Also by Eqs. (1), (2) and (3) $P_0 = \mathbf{75.4\ cm\ of\ Hg}$

57. The mole of air contained in bubble at the bottom of tank as well as on the surface remains same.

$$\text{Thus,} \quad n = \underset{\text{At bottom of the tank}}{\frac{P_1V_1}{RT_1}} = \underset{\text{At the surface}}{\frac{P_2V_2}{RT_2}}$$

or $\quad \frac{3 \times \frac{4}{3}\pi \times (0.5)^3}{R \times 278} = \frac{1 \times \frac{4}{3}\pi r^3}{R \times 298}$

$$\therefore \quad r = \mathbf{0.74\ cm}$$

58. Given, $\quad P_{N_2} + P_{H_2O} = 760\,\text{mm}$

H_2O is dried by drying agent and left pressure stands for N_2.

Thus, $\quad P_{N_2} = 745\,\text{mm}$

$\therefore \quad P_{H_2O} = 760 - 745 = 15\,\text{mm}$

(a) Since, $P_{N_2} = P_M \times$ mole fraction of N_2

$\therefore$ Mole fraction of $N_2 = \frac{745}{760} = 0.9803$

or % mole fraction of $N_2 = \mathbf{98.03\%}$

$\therefore$ % mole fraction of $H_2O = \mathbf{1.97\%}$

(b) The mass of H_2O in mixture = increase in mass of drying agent

$$= 0.15\,\text{g}$$

$\therefore$ Mole of $H_2O\,(n) = \frac{0.15}{18}$

Now use $PV = nRT$ for water vapours, in a flask of volume V.

$$\frac{15}{760} \times V = \frac{0.15}{18} \times 0.0821 \times 293$$

$$(\because T = 273 + 20 = 293\,\text{K})$$

$\therefore \quad V = \mathbf{10.16\ litre}$

59.

	$N_2 \rightleftharpoons$	$2N$
Initial mole	$\frac{1.4}{28}$	0
Mole after dissociation	$\frac{1.4}{28} \times \frac{70}{100}$	$\frac{1.4}{28} \times \frac{2 \times 30}{100}$

$$\therefore \quad \text{Total mole} = \frac{1.4}{28} \times \frac{70}{100} + \frac{1.4 \times 60}{100 \times 28} = \frac{1.4}{28} \times \left[\frac{130}{100}\right]$$

$$\therefore \quad P \times 5 = \frac{1.4 \times 130}{28 \times 100} \times 0.0821 \times 1800$$

$$\therefore \quad P = \mathbf{1.92\ atm}$$

60. Initially at **lower end :**

$P = 76\,\text{cm of Hg} + 76\,\text{cm of air} = 152\,\text{cm}, T = 300\,\text{K}, V = \frac{V_1}{2}$

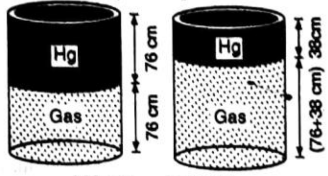
where V_1 is volume of cylinder

Finally at lower end :

$P = 76$ cm of air + 38 cm of Hg = 114 cm, $T = ?$,

$V = \frac{3V_1}{4}$

$$\therefore \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

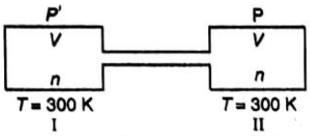


$$\frac{152 \times V_1}{2 \times 300} = \frac{114 \times 3V_1}{4 \times T}$$

$$\therefore \quad T = \frac{114 \times 3 \times 2 \times 300}{152 \times 4}$$

$$= \mathbf{337.5\ K}$$

61.



$P_T = 105 \times 10^3$ Pa

Let each vessel contains n, mole initially since, both are at same conditions.

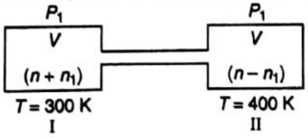
$$P' \times V = nR \times 300 \quad ...(1)$$

$$P \times V = nR \times 300 \quad ...(2)$$

$$P' + P = P_T = 105 \times 10^3 \text{ Pa}$$

$$\therefore \quad 2n \times R \times 300 = 105 \times 10^3 \times V \quad ...(3)$$

On putting one vessel at 400 K, mole from this vessel will move to the vessel at 300 K. Let n_1 mole move from II vessel to I. Also pressure in two vessel will be same.



$$P_1 \times V = (n + n_1) \times R \times 300 \quad n > n_1 \quad ...(4)$$

$$P_1 \times V = (n - n_1) \times R \times 400 \quad ...(5)$$

$$\therefore \quad \frac{n + n_1}{n - n_1} = \frac{400}{300}$$

$$300n + 300n_1 = 400n - 400n_1$$

$$n_1 = \frac{1}{7}n$$

Vessel I has, $n + \frac{n}{7}$ mole $= \frac{8n}{7}$

Vessel II has, $n - \frac{n}{7}$ mole $= \frac{6n}{7}$

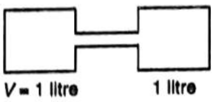
$\therefore$ Ratio of mole in vessel I and II $= \frac{8}{6} = \frac{4}{3}$

By Eqs. (3) and (4) $\frac{2n \times R \times 300}{8\frac{n}{7} \times R \times 300} = \frac{105 \times 10^3 \times V}{P_1 \times V}$

$$\therefore \quad P_1 = \frac{105 \times 10^3 \times 8}{2 \times 7} = 60000 \text{ Pa}$$

$\therefore$ Total pressure $= 2P_1 = 2 \times 60000 = 120000$ Pa = **120 kPa**

62.



The aqueous tension remains same in both the flask. Also flasks are at same temperature.

Thus, $\underset{\text{(Initially)}}{P_1V_1} = \underset{\text{(Finally)}}{P_2V_2}$

Initial pressure of gas $P_1 = 200 - 93 = 107$ mm

Final pressure of gas $= P$

$\therefore \quad 107 \times 1 = P \times 2 \quad \therefore \quad P = \frac{107}{2} = 53.5$ mm

Since, aqueous tension or P'_{H_2O}, is also present in flasks, equivalent to 93 mm.

$\therefore$ Pressure of gaseous mixture $= 93 + 53.5 =$ **146.5 mm**

63. $P_{\text{wet air}} = 760$ mm at 298 K

$P_{\text{dry air}} = 760 - 24 = 736$ mm at 298 K

Now $\frac{P_1}{P_2} = \frac{T_1}{T_2}$ (The temperature is raised to 100° C)

$$\frac{P_1}{736} = \frac{373}{298}$$

$$\therefore \quad P_1 = 921.23 \text{ mm Hg}$$

$P_{\text{wet air}}$ at 100° C $= P_1 + P_{H_2O}$ at 373 K $= 921.23 + 760$

$= \mathbf{1681.23\ mm\ Hg}$

64. Using $PV = \frac{w}{M}RT$

[For saturation vapour pressure of water $= 3.6 \times 10^3$ Pa, $V = 1$ litre $= 1 \times 10^{-3}$ m^3]

$$3.6 \times 10^3 \times 10^{-3} = \frac{w_{H_2O}}{18} \times 8.314 \times 300$$

$$\therefore \quad w_{H_2O} = 0.026 \text{ kg} = 26 \text{ g}$$

Since, relative humidity is 50%.

Thus, mass of water vapour is $= 26 \times 0.5 =$ **13 g**

65. For dry air: $P_{(N_2 + O_2)} = 760$ mm

$$\therefore \quad P_{N_2} = \frac{760 \times 79}{100} = 600.40 \text{ mm}$$

$$P_{O_2} = \frac{760 \times 21}{100} = 159.60 \text{ mm}$$

Let volume be 1 litre, then

mole of $N_2 = \frac{PV}{RT} = \frac{600.4 \times 1}{760 \times 0.0821 \times 298} = 3.23 \times 10^{-2}$

mole of $O_2 = \frac{159.6 \times 1}{760 \times 0.0821 \times 298} = 8.58 \times 10^{-3}$

$\therefore$ Density of dry air = mass of dry air in one litre

$= 3.23 \times 10^{-2} \times 28 + 8.58 \times 10^{-3} \times 32$

$= 90.44 \times 10^{-2} + 27.46 \times 10^{-2}$

$= \mathbf{1.179\ g / litre}$

For moist air:

$\therefore$ Partial pressure of water $= \frac{60}{100} \times 23.76 = 14.3$ mm

$\therefore$ Partial pressure of $(N_2 + O_2) = 760 - 14.3 = 745.7$ mm

$$\therefore \quad P_{N_2} = 745.7 \times \frac{79}{100} = 589.1 \text{ mm}$$

$$\therefore \quad P_{O_2} = 745.7 \times \frac{21}{100} = 156.6 \text{ mm}$$

Let the volume be 1 litre, then

Mole of water vapours

$$(n_1) = \frac{PV}{RT} = \frac{14.3 \times 1}{760 \times 0.082 \times 298} = 7.7 \times 10^{-4}$$

$$\text{Mole of } N_2 \ (n_2) = \frac{589.1 \times 1}{760 \times 0.082 \times 298} = 3.17 \times 10^{-2}$$

$$\text{Mole of } O_2 \ (n_3) = \frac{156.6 \times 1}{760 \times 0.082 \times 298} = 8.43 \times 10^{-3}$$

$\therefore$ Total mass in one litre

$$= 7.7 \times 10^{-4} \times 18 + 3.17 \times 10^{-2} \times 28 + 8.43 \times 10^{-3} \times 32 = 1.171 \text{ g}$$

$\therefore$ Density of moist air at 25° C $=$ **1.171 g litre^{-1}**

66. Given volume of container = 0.731 mL

Temperature = 23 + 273 = 296 K

$$P_{H_2O_v} + P_{CO_2} + P_{N_2} = 1.74 \text{ mm} \quad ...(1)$$

When H_2O_v is frozen out, the pressure exists for CO_2 and N_2 and therefore,

$$P_{CO_2} + P_{N_2} = 1.32 \text{ mm} \quad ...(2)$$

When CO_2 is frozen out, the pressure exist for N_2 only and therefore,

$$P_{N_2} = 0.53 \text{ mm} \quad ...(3)$$

By Eqs. (1), (2) and (3),

$$P_{CO_2} = 0.79 \text{ mm}, \qquad P_{H_2O_v} = 0.42 \text{ mm}$$

Now for N_2, $PV = nRT$

$$\therefore \quad n = \frac{PV}{RT} = \frac{0.53 \times 0.731}{760 \times 1000 \times 0.0821 \times 296} = \mathbf{2.1 \times 10^{-8}}$$

Similarly for CO_2 $\quad n = \mathbf{3.1 \times 10^{-8}}$

and H_2O $\quad n = \mathbf{1.7 \times 10^{-8}}$

67. Given, pressure of $N_2 = 0.965$ atm

Volume of $N_2 = 10$ litre, $\quad$ Temperature of $N_2 = 298$ K

$\therefore$ For N_2 when bag is fully expanded,

Volume of N_2 (alone) = 30 litre at 298 K

$$\because \quad P_1V_1 = P_2V_2$$

$$0.965 \times 10 = P_2 \times 30$$

$\therefore$ P_{N_2} (alone) in 30 litre bag at 298 K = 0.322 atm

Now

$$P_M = P_{O_2} + P_{N_2}$$

$$0.990 = P_{O_2} + 0.322$$

$$\therefore \quad P_{O_2} = \mathbf{0.668 \text{ atm}}$$

68.

$$P_{N_2} + P_{NO} + P_{NO_2} = 3.0 \text{ cm} \quad ...(1)$$

$$P_{N_2} + P_{NO} + P'_{H_2O} = 2.42 \text{ cm} \quad ...(2)$$

(H_2O absorbs NO_2 and P'_{H_2O} exist in gases)

$$P_{N_2} + P'_{2H_2O} = 1.24 \text{ cm} \quad ...(3)$$

($FeSO_4$ absorbs NO and P'_{2H_2O} exists in gases)

Given $\quad P'_{1H_2O} = 0.2 \text{ cm}$ and $P'_{2H_2O} = 0.18 \text{ cm}$

$\therefore$ By Eq. (3) $\quad P_{N_2} = 1.24 - 0.18 = 1.06 \text{ cm} \quad ...(4)$

By Eq. (2) and (3) $\quad P_{NO} = 2.42 - 1.06 - 0.2 = 1.16 \text{ cm}$

$$P_{NO_2} = 3.0 - 1.06 - 1.16 = 0.78 \text{ cm}$$

$$\therefore \quad \text{Mole \% of } N_2 = \frac{1.06}{3} \times 100 = \mathbf{35.33}$$

$$\text{Mole \% of NO} = \frac{1.06}{3} \times 100 = \mathbf{38.67}$$

$$\text{Mole \% of } NO_2 = \frac{0.78}{3} \times 100 = \mathbf{26.00}$$

69.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Mole	1.04	$\frac{20}{32}$	0
			(Before reaction)
Mole	0	$\left(\frac{20}{32} - \frac{1.04}{2}\right)$	1.04
			(After reaction)

$$\therefore \quad \text{Total mole before reaction} = 1.04 + \frac{20}{32} = 1.665$$

$$\text{Total mole after reaction} = \frac{20}{32} - \frac{1.04}{2} + 1.04 = 1.145$$

$\therefore$ Change in no. of mole during reaction

$$= 1.665 - 1.145 = 0.520$$

$\therefore$ Change in pressure

$$= \frac{\Delta nRT}{V} = \frac{0.52 \times 0.0821 \times 300}{20} = \mathbf{0.64 \text{ atm}}$$

70. Given reaction is $\quad 2H_2 + O_2 \longrightarrow 2H_2O(l)$

Volume before reaction	a	b	0
Volume after reaction	$(a - 2b)$	0	

Since at constant P and T, gases react in their volume ratio

Given $\quad a + b = 40, \quad a - 2b = 10$

$\therefore \quad a = 30$ mL, $\quad b = 10$ mL

Therefore, mole % of H_2

$$= \text{Volume \% of } H_2 = \frac{30}{40} \times 100 = \mathbf{75\%}$$

71.

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

(a) Since no. of mole after reaction $(n_2) = 2\times$ no. of mole before reaction (n_1) at same T and V, $P \propto n$

$$\therefore \quad \frac{P_1}{P_2} = \frac{n_1}{n_2} = \frac{1}{2}$$

$\therefore$ Pressure after reaction $=$ **2 atm**

(b) Given for NH_3, $p = 1$ atm, $V = 1$ litre, $T = 298$ K

$$\therefore \quad \text{Mole of } NH_3 = \frac{PV}{RT} = \frac{1 \times 1}{0.0821 \times 298} = 4.087 \times 10^{-2}$$

$$\therefore \quad \text{Mole of } N_2 \text{ formed} = \text{Mole of } NH_3 \times \frac{1}{2}$$

$$= \frac{4.087 \times 10^{-2}}{2} = \mathbf{2.0435 \times 10^{-2}}$$

$$\therefore \quad \text{Mole of } H_2 \text{ formed} = \text{Mole of } NH_3 \times \frac{3}{2}$$

$$= \frac{4.087 \times 10^{-2} \times 3}{2} = \mathbf{6.1305 \times 10^{-2}}$$

72. **For NO :** $V = 250\,\text{mL};\ T = 300\,\text{K};\ P = 1.053\,\text{atm}$

$$\therefore n_{NO} = \frac{PV}{RT} = \frac{1.053 \times 250}{0.0821 \times 300 \times 1000} = 1.069 \times 10^{-2}$$

For O_2 : $V = 100\,\text{mL};\ T = 300\,\text{K};\ P = 0.789\,\text{atm}$

$$\therefore \quad n_{O_2} = \frac{0.789 \times 100}{0.0821 \times 300 \times 1000} = 0.32 \times 10^{-2}$$

Now	$2NO$	+	O_2	$\longrightarrow$	N_2O_4
Mole before reaction	1.069×10^{-2}		0.32×10^{-2}		0
Mole after reaction	$(1.069 \times 10^{-2} - 2 \times 0.32 \times 10^{-2})$ $= 0.429 \times 10^{-2}$		0		0.32×10^{-2}

$\therefore$ Mole of NO left $= \mathbf{4.29 \times 10^{-3}}$

$$P_{NO} \times V = nRT$$

Given $T = 220\,\text{K}$, $\quad V = \frac{250 + 100}{1000} = \frac{350}{1000}$ litre

$$P_{NO} \times \frac{350}{1000} = 4.29 \times 10^{-3} \times 0.0821 \times 220$$

$$\therefore \quad P_{NO} \text{ left} = \mathbf{0.221\ atm}$$

73. Since A and A_2 are two states in gaseous phase having their mass ratio 50%, *i.e.*, 1 : 1

$$\therefore \quad \text{Mole of } A = \frac{96}{2} \times \frac{1}{48} = 1 \qquad \left(n = \frac{w}{m}\right)$$

$$\text{Mole of } A_2 = \frac{96}{2} \times \frac{1}{96} = \frac{1}{2}$$

$\therefore$ Total mole of A and A_2 are $= 1 + \frac{1}{2} = \frac{3}{2}$

Thus, $\quad PV = nRT$

$$P \times 33.6 = \frac{3}{2} \times 0.0821 \times 546$$

$$\therefore \quad P = \mathbf{2\ atm}$$

74.	Cl_2	+	Cl_2O_n	$\longrightarrow$	$2Cl_2$	+	$(n/2)O_2$
Before reaction	30 mL		30 mL		0		0
After reaction	0		0		60 mL		$15n$ mL

The volume of O_2 = Volume left after passing mixture through KOH (KOH absorbs Cl_2)

$$= 5$$

$$\therefore \quad 15n = 15$$

$$\therefore \quad n = 1$$

$\therefore$ Formula of $Cl_2O_n = \mathbf{Cl_2O}$

75.	$2H_2$	+	O_2	$\longrightarrow$	$2H_2O(g)$
Volume before reaction in litre	1		1		0
Volume after reaction in litre	0		0.5		1

(a) Mole of H_2O formed

$$= \frac{PV}{RT} = \frac{1 \times 1}{0.821 \times 273} = \mathbf{4.46 \times 10^{-2}}$$

$\therefore$ Mass of H_2O formed

$$= 4.46 \times 10^{-2} \times 18 = \mathbf{8.03 \times 10^{-1}\ g}$$

(b) Gas left is $O_2 = 0.5$ litre at STP $= \mathbf{2.23 \times 10^{-2}}$ **mole**

$\therefore$ Mass of O_2 left $= \frac{32 \times 0.5}{22.4}\,\text{g} = \mathbf{0.7143\ g}$

(c) At 100° C H_2O also exists as vapours

$\therefore$ Total mole present at 100° C

= mole of H_2O formed + mole of O_2 left

$= 4.46 \times 10^{-2} + 2.23 \times 10^{-2} = 6.69 \times 10^{-2}$

Volume of vessel = 2 litre

$$\therefore \quad P = \frac{nRT}{V} = \frac{6.69 \times 10^{-2} \times 0.0821 \times 373}{2} = \mathbf{1.02\ atm}$$

(d) Volume of O_2 used for formation of $H_2O = 0.5$ litre

$\therefore$ Mole of O_2 used for formation of H_2O

$$= \frac{0.5}{22.4} = \mathbf{2.23 \times 10^{-2}}$$

76. Mol. mass of mixture $= \frac{30 \times 4 + 20 \times 32 + 50 \times 28}{100} = 21.60$

Also, rate of diffusion in terms of change of P/sec for Ne = 0.3 torr/sec

Let rate of diffusion in terms of change of P/sec for mixture be $= r_2$ torr/sec

$$\therefore \quad \frac{0.3}{r_2} = \sqrt{\frac{21.60}{20}}$$

$$\text{or} \quad r_2 = \mathbf{0.289\ torr/sec}$$

77.

$$\frac{r_1}{r_2} = \frac{V_1}{t_1} \times \frac{t_2}{V_2} = \sqrt{\left(\frac{M_2}{M_1}\right)}$$

$$\text{or} \quad \frac{20}{60} \times \frac{30}{V} = \sqrt{\left(\frac{32}{64}\right)}$$

$$\therefore \quad V = \mathbf{14.14\ dm^3}$$

78. For gaseous mixture 80% O_2, 20% gas

$\therefore$ Average molar mass of mixture $(M_m) = \frac{32 \times 80 + 20 \times m}{100}$ ...(1)

Now for diffusion of gaseous mixture and pure O_2

$$\frac{r_{O_2}}{r_m} = \sqrt{\left(\frac{M_m}{M_{O_2}}\right)}$$

$$\text{or} \quad \frac{V_{O_2}}{t_{O_2}} \times \frac{t_m}{V_m} = \sqrt{\left(\frac{M_m}{M_{O_2}}\right)} \qquad (\because \text{ same volume diffuses})$$

$$\therefore \quad \frac{1}{224} \times \frac{234}{1} = \sqrt{\left(\frac{M_m}{32}\right)}$$

$$M_m = 34.92 \qquad \text{...(2)}$$

By Eqs. (1) and (2), molar mass of gas $m = \mathbf{46.6}$

79.

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2}$$

$$\text{or} \quad \frac{n_1}{t_1} \times \frac{t_2}{n_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2}$$

$$\text{or} \quad \frac{1}{38} \times \frac{57}{1} = \sqrt{\left(\frac{M_g}{28}\right)} \times \frac{0.8}{1.6}$$

$$\therefore \quad M_g = \left[\frac{57}{38} \times \frac{1.6}{0.8}\right]^2 \times 28$$

$$M_g = \mathbf{252;}$$

Thus, compound is XeF_6 because it can have only one xenon atom (since for two xenon atom, 2× Atomic mass of Xe = 2 × 131 = 262, *i.e.*, greater than 252).

80. $P = 4.18\,\text{bar},\ \ V = 3\text{L},\ \ T = 300\,\text{K}$

$$R = 0.083\ \text{bar-litre}\ K^{-1}\ \text{mol}^{-1}$$

$$\therefore \quad n_T = \frac{PV}{RT} = \frac{4.18 \times 3}{0.083 \times 300}$$

$$n_T = 0.50$$

Total mole of gases diffused = 0.50

Mole of unknown gas n_g diffused

$$= n_T - n_{N_2} = 0.50 - 0.40 = \mathbf{0.10}$$

Now, $\frac{n_g}{n_{N_2}} \times \frac{t_{N_2}}{t_g} = \sqrt{\frac{M_{N_2}}{M_g}}$ $(t_{N_2} = t_g = 10 \text{ min})$

or $\frac{0.1}{0.4} = \sqrt{\frac{28}{M_g}}$

$$\therefore \quad M_g = \mathbf{448\ g\ mol^{-1}}$$

81. Given $\frac{r_1}{r_2} = \frac{1}{4}; \quad \frac{w_1}{w_2} = \frac{2}{3}$

We have $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$

$$\therefore \quad \frac{1}{4} = \sqrt{\frac{M_2}{M_1}} \quad \text{or} \quad \frac{M_2}{M_1} = \frac{1}{16}$$

Also, mole ratio

$$= \frac{n_1}{n_2} = \frac{w_1/M_1}{w_2/M_2} = \frac{w_1}{w_2} \times \frac{M_2}{M_1} = \frac{2}{3} \times \frac{1}{16} = \mathbf{\frac{1}{24}}$$

82. $\frac{\gamma_{\text{mix}}}{\gamma_{\text{Kr}}} = \sqrt{\left(\frac{M_{\text{Kr}}}{M_{\text{Mix}}}\right)}$ or $1.16 = \sqrt{\left(\frac{84}{M}\right)}$

$\therefore \quad M = 62.425$

For $Cl_2 \rightleftharpoons 2Cl$

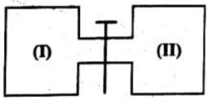
$$\begin{array}{cc} 1 & 0 \\ (1-\alpha) & 2\alpha \end{array}$$

$$\frac{\text{Normal molar mass}}{\text{Exp. molar mass}} = 1 + \alpha$$

$$\frac{71}{62.425} = 1 + \alpha$$

$\therefore \quad \alpha = \mathbf{0.137}$ or $\mathbf{13.7\%}$

83.



At STP

Before diffusion

$$\left.\begin{array}{l} D_2 = 1.12 \text{ lit. at STP} = 0.2\,g = 0.05 \text{ mole} \\ H_2 = 2.24 \text{ lit. at STP} = 0.2\,g = 0.1 \text{ mole} \end{array}\right\} \text{in I bulb}$$

When these mole are placed in the bulb, the partial pressure of gas will be different because V and T are constant. Also $P \propto n$

Thus, $\frac{P_{D_2}}{P_{H_2}} = \frac{0.05}{0.10} = \frac{1}{2}$

After diffusion D_2 left in I bulb = 0.1 g

or D_2 diffuses from I into II (bulb) = 0.2 − 0.1 = 0.1

Now for diffusion of D_2 and H_2

$$\frac{r_{D_2}}{r_{H_2}} = \sqrt{\left(\frac{M_{H_2}}{M_{D_2}}\right)} \times \frac{P_{D_2}}{P_{H_2}}$$

$$\because \quad \frac{w_{D_2}}{t_{D_2}} \times \frac{t_{H_2}}{w_{H_2}} = \sqrt{\left(\frac{M_{D_2}}{M_{H_2}}\right)} \times \frac{P_{D_2}}{P_{H_2}}$$

$$\therefore \quad \frac{0.1}{t} \times \frac{t}{w_{H_2}} = \sqrt{\left(\frac{4}{2}\right)} \times \frac{1}{2} \qquad \therefore w_{H_2} = 0.14\,g$$

∴ Mass of gases in II bulb

= mass of D_2 + mass of H_2 = 0.10 g + 0.14 g = 0.24 g

$$\therefore \quad \%\ D_2 \text{ by mass} = \frac{0.10}{0.24} \times 100 = \mathbf{41.66\%}$$

$$\%\ H_2 \text{ in bulb II} = \mathbf{58.33\%}$$

84. Molar mass of $^{235}UF_6 = 235 + 19 \times 6 = 349$

Molar mass of $^{238}UF_6 = 238 + 19 \times 6 = 352$

From Graham's law at same P and T

$$\frac{r_1}{r_2} = \sqrt{\left(\frac{M_2}{M_1}\right)}$$

$$\frac{r_{UF_6}^{235}}{r_{UF_6}^{238}} = \sqrt{\left(\frac{352}{349}\right)} = \mathbf{1.0043}$$

Also, $x = \dfrac{2\log\left(\dfrac{n'_A/n'_B}{n_A/n_B}\right)}{\log\left(\dfrac{M_B}{M_A}\right)}$

Here, $n_B = U^{235}$ in $U^{235}F_6 = 0.72$ and $M_B = M_{U^{238}F_6}$

$n_B = U^{238}$ in $U^{238}F_6 = 99.28$ and $M_A = M_{U^{235}F_6}$

$$n'_A = U^{235} \text{ in } U^{235}F_6 = 10$$

$$n'_B = U^{238} \text{ in } U^{238}F_6 = 90$$

$$\therefore \quad x = \frac{2\log\left[\dfrac{(10/90)}{(0.72/99.28)}\right]}{\log\left(\dfrac{352}{349}\right)}$$

$$x = \mathbf{638\ steps}$$

85. H_2 present has $_1^1H_1^1H$ and $_1^1H_1^2H$ in the ratio 99.8% and 0.2, *i.e.*, $n_{2_H} : n_{3_H}$. This has to be diffused to have the outcoming sample enriched to 99.8% $^1H^1H$.

$n_{2_H} = 90$ $\qquad n_{3_H} = 10$ $\qquad \therefore \frac{n_A}{n_B} = \frac{90}{10}$

$n_{2_H}^1 = 99.8$ $\qquad n_{3_H}^1 = 0.2$ $\qquad \therefore \frac{n'_A}{n'_B} = \frac{99.8}{0.2}$

$$\therefore \quad \text{Separation factor} = \frac{99.8 \times 10}{0.2 \times 90} = 55.44$$

$$\therefore \quad f = \frac{r_{2_H}}{r_{3_H}} = \sqrt{\frac{M_{3_H}}{M_{2_H}}} = \sqrt{\frac{3}{2}}$$

Now, $$(f')^X = \left[\frac{n_A^1/n_B^1}{n_A/n_B}\right]$$

∴ $$\left[\sqrt{\frac{3}{2}}\right]^X = 55.44$$

∴ $$\frac{X}{2}\log\frac{3}{2} = 55.44$$

$$X = 19.8 \simeq \mathbf{20\ steps}$$

86. At constant V and T for a gas $P \propto w$

Thus, for $N_2 : P_1 = 2\,\text{atm}, P_2 = \frac{1}{2}\,\text{atm}$, at $t = 1$ hr, $w_1 = 14$ kg, $w_2 = ?$

∵ $$\frac{P_1}{P_2} = \frac{w_1}{w_2}; \quad \frac{2}{1/2} = \frac{14}{w_2}$$

∴ $$w_2 = \frac{14}{4}\ \text{kg}\ N_2$$

∴ mass of N_2 diffused $= 14 - \frac{14}{4} = \frac{42}{4} = \frac{21}{2}$ kg

Similarly, for H_2 : $P_1 = 2\,\text{atm}$, $P_2 = \frac{1}{2}\,\text{atm}$, at $t = t$ hr, $w_1 = 1\,\text{kg}$, $w_2 = ?$

∵ $$\frac{P_1}{P_2} = \frac{w_1}{w_2}$$

$$\frac{2}{1/2} = \frac{1}{w_2} \quad \therefore \quad w_2 = \frac{1}{4}\ \text{kg}$$

∴ mass of H_2 diffused $= 1 - \frac{1}{4} = \frac{3}{4}$ kg

Now $$\frac{r_{N_2}}{r_{H_2}} = \sqrt{\left(\frac{M_{H_2}}{M_{N_2}}\right)}$$

for diffusion of N_2 and H_2

or $$\frac{w_{H_2}}{w_{N_2}} \times \frac{t_{N_2}}{t_{H_2}} = \sqrt{\left(\frac{M_{H_2}}{M_{N_2}}\right)}$$

$$\frac{3/4}{21/2} \times \frac{60}{t} = \sqrt{\left(\frac{2}{28}\right)} \quad (t_{N_2} = 1\ \text{hour} = 60\ \text{minute})$$

∴ $$t = \mathbf{16\ minute}$$

87. Mole of H_2 diffused = 0.7 in 20 minute

Mole of gas diffused $= n_1$ in 20 minute

For gaseous mixture after diffusion

$$PV = nRT$$

$$n = \frac{6 \times 3}{0.0821 \times 300} = 0.731$$

∵ Mixture contains, mole of H_2 + mole of gas diffused $= n$

∴ $$0.7 + n_1 = 0.731$$

∴ $$n_1 = 0.031$$

Now $$\frac{r_{H_2}}{r_g} = \sqrt{\left(\frac{M_g}{M_{H_2}}\right)}$$

$$\frac{n_{H_2}}{t} \times \frac{t}{n_g} = \sqrt{\left(\frac{M_g}{2}\right)}$$

$$\frac{0.7}{20} \times \frac{20}{0.031} = \sqrt{\left(\frac{M_g}{2}\right)}$$

∴ $$\frac{M_g}{2} = \frac{0.7 \times 0.7}{0.031 \times 0.031}$$

∴ $$M_g = \mathbf{1019.77}$$

88. Before diffusion:

Mole of CO = 0.5

Mole of CO_2 = 0.5

Total mole diffused out $= A$

Let Mole of CO diffused $= a$

∴ Mole of CO_2 diffused $= b$

Then, $$a + b = A \qquad ...(1)$$

Now,

M_1 = Mean molar mass of diffused portion

$$M_1 = \frac{a \times 28 + 44 \times b}{(a+b)} = \frac{28a + 44b}{A} \qquad ...(2)$$

Also, M_2 = Mean molar mass of left portion

$$= \frac{(0.5-a) \times 28 + (0.5-b) \times 44}{(0.5-a) + (0.5-b)} = \frac{14 - 28a + 22 - 44b}{1 - (a+b)}$$

$$= \frac{36 - 28a - 44b}{1 - A}$$

using Eq. (1)

$$M_2 = \frac{36}{1-A} - \frac{28a + 44b}{1-A}$$

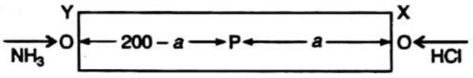
$$M_2 = \frac{36}{1-A} - \frac{M_1 A}{1-A}$$

using Eq. (2)

∴ $$M_2(1-A) = 36 - M_1 A$$

or $$\boldsymbol{M_1 A + M_2(1-A) = 36}$$

89.



Let distance of P from X end is a cm.

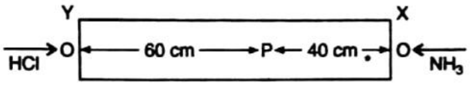
For diffusion of NH_3 and HCl at same P

$$\frac{d_{NH_3}}{t_{NH_3}} \times \frac{t_{HCl}}{d_{HCl}} = \sqrt{\left(\frac{M_{HCl}}{M_{NH_3}}\right)}$$

$$\frac{200-a}{t} \times \frac{t}{a} = \sqrt{\left(\frac{36.5}{17}\right)} \qquad \text{(time is same)}$$

∴ $$a = \mathbf{81.1\ cm}$$

90.



For diffusion of NH_3 and HCl

Let pressure of HCl $= P$ atm

Let pressure of NH_3 = 1 atm

$$\frac{r_{NH_3}}{r_{HCl}} = \sqrt{\left(\frac{M_{HCl}}{M_{NH_3}}\right)} \times \frac{P_{NH_3}}{P_{HCl}}$$

$$\frac{d_{NH_3}}{t_{NH_3}}\times\frac{t_{HCl}}{d_{HCl}}=\sqrt{\left(\frac{M_{HCl}}{M_{NH_3}}\right)}\times\frac{P_{NH_3}}{P_{HCl}}$$

$$\frac{40}{t}\times\frac{t}{60}=\sqrt{\left(\frac{36.5}{17}\right)}\times\frac{1}{P} \qquad \text{(time is same)}$$

$\therefore$ $\quad$ $P = \mathbf{2.198\ atm}$

91. 2000 mm pressure of $O_2 \xrightarrow{t=47\text{ min}} 1500$ mm

4000 mm pressure of mixture $\xrightarrow{t=74\text{ min}} 1:1\,(O_2+\text{gas})$

For pure O_2, $\quad \frac{P_1}{P_2}=\frac{n_1}{n_2}$

When n_1 and n_2 are original no. of mole of O_2 and mole of O_2 after 47 minute.

$\therefore$ $\quad \frac{n_1}{n_2}=\frac{2000}{1500}$

$\therefore$ $\quad n_2=(3/4)n_1$

or mole of O_2 diffused in 47 min $= n_1-\frac{3n_1}{4}=\frac{n_1}{4}$

or mole of O_2 diffused in 74 min $=\frac{n_1\times 74}{47\times 4}$

$= 0.3936 \qquad (\text{if } n_1 = 1)$

Since, diffusion of O_2 in mixture also occurs at partial pressure of 2000 mm. (The ratio of gas and O_2 being 1:1) Now gas and O_2 both diffusing in form of mixture through same orifice at the partial pressure of 2000 mm each.

$\therefore$ $\quad \frac{n_{O_2}}{74}\times\frac{74}{n_g}=\sqrt{\left(\frac{79}{32}\right)}$

$\therefore$ $\quad n_g=n_{O_2}\times\sqrt{\left(\frac{32}{79}\right)}=\frac{74}{188}\times\sqrt{\left(\frac{32}{79}\right)}=0.249$

$\therefore$ Mole of O_2 left after 74 minute $= 1-0.3936 = 0.6064$

Mole of gas left after 74 minute $= 1-0.249 = 0.7510$

$\therefore$ $\quad O_2 : \text{gas} :: 0.6064 : 0.7510$

$\quad :: \mathbf{1 : 1.236}$

92. Molar ratio of He and CH_4 is 4 : 1

$\therefore$ Partial pressure ratio of He and CH_4 is 16 : 4

($\because$ total pressure = 20bar)

$$\frac{n_{He}}{n_{CH_4}}=\sqrt{\frac{M_{CH_4}}{M_{He}}}\times\frac{P_{He}}{P_{CH_4}}$$

($\because$ time of diffusion for both is same)

$$=\sqrt{\frac{16}{4}}\times\frac{16}{4}=8:1$$

The composition of mixture initially gone out for He and CH_4 is **8 : 1**

93. $u_{rms}=\sqrt{\frac{n_1u_1^2+n_2u_2^2+n_3u_3^2+\ldots}{n_1+n_2+n_3+\ldots}}$

$$=\sqrt{\frac{5\times(15\times10^2)^2+10\times(5\times10^2)^2+15\times(10\times10^2)^2}{5+10+15}}$$

$= \mathbf{9.79\times10^2\ m\ sec^{-1}}$

Also, $\quad u_{AV}=\frac{n_1u_1+n_2u_2+n_3u_3+\ldots}{n_1+n_2+n_3+\ldots}$

$$=\frac{(5\times15\times10^2)+(10\times5\times10^2)+(15\times10\times10^2)}{5+10+15}$$

$= \mathbf{9.17\times10^2\ m\ sec^{-1}}$

94. It T is given always use

$$u_{rms}=\sqrt{\left(\frac{3RT}{M}\right)}$$

(a) at STP $\quad T = 273$ K

$\therefore u_{rms}$ for $O_2=\sqrt{\left(\frac{3RT}{M}\right)}=\sqrt{\left(\frac{3\times8.314\times10^7\times273}{32}\right)}$

$= \mathbf{4.61\times10^4\ cm\ sec^{-1}}$

Now $\quad u_{MP}=u_{rms}\times0.816 \qquad$ ...(1)

and $\quad u_{AV}=u_{rms}\times0.9213 \qquad$ ...(2)

$\therefore$ $\quad u_{MP}=\mathbf{3.76\times10^4\ cm\ sec^{-1}}$

and $\quad u_{AV}=\mathbf{4.25\times10^4\ cm\ sec^{-1}}$

(b) $\quad u_{rms}$ of $C_2H_6=\sqrt{\left(\frac{3RT}{M}\right)}$

$M = 30, \qquad T = 27+273 = 300$ K

$\therefore$ $\quad u_{rms}=\sqrt{\left(\frac{3\times8.314\times10^7\times300}{30}\right)}$

$u_{rms}=\mathbf{4.99\times10^4\ cm\ sec^{-1}}$

By Eq. (1), $\quad u_{MP}=\mathbf{4.07\times10^4\ cm\ sec^{-1}}$

By Eq. (2), $\quad u_{AV}=\mathbf{4.60\times10^4\ cm\ sec^{-1}}$

(c) $\quad u_{rms}$ of $O_2=\sqrt{\left(\frac{3RT}{M}\right)}$

at $\quad T = 17+273 = 290$ K

$u_{rms}=\sqrt{\left(\frac{3\times8.314\times10^7\times290}{32}\right)}$

$= \mathbf{4.75\times10^4\ cm\ sec^{-1}}$

By Eq. (1), $\quad u_{MP}=\mathbf{3.88\times10^4\ cm\ sec^{-1}}$

By Eq. (2), $\quad u_{AV}=\mathbf{4.38\times10^4\ cm\ sec^{-1}}$

(d) Density of $O_2 = 0.0081\text{g mL}^{-1} = 0.0081\text{g cm}^{-3}$

and $\quad P = 1\text{atm} = 1\times76\times13.6\times981\text{dyne cm}^{-2}$

Now, $\quad u_{rms}=\sqrt{\left(\frac{3P}{d}\right)}=\sqrt{\left(\frac{3\times1\times76\times13.6\times981}{0.0081}\right)}$

$= \mathbf{1.94\times10^4\ cm\ sec^{-1}}$

By Eq. (1), $\quad u_{MP}=\mathbf{1.58\times10^4\ cm\ sec^{-1}}$

By Eq. (2), $\quad u_{AV}=\mathbf{1.78\times10^4\ cm\ sec^{-1}}$

(e) Given for O_2, $\quad w = 6.431\,g,\ V = 5$ litre

$P = 750\text{ mm} = 75\text{ cm} = \frac{75}{76}\text{ atm}$

$\because$ $\quad PV=\frac{w}{M}RT$

$\frac{75}{76}\times5=\frac{6.431}{32}\times0.0821\times T$

$\therefore$ $\quad T = 299.05$ K

Now

$$u_{\text{rms}} = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3 \times 8.314 \times 10^7 \times 299.05}{32}\right)}$$

$$\boldsymbol{u_{\text{rms}} = 4.83 \times 10^4 \text{ cm sec}^{-1}}$$

By Eq. (1), $\boldsymbol{u_{\text{MP}} = 3.94 \times 10^4 \text{ cm sec}^{-1}}$

By Eq. (2), $\boldsymbol{u_{\text{AV}} = 4.45 \times 10^4 \text{ cm sec}^{-1}}$

(f) For O_3 : $T = 20 + 273 = 293$ K

$$\therefore \quad u_{\text{rms}} = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3 \times 8.314 \times 10^7 \times 293}{48}\right)}$$

$$\boldsymbol{u_{\text{rms}} = 3.9 \times 10^4 \text{ cm sec}^{-1}}$$

By Eq. (1), $\boldsymbol{u_{\text{MP}} = 3.18 \times 10^4 \text{ cm sec}^{-1}}$

By Eq. (2), $\boldsymbol{u_{\text{AV}} = 3.59 \times 10^4 \text{ cm sec}^{-1}}$

95. $u_{\text{AV}} = \sqrt{\left(\frac{8RT}{\pi M}\right)}, \quad u_{\text{MP}} = \sqrt{\left(\frac{2RT}{M}\right)}$

Average speed at T_1 K = MP speed at T_2 K for CO_2

$$\sqrt{\left(\frac{8RT_1}{\pi M}\right)} = \sqrt{\left(\frac{2RT_2}{M}\right)}$$

$$\therefore \quad \frac{T_1}{T_2} = \frac{\pi}{4} \quad \text{...(1)}$$

Also, for CO_2 $\quad u_{\text{MP}} = \sqrt{\left(\frac{2RT}{M}\right)} = 9 \times 10^4$

$$\therefore \quad \sqrt{\left(\frac{2 \times 8.314 \times 10^7 \times T_2}{44}\right)} = 9 \times 10^4$$

$$\therefore \quad \boldsymbol{T_2 = 2143.37 \text{ K}}$$

$\therefore$ By Eq. (1), $\quad \boldsymbol{T_1 = 1684.0 \text{ K}}$

96. $$u_{\text{AV}} = \sqrt{\left(\frac{8RT}{\pi M}\right)}$$

Given $u_{\text{AV}} = 0.3 \text{ m sec}^{-1}$ at 300 K

$$\therefore \quad u_1 = 0.3 = \sqrt{\left(\frac{8R \times 300}{\pi M}\right)} \quad \text{...(1)}$$

at $T = 273 + 927 = 1200$ K

$$\therefore \quad u_2 = \sqrt{\left(\frac{8R \times 1200}{\pi M}\right)} \quad \text{...(2)}$$

$$\therefore \quad \frac{u_2}{0.3} = \sqrt{\left(\frac{1200}{300}\right)}$$

$$\therefore \quad \boldsymbol{u_2 = 0.6 \text{ m sec}^{-1}}$$

97. $u_{\text{rms}} = \sqrt{\left(\frac{3RT}{M}\right)}, \quad u_{\text{AV}} = \sqrt{\left(\frac{8RT}{\pi M}\right)}, \quad u_{\text{MP}} = \sqrt{\left(\frac{2RT}{M}\right)}$

$$\therefore \quad u_{\text{rms}} : u_{\text{AV}} : u_{\text{MP}} = 1 : \sqrt{\left(\frac{8}{3\pi}\right)} : \sqrt{\left(\frac{2}{3}\right)}$$

$$\boldsymbol{= 1 : 0.9213 : 0.816}$$

Also $\quad \boldsymbol{u_{\text{MP}} : u_{\text{AV}} : u_{\text{rms}} = 1 : \sqrt{(4/\pi)} : \sqrt{(3/2)}}$

$$\boldsymbol{= 1 : 1.128 : 1.224}$$

98. $$u_{\text{AV}} = \sqrt{\frac{8RT}{\pi M}} \quad \text{...(1)}$$

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad \text{...(2)}$$

By Eqs. (1) and (2), $\quad u_{\text{rms}} = u_{\text{AV}} \times \sqrt{\frac{3\pi}{8}}$

$$= 400 \times \sqrt{\frac{3 \times 3.14}{8}} = \boldsymbol{434 \text{ m/sec}}$$

99. Given, $\quad m_A = 2m_B$

$\therefore$ Molar mass of $A = 2 \times$ Molar mass of B ...(1)

Given $\quad u_{\text{rms}}$ of $A = 2 \times u_{\text{rms}}$ of B ...(2)

Also no. of molecules of A = No. of molecules of B ...(3)

For gas A $\quad P_A V_A = \frac{1}{3} M_A u^2_{\text{rms } A}$

For gas B $\quad P_B V_B = \frac{1}{3} M_B u^2_{\text{rms } B}$

$$\therefore \quad \frac{P_A V_A}{P_B V_B} = \frac{M_A}{M_B} \times \frac{u_A^2}{u_B^2} \quad \text{...(4)}$$

Given $\quad V_A = V_B$ ...(5)

$\therefore$ By Eqs. (1), (2), (4) and (5), $\quad \frac{P_A}{P_B} = 2 \times (2)^2 = 8$

$$\therefore \quad \boldsymbol{P_A = 8P_B}$$

100. For gas $\quad PV = \frac{w}{M} RT$

$$3 \times 12.5 = \frac{15}{M} \times 0.0821 \times T$$

$$\therefore \quad \frac{T}{M} = 30.45$$

Now $\quad u_{\text{AV}} = \sqrt{\left(\frac{8RT}{\pi M}\right)} = \sqrt{\left(\frac{8 \times 8.314 \times 10^7 \times 30.4 \times 7}{22}\right)}$

$$\boldsymbol{= 8.028 \times 10^4 \text{ cm sec}^{-1}}$$

101. Given, $n = 10^{23}$, $\quad m = 10^{-22}$ g, $\quad V = 1 \text{ litre} = 10^3 \text{ cm}^3$

$$u_{\text{rms}} = 10^5 \text{ cm sec}^{-1}$$

$$\because \quad PV = \frac{1}{3} mnu^2_{\text{rms}}$$

$$\therefore \quad P \times 10^3 = \frac{1}{3} \times 10^{-22} \times 10^{23} \times (10^5)^2$$

$$\therefore \quad \boldsymbol{P = 3.3 \times 10^7 \text{ dyne cm}^{-2}}$$

102. $\quad T = 27 + 273 = 300$ K, $\quad R = 8.314 \times 10^7$ erg

$$u_{\text{rms}} \text{ for } CH_4 = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3 \times 8.314 \times 10^7 \times 300}{16}\right)}$$

$$\boldsymbol{= 6.84 \times 10^4 \text{ cm sec}^{-1}}$$

Now, $\quad$ K.E./mol $CH_4 = \frac{1}{2} Mu^2 = \frac{1}{2} \times 16 \times (6.84 \times 10^4)^2$

$$= 374.28 \times 10^8 \text{ erg mol}^{-1}$$

$\therefore$ K.E. for $\frac{1}{2}$ mole $CH_4 = \frac{374.28 \times 10^8}{2}$ erg

$$= \frac{374.28 \times 10^8}{2 \times 10^7} \text{ joule}$$

$$\boldsymbol{= 1871.42 \text{ joule}}$$

Average kinetic energy

$$= \frac{\text{K.E./mol}}{\text{Av. No.}} = \frac{374.28 \times 10^8}{6.023 \times 10^{23}} = 62.14 \times 10^{-15} \text{ erg}$$

$$= \mathbf{62.14 \times 10^{-22} \text{ joule}}$$

103. Average kinetic energy $= \frac{\text{K.E./mol}}{\text{Av. No.}} = \frac{3RT}{2 \times N} = \frac{3}{2}kT$

$\therefore$ $k = \frac{5.621 \times 10^{-14} \times 2}{3 \times 273}$ $(\because T = 273 \text{ K})$

$= \mathbf{1.372 \times 10^{-16} \text{ erg molecule}^{-1} \text{ K}}$

Now Avogadro's no.

$$= \frac{R}{k} = \frac{8.314 \times 10^7}{1.372 \times 10^{-16}} = \mathbf{6.059 \times 10^{23}}$$

104. Given, $P = 7.57 \times 10^3 \text{ Nm}^{-2}$, $V = 1 \text{ litre} = 10^{-3} \text{ m}^3$

$R = 8.314 \text{ J}$, $n = \frac{2 \times 10^{21}}{6.023 \times 10^{23}}$ mole

Using $PV = nRT$

$$7.57 \times 10^3 \times 10^{-3} = \frac{2 \times 10^{21}}{6.023 \times 10^{23}} \times 8.314 \times T$$

$\therefore$ $T = 274.2 \text{ K}$

$\therefore$ $u_{\text{rms}} = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3 \times 8.314 \times 274.2}{28 \times 10^{-3}}\right)}$ (M in kg)

$= \mathbf{494.22 \text{ m sec}^{-1}}$

Now, $\frac{u_{\text{MP}}}{u_{\text{rms}}} = 0.82$

$\therefore$ $u_{\text{MP}} = \mathbf{405.26 \text{ m sec}^{-1}}$

105. Let the u_{rms} of He and SO_2, be u_1 and u_2 respectively,

(i) **For He :** $u_1 = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3RT}{4}\right)}$

For SO_2 : $u_2 = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3RT}{64}\right)}$ (temp. is same)

$\therefore$ $\frac{u_1}{u_2} = \mathbf{4}$

(ii) Given, u_{rms} of $SO_2 = \frac{1}{2} u_{\text{rms}}$ of He

$\therefore$ $\sqrt{\left(\frac{3RT}{64}\right)} = \frac{1}{2}\sqrt{\left(\frac{3R \times 300}{4}\right)}$

($T = 300$ K for He)

$\therefore$ $T = \mathbf{1200 \text{ K}}$

(iii) Since speed is independent of P and V terms and thus no effect on speed by changing volume.

(iv) Since u_{rms} is independent of no. of molecules and thus, no effect on speed by changing no. of molecules.

106. Let mass of mist particle be m, then K.E. of this particle $= \frac{1}{2}mu^2$, where u is its rms velocity.

Also K.E. per molecule $= \frac{3RT}{2 \times N}$

Therefore, $\frac{1}{2}mu^2 = \frac{3RT}{2 \times N}$

$$u = \sqrt{\left[3\frac{R}{N} \times \frac{T}{m}\right]}$$

$\because$ $m = 10^{-12}$ g; $R = 8.314 \times 10^7$ erg, $T = 300 \text{ K}$

$\therefore$ $u = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 300}{6.023 \times 10^{23} \times 10^{-12}}} = \mathbf{0.35 \text{ cm sec}^{-1}}$

107. **For H_2 :** $u_{\text{AV}} = \sqrt{\left(\frac{8R \times 300}{\pi \times 2}\right)}$

$(\because T = 300 \text{ K}$ and molar mass $= 2)$

For C_2H_6: $u_{\text{AV}} = \sqrt{\left(\frac{8R \times 900}{\pi \times 30}\right)}$

$(\because T = 900 \text{ K}$ and molar mass $= 30)$

$\therefore$ $\frac{u_{\text{AVH}_2}}{u_{\text{AVC}_2\text{H}_6}} = \sqrt{\left(\frac{300 \times 30}{900 \times 2}\right)} = \mathbf{2.237 : 1}$

108. (a) Volume of 1 molecule $= \frac{4}{3}\pi r^3$ (spherical shape)

$(\because r = 150 \text{ pm} = 150 \times 10^{-10} \text{ cm})$

$\therefore$ Volume of 1 molecule $= \frac{4}{3} \times \frac{22}{7} \times [150 \times 10^{-10}]^3$

$(V_1) = \mathbf{1.41 \times 10^{-23} \text{ cm}^3}$

(b) Thus, volume occupied by N molecules $= N \times V_1$

$= 6.023 \times 10^{23} \times 1.41 \times 10^{-23} = 8.49 \text{ cm}^3$ per mol

Also volume of 1 mole of $N_2 = 22400 \text{ cm}^3$ at STP

Thus, empty space $= 22400 - 8.49 = 22391.51$

or % empty space $= \frac{22391.51}{22400} \times 100 = \mathbf{99.96\%}$

(c) 99.96% is empty space and this accounts that most of the space in container is empty in which a molecule can move. Also it suggests for compressibility of gases to higher extent.

109. $PV = nRT$ ...(1) for ideal gas

$PV^2 = K$ ...(2) additional law

or $PV = \frac{K}{V}$ ...(3)

By Eqs. (1) and (3)

$\therefore$ $\frac{K}{V} = nRT$

Initially $\frac{K}{V} = nRT$

Finally $\frac{K}{2V} = nRT_1$

$\therefore$ $2 = \frac{T}{T_1}$

or $T_1 = \frac{T}{2}$

110. Let P, V represent pressure and volume at temperature T.

$PV = nRT$ ...(1)

At $V = V_0$, $P = \frac{P^\circ}{1 + (1)^2} = \frac{P^\circ}{2}$ $\left[\because P = \frac{P^\circ}{1 + \left(\frac{V}{V_0}\right)^2}\right]$

$\therefore$ By Eq. (1), $\frac{P^\circ}{2} \times V_0 = nRT$

$$\therefore \qquad T = \frac{P^\circ V^\circ}{2R} \quad (n = 1)$$

111. Pressure correction $= \frac{n^2 a}{V^2} = \frac{(4.4)^2 \times 3.6}{(44)^2 \times 1 \times 1} \qquad \left(n = \frac{4.4}{44}\right)$

$= \mathbf{0.036\ atm}$

Volume correction $= nb = \frac{4.4}{44} \times 0.04 = \mathbf{0.004\ litre}$

112. $\because \ b = 4N \times v$

[where v is volume of 1 molecule (of steam)]

$\therefore$ Volume of 1 mole of steam

$= \frac{b}{4} = \frac{0.0305}{4}$ litre $= \frac{0.0305}{4} \times 10^3$ mL $= 7.625$ mL

Also, volume of 1 mole of $H_2O(l) = \frac{18}{0.958}$ mL

$$\therefore \quad \frac{\text{Volume of 1 mole steam}}{\text{Volume of 1 mole } H_2O} = \frac{7.625 \times 0.958}{18} = 0.4058$$

$\therefore$ Volume of 1 mole of steam $=$ **40%** of volume of 1 mole of H_2O

113. For gaseous water, $\qquad PV = nRT$

Thus, volume occupied by 1 mole gaseous water can be derived as ($T = 273 + 100 = 373$ K)

$$V = \frac{nRT}{P} = \frac{1 \times 0.0821 \times 373}{1} = 30.62 \text{ litre}$$

Also volume of 1 mole of liquid water $= \frac{\text{mass}}{\text{density}}$

$$= \frac{18}{0.958} = 18.79 \text{ mL} = 18.79 \times 10^{-3} \text{ litre}$$

Thus, volume percentage occupied by water molecules in gaseous state

$$= \frac{18.79 \times 10^{-3}}{30.62} \times 100 = 0.0614$$

Therefore, percentage of free volume

$= 100 - 0.0614 = \mathbf{99.9386}$

114. $\because \ 6.023 \times 10^{23}$ molecules of N_2 occupy 22400cm^3

$\therefore$ one molecule of N_2 occupies $\frac{22400}{6.023 \times 10^{23}}$ cm^3

or volume of one molecule of $N_2 = 3.72 \times 10^{-20}$ cm^3

Also, the average distance between two molecules $= 2r$

and $\quad \frac{4}{3}\pi r^3 = 3.72 \times 10^{-20}$

$$\therefore \qquad r^3 = \frac{3.72 \times 10^{-20} \times 3 \times 7}{4 \times 22}$$

$$\therefore \qquad r = 20.7 \times 10^{-8} \text{ cm}$$

Thus, $\qquad$ average distance $= 2 \times 20.7 \times 10^{-8}$

$= \mathbf{41.4 \times 10^{-8}\ cm}$

115. $b = 4 \times$ Volume occupied by the molecules in one mole of gas

$= 4 \times N \times \left(\frac{4}{3}\pi r^3\right)$

$$\therefore \quad r = \left[\frac{3 \times 24}{16 \times (22/7) \times 6.023 \times 10^{23}}\right]^{1/3} = 1.355 \times 10^{-8} \text{ cm}$$

$\therefore \ d = 2 \times r = 2 \times 1.355 \times 10^{-8}$ cm $=$ **2.71 Å**

116. (i) The volume of sphere $= \frac{4}{3}\pi r^3$

Thus, volume of one N_2 molecule

$= \frac{4}{3} \times \frac{22}{7} \times (2 \times 10^{-10})^3$ m^3 $= \mathbf{3.35 \times 10^{-23}\ cm^3}$

(ii) The total volume of one mole of gas at STP $= 22400 \text{cm}^3$

Also the volume of one mole of gas

$= N \times$ volume of one molecule

$= 6.023 \times 10^{23} \times 3.35 \times 10^{-23}$ cm^3 $= 20.2 \text{cm}^3$

$\therefore$ Empty space $= 22400 - 20.2 = 22379.8 \text{cm}^3$

$\therefore$ Percentage empty space $= \frac{22379.8}{22400} \times 100 = \mathbf{99.9\%}$

[**NOTE :** This result clearly indicates that particles of gas occupy only a tiny fraction of the total gaseous volume.]

117. Given, $n = 5; V = 1$ litre; $T = 47 + 273 = 320$ K

$a = 3.592; \qquad b = 0.0427$

Using van der Waals' equation for n mole

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$$\left[P + \frac{25 \times 3.592}{1}\right][1 - 5 \times 0.0427] = 5 \times 0.0821 \times 320$$

$$\therefore \qquad P = \mathbf{77.218\ atm}$$

Also, if gas behaves ideally, then $PV = nRT$

$P \times 1 = 5 \times 0.0821 \times 320 = \mathbf{131.36\ atm}$

118. For 1 mole : $\left[P + \frac{a}{V^2}\right][V - b] = RT$

if b is negligible, $\qquad P = \frac{RT}{V} - \frac{a}{V^2}$

or $\qquad PV^2 - RTV + a = 0$

The equation is quadratic in V, thus

$$V = \frac{+RT \pm \sqrt{R^2T^2 - 4aP}}{2P}$$

Since, V has one value at given P and T, thus numerical value of discriminant $= 0$

or $\qquad R^2T^2 = 4aP$

$$\therefore \qquad P = \frac{R^2T^2}{4a} = \frac{(0.0821)^2 \times (273)^2}{4 \times 3.592} = \mathbf{34.96\ atm}$$

119. $\qquad Z = \frac{PV}{RT} = 0.5$

$$\therefore \qquad \frac{100 \times V}{0.082 \times 273} = 0.5$$

$$\therefore \qquad V = 0.112 \text{ litre}$$

Now using van der Waals' equation,

$\left[P + \frac{a}{V^2}\right][V] = RT \qquad (\because b$ is negligible) or $$\left[P+\frac{a}{V^2}\right]=\frac{RT}{V}$$

$\therefore$ $$\left[100+\frac{a}{(0.112)^2}\right]=\frac{0.082\times 273}{0.112}=199.88$$

$\therefore$ $$\frac{a}{(0.112)^2}=99.88$$

$\therefore$ $$a=\mathbf{1.253\ litre^2\ mol^2\ atm}$$

120. Compressibility factor $(Z)=\dfrac{PV}{nRT}$

$$Z=\frac{40\times 0.4}{1\times 0.0821\times 300}=\mathbf{0.65}$$

Since, Z value is lesser than 1 and thus, $nRT > PV$. In order to have $Z=1$, volume of CO_2 must have been more at same P and T or CO_2 is more compressible than ideal gas.

121. For real gas $PV=Z\cdot nRT=\dfrac{Z\cdot wRT}{M}$

Given compressibility factor $Z=0.927$, $T=273\,K$, $P=100\,atm, V=100$ litre

$\therefore$ $$100\times 100=0.927\times\frac{w}{30}\times 0.0821\times 273$$

$$w=14.439\times 10^3\ g$$

$$w=\mathbf{14.439\ kg}$$

122. (a) (i) $$\frac{r_{(v)}}{r_{(O_2)}}=\sqrt{\frac{M_{(O_2)}}{M_{(v)}}}$$

$\therefore$ $$1.33=\sqrt{\frac{32}{M_{(v)}}}$$

$\therefore$ $$M_{(v)}=\mathbf{18.1}$$

(ii) Molar volume at 500 K

$$(\bar{V})=\frac{\text{Molar mass}}{\text{Density of 1 mole}}=\frac{18.1\times 10^{-3}}{0.36}$$

$$=\mathbf{50.25\times 10^{-3}\ m^3}$$

(iii) Compression factor

$$(Z)=\frac{P\bar{V}}{RT}=\frac{101325\times 50.25\times 10^{-3}}{8.314\times 500}=\mathbf{1.225}$$

$$[P=101325\ Nm^{-2}=1\,atm]$$

(iv) Repulsive forces operates among molecules since $Z>1$

(b) $$\text{Average K.E.}=\frac{3}{2}kT=\frac{3}{2}\times 1.38\times 10^{-23}\times 1000$$

$$=\mathbf{2.07\times 10^{-20}\ J/\ molecule}$$

123. van der Waals' equation for n mole of gas is

$$\left[P+\frac{n^2a}{V^2}\right][V-nb]=nRT$$

Given, $V=4$ litre; $P=11.0\,atm$; $T=300\,K$; $b=0.05$ litre mol^{-1}; $n=2$

Thus, $$\left[11+\frac{2^2a}{4^2}\right][4-2\times 0.05]=2\times 0.082\times 300$$

$$a=\mathbf{6.46\ atm\ litre^2\ mol^{-2}}$$

124. $\because$ $$n=\frac{PV}{RT}=\frac{1\times 5.6}{0.0821\times 273}=0.25$$

Also, $$q=m\cdot S\cdot\Delta T=0.25\times C_v\times 10$$

$\therefore$ $$12.5=0.25\times C_v\times 10$$

$\therefore$ $$C_v=\mathbf{5\ calorie}$$

Also, $$C_p=C_v+R=5+2=7\,\text{calorie}$$

So, $$\gamma=\frac{C_p}{C_v}=\frac{7}{5}=\mathbf{1.40}$$

Thus, gas is **diatomic.**

125. Given, $P=50\,atm$, $V=25$ litre, $n=10$

$a=5.46\,atm\ litre^2\ mol^{-2}$, $b=0.031$ litre mol^{-1}

Now van der Waals' equation for n mole of gas.

$$\left[P+\frac{n^2a}{V^2}\right][V-nb]=nRT$$

$$\left[50+\frac{100\times 5.46}{625}\right][25-10\times 0.031]=10\times 0.0821\times T$$

$\therefore$ $$T=1529.93\,K=\mathbf{1256.93°\,C}$$

126. We have, $Z=\dfrac{PV}{nRT}$

$\therefore$ Mole of $N_2=\dfrac{PV}{ZRT}=\dfrac{800\times 100}{1.95\times 0.0821\times 223}=\mathbf{2240.8}$

127. Given, $T_c=374°\,C=374+273=647\,K$, $P_c=218\,atm$

$V_c=0.0566$ litre mol^{-1}

$\because$ $$b=\frac{V_c}{3}=\frac{0.0566}{3}=\mathbf{0.0189\ litre\ mol^{-1}}$$

$$a=3P_cV_c^2=3\times 218\times(0.0566)^2=\mathbf{2.095\ litre^2\ atm\ mol^{-2}}$$

$$R=\frac{8}{3}\frac{P_cV_c}{T_c}=\frac{8\times 218\times 0.0566}{3\times 647}=\mathbf{0.05086\ litre\ atm\ K^{-1}\ mol^{-1}}$$

128. According to van der Waals' equation

$$\left[P+\frac{a}{V^2}\right][V-b]=RT$$

or $$P=\frac{RT}{(V-b)}-\frac{a}{V^2}$$

Multiply by V, then $$PV=\frac{RTV}{(V-b)}-\frac{a}{V}$$

or $$PV=RT\left[\frac{V}{V-b}-\frac{a}{VRT}\right]$$

or $$PV=RT\left[\left(1-\frac{b}{V}\right)^{-1}-\frac{a}{VRT}\right]$$

$\because$ $$\left[1-\frac{b}{V}\right]^{-1}=1+\frac{b}{V}+\left(\frac{b}{V}\right)^2+\ldots$$

$\therefore$ $$PV=RT\left[1+\frac{b}{V}+\ldots-\frac{a}{VRT}\right]$$

$$PV=RT\left[1+\left(b-\frac{a}{RT}\right)\cdot\frac{1}{V}+\ldots\right]$$

$\therefore$ $$\mathbf{B=b-\frac{a}{RT}}$$

129. $$nA\rightleftharpoons[A]_n$$

Before association	1	0
After association	$1-\alpha$	$\frac{\alpha}{n}$

$$\therefore \qquad K_C = \frac{[A_n]}{[A]^n} = \frac{\alpha}{n\cdot V\left[\frac{1-\alpha}{V}\right]^n} = \frac{\alpha\cdot V^{n-1}}{n\,(1-\alpha)^n}$$

Since α is small, thus $\frac{\alpha}{n} = \frac{K_C}{V^{n-1}}$ ...(1)

Total mole of gas at equilibrium $= 1-\alpha+\frac{\alpha}{n}$

$$\therefore \qquad PV = \left[1-\alpha+\frac{\alpha}{n}\right]RT$$

or $\frac{PV}{RT} = 1-\alpha+\frac{\alpha}{n} = \frac{n-n\alpha\div\alpha}{n} = \left[1-(n-1)\cdot\frac{\alpha}{n}\right]$

$\therefore$ By Eq. (1), $\frac{PV}{RT} = \left[1-\frac{(n-1)\cdot K_C}{V^{n-1}}\right]$

130. For real gas: $\left[P+\frac{a}{V^2}\right][V-b] = RT$

or $P\,[V-b] = RT$ (neglecting a)

$\therefore \frac{10.1325\times10^6}{101325}[V_1-b] = 0.0821\times273 (101325\text{ Pa} = 1\text{ atm})$

or $100[V_1-b] = 0.0821\times273 = 22.41$ ...(i)

$\frac{101.325\times10^3}{101325}[V_2-b] = 0.0821\times273$

or $[V_2-b] = 22.41$ ...(ii)

By Eq. (i), $V_1 = 0.2241+b$ ...(iii)

By Eq. (ii), $V_2 = 22.41+b$ ...(iv)

By Eqs. (iii) and (iv), $\frac{V_1}{V_2} = \frac{0.2241+b}{22.41+b}$

$\frac{0.011075V_2}{V_2} = \frac{0.2241+b}{22.41+b}$

($V_1 = 0.011075V_2$ is given)

$\therefore \; b = 0.024\text{ litre mol}^{-1} = 24\text{ cm}^3\text{ mol}^{-1}$

$\because \; b = 4N\times v = 4\times6.023\times10^{23}\times\frac{4}{3}\pi r^3$

or $24 = 4\times6.023\times10^{23}\times\frac{4}{3}\times\frac{22}{7}\times r^3$

$\therefore \; r = \mathbf{1.33\times10^{-8}}$ **cm**

131. (a) Given $P(V-b) = nRT$

$1\times(25-b) = 1\times0.0821\times273$

($\because V = 25\text{ dm}^3 = 25$ litre)

$\therefore \; b = 2.586$ litre

Also, diameter of molecule $d = 2r$

We have $b = 4\times N\times$ Volume of molecule

$= 4\times6.023\times10^{23}\times\frac{4}{3}\pi r^3$

$\therefore \; 2.586 = 4\times6.023\times10^{23}\times\frac{4}{3}\times\frac{22}{7}\times\left(\frac{d}{2}\right)^3$

$\therefore \; d = \mathbf{1.270\times10^{-8}}$ **cm**

(b) Given $P(V-b) = nRT, \quad PV-Pb = nRT$

$\frac{PV}{nRT}-\frac{Pb}{nRT} = 1$

or $Z-\frac{Pb}{nRT} = 1$

($\because \frac{PV}{nRT} = Z$, *i.e.*, compressibility factor)

or $Z = 1+\frac{Pb}{nRT} = 1+\frac{1\times2.586}{1\times0.0821\times273} = \mathbf{1.115}$

132. $T_C = \frac{8a}{27Rb}$ and $P_C = \frac{a}{27b^2}$

$\therefore \; \frac{T_C}{P_C} = \frac{8b}{R}$ or $b = \frac{RT_C}{8P_C}$

$\therefore \; b = \frac{0.0821\times303}{8\times72} = \mathbf{0.043}$ **litre mol^{-1}**

$a = 27P_C\times b^2 = 27\times72\times(0.043)^2 = \mathbf{3.59}$ **litre^2 atm mol^{-2}**

133. **For O_2 :** $T_{r_1} = \frac{T}{T_{C_1}} = \frac{300}{155}$

For N_2 : $T_{r_2} = \frac{T}{T_{C_2}} = \frac{300}{126}$

$\therefore \; \frac{T_{r_1}}{T_{r_2}} = \frac{126}{155} = \mathbf{0.812}$

134. According to law of corresponding state

$$\left[P_r+\frac{3}{V_r^2}\right][3V_r-1] = 8RT_r$$

$$\left[P_r+\frac{3}{(0.4)^2}\right][3\times0.4-1] = 8\times0.7277$$

$\therefore \; P_r = \mathbf{10.350}$

135. Inversion temperature,

$$T_i = \frac{2a}{R\cdot b} = \frac{2\times0.246}{0.0821\times0.0267} = \mathbf{224.4\text{ K}}$$

Boyle temperature,

$$T_b = \frac{a}{R\cdot b} = \frac{0.246}{0.0821\times0.0267} = \mathbf{112.2\text{ K}}$$

136. Let pressure of gas left in vessel after I operation be P_1. Let n_1 mole are removed from vessel after I operation. Let n mole were present initially.

Thus, Initial state $PV = nRT$ ...(i)

$\therefore \; P_1V = (n-n_1)RT$ ...(ii)

$P_1V = nRT-n_1RT$

$P_1V = PV-n_1RT$ ...(iii)

The n_1 mole taken out has volume v at pressure P_1

Thus, $P_1v = n_1RT$ ...(iv)

By Eqs. (iii) and (iv), $P_1V = PV-P_1v$

or $P_1 = P\left[\frac{V}{V+v}\right]$ ...(v)

Similarly, for II operation: $P_2 = P_1\left[\frac{V}{V+v}\right] = P\left[\frac{V}{V+v}\right]^2$

Thus, for n operations $\mathbf{P_n = P\left[\frac{V}{V+v}\right]^n}$

137. For real gases, van der Waals' equation for one mole is:

$$\left[P+\frac{a}{V_m^2}\right][V_m-b] = RT$$

or $$PV_m - Pb + \frac{a}{V_m} - \frac{ab}{V_m^2} = RT \qquad ...(1)$$

For intercept of PV_m *vs.* P graph at y-axis, $P = 0$ and thus, $v_m \rightarrow \infty$. Thus neglecting $\frac{a}{V_m}$ and $\frac{ab}{V_m^2}$ terms in Eq. (1)

or $$\boldsymbol{PV_m = Pb + RT} \qquad ...(2)$$

Thus, a graph between PV_m *vs.* P will lead to an intercept RT as Eq. (2) represents a straight line equation ($y = mx + c$).

138. $$\text{Mole of He} = \frac{1}{4}$$

$$\text{Mole of O}_2 = \frac{4}{32} = \frac{1}{8}$$

$\because$ $$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

For O_2 : $$1000 = \sqrt{\frac{3 \times 8.314 \times T}{32 \times 10^{-3}}}$$

$$[M_{O_2} = 32 \times 10^{-3} \text{ kg}]$$

$\therefore$ $$T_{O_2} = 1283.0 \text{ K}$$

For He : $$1000 = \sqrt{\frac{3 \times 8.314 \times T}{4 \times 10^{-3}}}$$

$$[M_{\text{He}} = 4 \times 10^{-3} \text{ kg}]$$

$$T_{\text{He}} = 160.37 \text{ K}$$

$\therefore$ K.E. per $\frac{1}{4}$ mole He $= \frac{3}{2} \times \frac{1}{4} \times 8.314 \times 160.3 = 500$ J

K.E. per $\frac{1}{8}$ mole $O_2 = \frac{3}{2} \times \frac{1}{8} \times 8.314 \times 1283.0 = 2000.036$ J

At thermal equilibrium temperature (T) becomes constant as O_2 molecules provide heat energy to He molecules.

Heat given is expressed as $n \times c_v \times \Delta T$

$$\left(c_v = \frac{3}{2}R \text{ for He and } \frac{5}{2}R \text{ for O}_2\right)$$

$$\text{Heat given by O}_2 = \text{Heat taken up by H}_2$$

$$\frac{1}{8} \times \frac{5}{2} R \times (1283 - T) = \frac{1}{4} \times \frac{3}{2} R \times (T - 160.37)$$

$\therefore$ $$5(1283 - T) = 2 \times 3\,(T - 160.37)$$

$$6415 - 5T = 6T - 962.22$$

$\therefore$ $$T = 670.7 \text{ K}$$

Thus, $$u_{\text{rms}} \text{ for O}_2 = \sqrt{\frac{3 \times 8.314 \times 670.7}{32 \times 10^{-3}}} = \mathbf{723\ m/s}$$

$$u_{\text{rms}} \text{ for He} = \sqrt{\frac{3 \times 8.314 \times 670.7}{4 \times 10^{-3}}} = \mathbf{2045\ m/s}$$

139. According to Maxwell's molecular speed distribution :

(a) The number of molecules of a given gas having their speed near to u_{MP} increases with temperature.

(b) The number of molecules having their speed near to u_{MP} decreases with increase in molar mass for gases at constant temperature.

(c) The number of molecules having their speed near to u_{MP} increases with increase in u_{MP}.

Also, $$n \propto u_{MP}$$

$\therefore$ $$n_1 \propto \sqrt{\frac{2RT_1}{M_1}}, \quad n_2 \propto \sqrt{\frac{2RT_2}{M_2}}$$

$\because$ $$M_1 = M_2$$

$\therefore$ $$\frac{n_1}{n_2} = \sqrt{\frac{T_1}{T_2}}$$

$$T_2 = 300, \quad n_1 = \frac{n_2}{2}$$

$\therefore$ $$\frac{1}{2} = \sqrt{\frac{T}{300}} \qquad \therefore \ \mathbf{T = 75\ K}$$

140. According to Maxwell's molecular speed distribution :

$$\frac{n_g}{\Sigma n_g} \propto \frac{1}{u_{\text{rms}}}$$

$\therefore$ $$u_{\text{rms}} \propto \frac{\Sigma n_g}{n_g} \propto \frac{N}{n_g} \quad (\because \ \text{1 mole of both gases})$$

$$u_{\text{rms Ar}} \propto \frac{N}{n_{\text{Ar}}}, \quad u_{\text{rms He}} \propto \frac{N}{n_{\text{He}}}$$

$\therefore$ $$\frac{n_{\text{He}}}{n_{\text{Ar}}} = \frac{u_{\text{rms Ar}}}{u_{\text{rms He}}} = \frac{467}{1477} = \mathbf{0.316}$$

• SINGLE INTEGER ANSWER PROBLEMS •

1. A container having 3 mole of ideal gas occupies 60 litres at pressure P and temperature T. If 0.1 mole of gas is introduced at same P and T in container the change in volume will be ...... litre.

2. An ideal gas on heating from 100 K to 109 K shows an increase by $a\%$ in its volume at constant P. The value of a is ..9...

3. The ratio of inversion temperature and Boyle's temperature for a real gas is ..2..

4. The specific heat of a gas are 0.125 and 0.075 cal/g. The $1/10^{th}$ value of its molar mass is ......

5. A bulb is having ideal gas at 27° C. On heating the bulb to 227° C, 2 litre of gas measured at 227° C is expelled out. The volume of bulb in litre is ......

6. The mass of molecule A is twice the mass of molecule B. The rms speed of A is twice the rms speed of B. If two samples of A and B contain same number of molecule, the ratio of pressure of gas samples of A and B in separate containers of equal volume is ......

7. Molar mass of air is 28.80 g mol^{-1}. The volume of N_2 (in mL) in 10 mL of sample of this air is ......

8. A cylinder containing 5 litre of O_2 at 25° C was leaking. When the leakage was detected and checked, the pressure inside cylinder was reduced from 8 atm to 2 atm. The ratio of mass of O_2 initially present to that left after leakage is equal to ......

9. 16 mL of He gas effuses through a pin hole in 4 sec from a container having P_{He} equal to 1 atm. If same container is filled with CH_4 having pressure 2 atm, how much volume (in mL) of CH_4 will be leaked through same pin hole in 2 sec?

10. U_{rms} of CH_4 at T K is 6 times of U_{mp} of SO_2 at T_1 K. The temperature of CH_4 gas is ...... times of SO_2.

11. Root mean square speed of a gas is 5 ms^{-1}. If some molecules out of 10 molecules in all are moving with 7 ms^{-1} and rest all the molecules moving with 3 m sec^{-1}, then number of molecules moving with higher speed is ......

12. A metallic carbonyl $M\,(CO)_X$ is in gaseous state. The rate of diffusion of CH_4 is 3.31 time faster than this gas under identical conditions. If at. mass of metal is 63.29, the closest integer value of X is ......

13. The ratio of rate of diffusion of He (at 4 atm) and CH_4 (1 atm) through same pin hole at constant temperature is ......

14. 5 mL of a liquid [$V.P.$ = 8 cm at 400 K] having density 0.02 g/mL is placed in a container of 4 litre. It is connected to another empty container of 4 litre at 400 K. The resultant pressure of liquid shown is ......

15. A gas having molecular formula O_n. If its vapour density is 24. The value of n is ......

16. The percentage decrease in volume of gas at constant temperature if percentage increase in pressure is 5.26, is ......

17. An ideal gas on heating shows a rise in temperature by 8% at constant pressure. The % increase in volume of gas is ......

18. The density of vapours of a substance at 1 atm P and 500 K is 0.3 kg m^{-3}. The vapours effuse 0.4216 times faster than O_2 through a pin hole under identical conditions. If R = 0.08 litre atm $K^{-1}mol^{-1}$. The molar volume of gas is $a \times 10^2$ litre. The value of a is ....

19. What mass of N_2 should be mixed with 11g of CO to give a mean molar mass of mixture equal to 36 ?

20. A flask of capacity 5 litre containing air is heated from 27°C to 227°C. The volume (in litre) of air left in flask on heating is ....

21. A flask of capacity 10 litre containing air is heated from 27°C to 227°C. The ratio of mole of air present at 27°C to mole present at 227°C is ....

22. w_1 g of gas A and w_2 g of gas B shows a mixture of molar mass 72. This $(w_1 + w_2)$ g mixture is placed in a container of volume V litre at 1 atm and 300 K. The density of mixture at these conditions is ..... kg m^{-3}.
(R = 0.08 litre-atom K^{-1} mol^{-1})

23. A certain quantity of gas occupies 960 litre when collected over water at 300 K and 760 mm pressure. However the same quantity of dry gas occupies 608 litre at 2 atm and 400 K. The number of mole of water vapours present in wet gas is (R = 0.08 litre atm K^{-1} mol^{-1})....

24. 0.75 mole of solid A_4 and 2 mole of gaseous O_2 are heated to react completely in a sealed bottle to produce gaseous compound A_3O_n. After the compound is formed, the vessel is brought to initial temperature, the pressure is found to half of initial pressure. The value of n is ....

25. A graph is plotted for a van der Waals' gas between PV_m vs P leading to an intercept of 22.16 litre-atm. The temperature of gas at which these observations of P and V_M were made is ....°C.
(R = 0.08 litre atm K^{-1} mol^{-1})

26. Two boxes A and B having their volume ratio 1 : 4 and filled with Ne are inter connected through a narrow tube of negligible volume. Box A is kept at 300 K and box B at 600 K. The ratio of mole of Ne gas in box B to box A is ....

27. The density of the vapours of a substance at 1 atm and 500 K is 0.36 kg m^{-3}. If molar mass of gas is 18 g mol^{-1}, the molar volume of gas is 5×10^a m^{-3}. What is the value of a?

28. The root mean square speed of the molecules of diatomic gas is u at temperature T. On increasing the temperature to $2T$, the molecules are dissociated. At this time u_{rms} of the atoms is au. The value of a is ....

29. The u_{rms} of the molecules of a gas of density 4 kg m^{-3} and pressure 1.2×10^5 Nm^{-2} is 3×10^a cm/sec. The value of a is ....

30. One litre of N_2 and 7/8 litre of O_2 under identical conditions of P and T are mixed. The mass ratio of N_2 and O_2 is ....

31. Density of a gas is found 5.46 g/L at 27°C and 2 atm pressure. What will be its density at STP in g/L ?

32. A balloon is filled with 2.4×10^{-3} mole of He at 27°C and 80 mm pressure. An additional amount of He (1.2×10^{-3} mole) is added at the same temperature showing a rise in volume by 50%. The final pressure of gas in balloon in cm is ....

33. A given sample of gas occupies 40.5 mL at a certain P and T. If mass of the gas is doubled and absolute temperature is lowered to $T/3$ but pressure increases to $9P$, the volume occupied by gas will be .... mL.

34. The composition of air is 20% O_2 and 80% N_2 by volume. If 10 litre of air is placed at 24.9584 atm and 304 K, the mole of O_2 present to closest integer values are....

35. A closed container of volume $0.02 m^3$ consists 28g of mixture of neon and argon at temperature 27°C and pressure 1×10^5 Nm^{-2}. If atomic mass of Ne and Ar are 20 and 40 respectively, the mass of Ne in mixture in (g) is ....

36. If pressure of gases at sun is 1.4×10^9 atm, density is 1.4 g /mL and average molar mass of gaseous mixture is 2, the temperature of sun is 2.4×10^a K. The value of a is ....

37. A flask contains a mixture of N_2 and CO_2 at 1.5 atm and 27°C. If CO_2 is removed the pressure falls to 0.5 atm and the mass of the flask drops by 22g. The mass of N_2 in g in flask is ......

38. If $T_A : T_B$ is 2 :1, the ratio of u_{rms} of two gases A and B is $2\sqrt{2} : 1$ respectively. What would be the ratio of the rate of diffusion of two gases A and B under same P and T?

39. A mixture of H_2 and O_2 in 2 :1 volume ratio is allowed to diffuse through a porous partition. The composition ratio of $H_2 : O_2$ coming out initially would be ....

40. A cylinder containing 5.0 litre O_2 at 25°C was leaking. When the balloon leakage was detected and stopped, there was a change in the pressure of the gas from 3.0 atm to 2.235 atm. The massing of O_2 leaked out is ......

41. By how many times the absolute temperature of a gas would increase when u_{rms} of a gas in a container of fixed volume is increased from 5×10^4 cm sec^{-1} to 10×10^4 cm sec^{-1}?

42. The ratio of pressure of a gas when u_{rms} of a gas in a container is increased from 5×10^4 cm sec^{-1} to 10×10^4 cm sec^{-1}.

43. 11.2 litre of a gas at NTP requires 40 cal heat to raise its temperature from 0°C to 10°C. The specific heat at constant volume of gas in calories is ......

44. The ratio of root mean square speed of He and SO_2 gases placed in two containers of identical volume at same P and T is ......

45. A vessel having movable piston containers has 6.0 mole of a gas at 8.0 atm pressure and volume 5.0 litre. 1.5 mole of gas are withdrawn as well as piston is pulled isothermally onwards to make volume of vessel 10.0 litre. The final pressure of gas will be ......

46. The isothermal compressibility factor 'α' for an ideal gas at 0.25 atm pressure is ......

47. The mixture of one mole of monoatomic gas and one mole diatomic gas has molar specific heat at constant volume (in cal) equal to ....

48. The heat used in calorie in doing work during the heating of 1 mole diatomic gas at constant pressure in order to increase the temperature of gas through 1°C.

49. At 400 K, the root mean square speed of a gas (molar mass= 40) is equal to the most probable speed of gas y at 60 K. The molar mass of the gas y is .... **(IIT 2009)**

50. To an evacuated vessel with movable piston under external pressure of 1 atm., 0.1 mol of He and 1.0 mol of an unknown compound (vapour pressure 0.68 atm. at 0°C) are introduced. Considering the ideal gas behaviour, the total volume (in litre) of the gases at 0°C is close to ...... **(IIT 2011)**

ANSWERS

1. Two **2.** Nine **3.** Two **4.** Four **5.** Three **6.** Eight **7.** Eight **8.** Four **9.** Eight **10.** Six **11.** Four **12.** Four
13. Eight **14.** Eight **15.** Three **16.** Five **17.** Eight **18.** Six **19.** Seven **20.** Five **21.** Two **22.** Three **23.** Two **24.** Four
25. Four **26.** Two **27.** Three **28.** Two **29.** Four **30.** One **31.** Three **32.** Eight **33.** Three **34.** Two **35.** Four **36.** Seven
Seven **38.** Two **39.** Eight **40.** Five **41.** Four **42.** One **43.** Eight **44.** One **45.** Four **46.** Four **47.** Four **48.** Two
Four **50.** Seven (Saturated vapours do not obey gas laws except Dalton's law of vapour pressure)

OBJECTIVE PROBLEMS (One Answer Correct)

1. If X_M, X_P and X_V are mole fraction, pressure fraction and volume fraction respectively of a gaseous mixture, then :

(a) $X_M = \frac{1}{X_P} = \frac{1}{X_V}$ (b) $\frac{1}{X_M} = X_P = \frac{1}{X_V}$

(c) $X_M = X_P = X_V$ (d) $\frac{1}{X_M} = \frac{1}{X_P} = \frac{1}{X_V}$

2. Virial equation is :

$$PV_M = RT\left[A + \frac{B}{V_M} + \frac{C}{V_M^2} + ...\right]$$

where A, B, C are first, second, third .... virial coefficient respectively. For an ideal gases:

(a) A = unity and B, C are zero

(b) A, B, C are all equal to unity

(c) A is dependent of temperature

(d) All A, B, C depend on temperature

3. Which of the following is intensive property?

(a) P (b) V

(c) Mole (d) T

4. Which one is not correct for gaseous state obeying van der Waals' equation ?

(a) Compressibility factor at critical temperature ≈ 0.375

(b) For a gas if van der Waals' constant $a = 0, T_C = 0$

(c) Ideal gases do not have critical temperature

(d) Gaseous molecules showing H-bonding show minimum deviations from $Z \approx 0.375$

5. One mole of a gas is present in a vessel at STP. The volume of container in which neither of the gas molecule is present is :

(a) 22.4 litre (b) 2.24 litre

(c) 2.24×10^{-1} litre (d) 22.3776 litre

6. The compressibility factor for definite mass of a van der Waals' gas at 0°C and 100 atmosphere is found to be 0.5. Assuming the volume of gas molecules negligible, the van der Waals' constant 'a' for a gas is :

(a) 1.256 $\text{litre}^2\ \text{mol}^{-2}$ atm

(b) 0.256 $\text{litre}^2\ \text{mol}^{-2}$ atm

(c) 2.256 $\text{litre}^2\ \text{mol}^{-2}$ atm

(d) 0.0256 $\text{litre}^2\ \text{mol}^{-2}$ atm

7. The pressure exerted by 1 mole of CO_2 at 273 K, is 34.98 atm. Assuming that volume occupied by CO_2 molecules is negligible, the value of van der Waals' constant for attraction of CO_2 gas is :

(a) 3.59 dm^6 atm mol^{-2} (b) 2.59 dm^6 atm mol^{-2}

(c) 1.25 dm^6 atm mol^{-2} (d) 1.59 dm^6 atm mol^{-2}

8. Relative humidity of air is 60% and the saturation vapour pressure of water vapour in air is 3.6 kPa. The mass of water vapours present in 2 litre air at 300 K is :

(a) 52 g (b) 31.2 g

(c) 26 g (d) 5.2 g

9. A 3 : 2 molar mixture of N_2 and CO is present in a vessel at 500 bar pressure. Due to hole in the vessel, the gas mixture leaks out. The composition of mixture effusing out initially is :

(a) $n_{N_2} : n_{CO} :: 1 : 2$ (b) $n_{N_2} : n_{CO} :: 6 : 1$

(c) $n_{CO} : n_{N_2} :: 1 : 2$ (d) $n_{CO} : n_{N_2} :: 2 : 3$

10. Number of N_2 molecules present in 1 litre vessel at NTP when compressibility factor is 1.2 is :

(a) 2.23×10^{24} (b) 2.23×10^{22}

(c) 2.7×10^{22} (d) 2.7×10^{24}

11. Select the correct statement :

(a) A mixture of ideal gases is cooled up to liquid the temperature (4.22 K) to form ideal solution.

(b) Ideal gas can be liquefied on applying pressure and lowering temperature.

(c) Kinetic energy of a gas is zero at 0° C.

(d) Ideal gas on subjecting to Joule-Thomson effect do not show cooling on account of absence of molecular forces of attraction.

12. Select the incorrect statement :

(a) Compressibility factor for an ideal gas is unity.

(b) A real gas approaches ideal gas nature at high temperature and low pressure.

(c) The compressibility factor $Z > 1$, then for a gas when repulsive forces predominate.

(d) van der Waals' constant 'a' for NH_3 is smaller than N_2.

13. 0.44 g dry ice is placed in an evacuated chamber of 5 litre at 27°C. The pressure inside the vessel when whole dry ice has been evaporated to gaseous state is:

(a) 0.49 atm (b) 0.049 atm

(c) 4.9×10^{-3} atm (d) 4.9 atm

14. An oxide of nitrogen has density 1.33 g/litre at 764 mm Hg and 150° C. The oxide of nitrogen is:

(a) N_2O_5 (b) NO_2

(c) N_2O (d) NO

15. If P_g and P_v are partial pressure of H_2O_v and saturated vapour pressure of H_2O_v respectively, than % relative humidity is given by:

(a) $\frac{P_v}{P_g} \times 100$ (b) $\frac{P_g}{P_v} \times 100$

(c) $\frac{P_g + P_v}{P} \times 100$ (d) $\frac{P_g - P_v}{P_g} \times 100$

16. A graph plotted between *Pd vs. P* where *P* is pressure of C_2H_6 gas (assume ideal gas) and *d* is its density in g/L at particular temperature $\left[\frac{d\,Pd}{dP}\right]=20$ when $P = 8.21$ atm, the temperature of gas will be :

(a) 400 K (b) 1200 K
(c) 300 K (d) 600 K

17. At low pressure when *b* is negligible for a van der Waals' gas $RT = 2\sqrt{aP}$, then volume occupied by gas is :

(a) $\frac{RT}{2P}$ (b) $\frac{2RT}{P}$
(c) $\frac{2P}{RT}$ (d) $\frac{P}{RT}$

18. The pressure exerted by sodium vapours in a 2 litre container is 50 bar at 1000°C. The number of atoms of sodium in the container is :

(a) 5.76×10^{16} (b) 5.76×10^{23}
(c) 5.76×10^{17} (d) 5.76×10^{19}

19. The quantity $\frac{PV}{kT}$, where *k* represents Boltzman's constant represents :

(a) Number of mole of gas
(b) Number of molecules of gas
(c) Mass of gas
(d) K.E./molecule of gas

20. A mixture containing Ne and Ar in a vessel at 250 K has a total translational kinetic energy = 3 kJ. The total mass of mixture is 30g. What is the mass % of Ar in mixture ?

(a) 28.3 (b) 71.7
(c) 50.3 (d) 30.2

21. An electric lamp is filled with an ideal gas having density $0.75\ \text{kg/m}^3$ and pressure 4×10^4 Pa. On switching on the lamp, the temperature of gas molecules increases so that new pressure becomes 9×10^4 Pa. The increase in u_{rms} of gas molecules in m/sec,is :

(a) 200 (b) 300
(c) 100 (d) 400

22. One mole of a monoatomic gas $\left(\gamma=\frac{5}{3}\right)$ and one mole of a diatomic gas $\left(\gamma=\frac{7}{5}\right)$ are mixed in a vessel. The value of γ for the mixture is :

(a) 1.5 (b) 3.06
(c) 1.53 (d) 1.43

23. At 10°C the density of a fixed mass of an ideal gas divided by its pressure is *X*. At 110°C, this ratio would be :

(a) $\frac{10x}{110}$ (b) $\frac{283x}{383}$
(c) x (d) $\frac{383}{283}x$

24. The no. of atoms of a triatomic gas in 0.1 mol is :

(a) 1.8×10^{22} (b) 6.02×10^{23}
(c) 1.8×10^{23} (d) 3.6×10^{23}

25. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is :

(a) 1/3 (b) 1/2
(c) 2/3 (d) $\frac{1}{3}\times\frac{273}{298}$

26. The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is :

(a) Critical temperature
(b) Boyle's temperature
(c) Inversion temperature
(d) Reduced temperature

27. The ratio of root mean square speed to average speed of a gas molecule at a particular temperature is :

(a) 1.886 (b) 1.086
(c) 0.9213 (d) 1.426

28. Helium atom is two times heavier than a hydrogen molecule. At 298K, the average kinetic energy of a helium atom is :

(a) Two times of a H_2 molecule
(b) Same as of H_2 molecule
(c) Four times of a H_2 molecule
(d) 1/2 of H_2 molecule

29. Equal masses of methane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is :

(a) 1/2 (b) 8/9
(c) 1/9 (d) 16/17

30. The value of van der Waals' constant '*a*' for the gases O_2, N_2, NH_3 and CH_4 are 1.360, 1.390, 4.170 and 2.253 L^2 atm mol^{-2} respectively. The gas which can most easily be liquefied is :

(a) O_2 (b) N_2
(c) NH_3 (d) CH_4

31. A liquid is in equilibrium with its vapours at it's boiling point. On the average, the molecules in the two phases have equal :

(a) inter-molecular forces
(b) potential energy
(c) kinetic energy
(d) total energy

32. Rate of diffusion of a gas is :

(a) directly proportional to its density
(b) directly proportional to its molar mass
(c) directly proportional to the square root of its molar mass
(d) inversely proportional to the square root of its molar mass

33. The average speed of an ideal gas molecule at 27°C is 0.3 m/s. The average speed at 927°C will be :
(a) 0.6 m/s (b) 0.3 m/s
(c) 0.9 m/s (d) 3.0 m/s

34. In van der Waals' equation of state for a non-ideal gas, the term that accounts for intermolecular forces is :
(a) $(V-b)$ (b) RT
(c) $\left(P+\frac{a}{V^2}\right)$ (d) $(RT)^{-1}$

35. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends. The white ammonium chloride ring first formed will be :
(a) at the centre of the tube
(b) near the hydrogen chloride bottle
(c) near the ammonia bottle
(d) throughout the length of the tube

36. The density of neon will be highest at :
(a) STP (b) 0°C, 2 atm
(c) 273°C, 1 atm (d) 273°C, 2 atm

37. The rate of diffusion of methane at a given temperature is twice that of a gas *X*. The molar mass of *X* is :
(a) 64.0 (b) 32.0
(c) 4.0 (d) 8.0

38. According to the kinetic theory of gases for a diatomic molecule :
(a) the pressure exerted by the gas is proportional to the root mean square speed of the molecule
(b) the pressure exerted by the gas is proportional to the mean speed of the molecule
(c) the root mean square speed of the molecule is inversely proportional of the temperature
(d) the mean translational kinetic energy of the molecule is proportional to the absolute temperature

39. At constant volume, for a fixed number of mole of a gas, the pressure of the gas increases with rise of temperature due to :
(a) increase in average molecular speed
(b) increase rate of collisions amongst molecules
(c) increase in molecular attraction
(d) decrease in mean free path

40. Equal masss of ethane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is :
(a) 1 : 1 (b) 1 : 2
(c) 1 : 16 (d) 15 : 16

41. The van der Waals' constant '*a*' in L^2 atm mol^{-2} with gases (not reported in order are given in list A and B.)

List A	List B
(1) $C_6H_6(g)$	(a) 0.217
(2) $C_6H_5CH_3(g)$	(b) 5.464
(3) $Ne(g)$	(c) 18.00
(4) $H_2O(g)$	(d) 24.060

Which one is the correct match?
(a) 1-a, 2-d, 3-c, 4-b (b) 1-d, 2-a, 3-b, 4-c
(c) 1-c, 2-d, 3-a, 4-b (d) 1-b, 2-c, 3-a, 4-d

42. Which of the following gas molecules has the largest mean free path ?
(a) H_2 (b) N_2
(c) O_2 (d) Cl_2

43. The ratio between the root mean square speed of H_2 at 50 K and that of O_2 at 800 K is :
(a) 4 (b) 2
(c) 1 (d) 1/4

44. *X* mL of H_2 gas effuses through a hole in container in 5 seconds. The time taken for the effusion of the same volume of the gas specified below under identical conditions is :
(a) 10 s : He (b) 20 s : O_2
(c) 25 s : CO (d) 55 s : CO_2

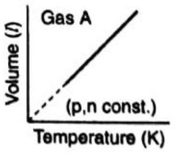
45. The compressibility factor for an ideal gas is :
(a) 1.5 (b) 1.0
(c) 2.0 (d) ∞

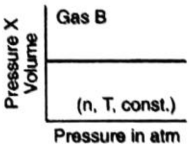
46. The critical temperature of H_2O is higher than O_2 because the H_2O molecule has :
(a) A fewer electron than O_2
(b) Two covalent bond
(c) V shape
(d) Dipole moment

47. According to Graham's law, at a given temperature the ratio of the rates of diffusion $\frac{r_A}{r_B}$ of gases *A* and *B* are given by :
(a) $\left(\frac{P_A}{P_B}\right)\left(\frac{M_A}{M_B}\right)^{\frac{1}{2}}$ (b) $\left(\frac{M_A}{M_B}\right)\left(\frac{P_A}{P_B}\right)^{\frac{1}{2}}$
(c) $\left(\frac{P_A}{P_B}\right)\left(\frac{M_B}{M_A}\right)^{\frac{1}{2}}$ (d) $\left(\frac{M_A}{M_B}\right)\left(\frac{P_B}{P_A}\right)^{\frac{1}{2}}$
(where *P* and *M* are pressures and molar masss of gases *A* and *B* respectively).

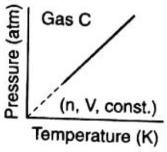
48. A gas will approach ideal behaviour at :
(a) low temperature and low pressure
(b) low temperature and high pressure
(c) high temperature and low pressure
(d) high temperature and high pressure

49. Which of these gases exhibits behaviour that deviates most significantly from that expected for an ideal gas?

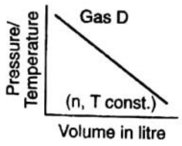
(a)


(b)


(c)

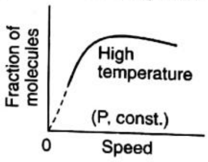


(d)

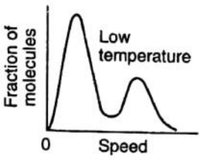


50. Which of the following graph is in accordance to the Maxwell distribution of molecular speeds and its dependence on temperature?

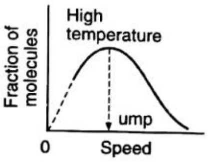
(a)



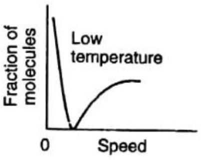
(b)



(c)

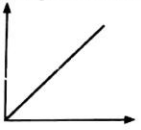


(d)

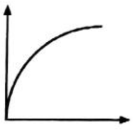


51. Which of the following graphs represents $\frac{1}{V^2}$ *vs* P curve for ideal gas at constant T and n ?

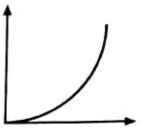
(a)



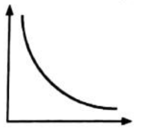
(b)



(c)

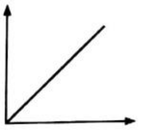


(d)

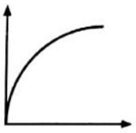


52. Which of the following graph represents V *vs* $\frac{1}{P^2}$ for ideal gas at constant T and n ?

(a)

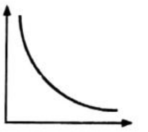


(b)



(c)

(d)



53. The ratio of rates of diffusion of SO_2 and CH_4 placed in a container in the mass ratio of 8 : 1 at the same temperature is :

(a) 1 (b) 2
(c) 3 (d) 4

54. The inversion temperature T_i (K) of hydrogen is ... (Given van der Waals' constants a and b are 0.244 atm litre^{2}mol^{-2} and 0.027 litre mol^{-1} respectively) :

(a) 440 (b) 220
(c) 110 (d) 330

55. The compressibility of gas is less than unity at STP. Therefore : **(IIT 2000)**

(a) $V_m > 22.4$ litre (b) $V_m < 22.4$ litre
(c) $V_m = 22.4$ litre (d) $V_m > 44.8$ litre

56. The rms speed of hydrogen is $\sqrt{7}$ times the rms speed of nitrogen. If T is the temperature of the gas, then : **(IIT 2000)**

(a) $T(H_2) = T(N_2)$ (b) $T(H_2) > T(N_2)$
(c) $T(H_2) < T(N_2)$ (d) $T(H_2) = \sqrt{7}\, T(N_2)$

57. At 100°C and 1 atm, if the density of liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm^{-3}, then the volume occupied by water molecules in 1 litre of steam at that temperature is : **(IIT 2000)**

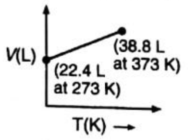
(a) 6 cm^3 (b) 60 cm^3
(c) 0.6 cm^3 (d) 0.06 cm^3

58. The root mean square speed of an ideal gas at constant pressure varies with density d as: **(IIT 2001)**

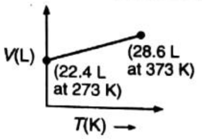
(a) d^2 (b) d
(c) $\sqrt{d}$ (d) $\frac{1}{\sqrt{d}}$

59. Which of the following volume (V) *vs.* temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure : **(IIT 2002)**

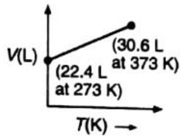
(a)



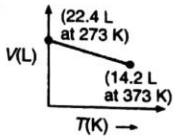
(b)



(c)



(d)



60. When the temperature is increased surface tension of water : **(IIT 2002)**

(a) increases
(b) decreases
(c) remains constant
(d) show irregular behaviour

61. Positive deviations from ideal gas behaviour takes place because of : **(IIT 2003)**

(a) molecular interaction between atoms and $\frac{PV}{nRT} > 1$

(b) molecular interaction between atoms and $\frac{PV}{nRT} < 1$

(c) finite size of atoms and $\frac{PV}{nRT} > 1$

(d) finite size of atoms and $\frac{PV}{nRT} < 1$

62. The root mean square speed of one mole of a monoatomic gas having molar mass M is u_{rms}. The relation between the average kinetic energy (E) of the gas and u_{rms} is : **(IIT 2004)**

(a) $u_{rms} = \sqrt{\frac{3E}{2M}}$ (b) $u_{rms} = \sqrt{\frac{2E}{3M}}$

(c) $u_{rms} = \sqrt{\frac{2E}{M}}$ (d) $u_{rms} = \sqrt{\frac{E}{3M}}$

63. The ratio of the rate of diffusion of helium and methane under identical conditions of pressure and temperature is : **(IIT 2005)**

(a) 4 (b) 2

(c) 1 (d) 0.5

64. A monoatomic ideal gas undergoes a process in which the ratio of P to V at any instant is constant and equal to unity. The molar heat capacity of gas is : **(IIT 2006)**

(a) $2.0\,R$ (b) $1.5\,R$

(c) $2.5\,R$ (d) 0

65. The term that accounts for the attractive forces present in a real gas in the van der Waals' equation is : **(IIT 2009)**

(a) nb (b) $\frac{n^2a}{V^2}$

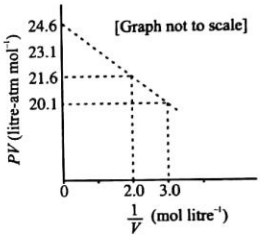
(c) $-\frac{an^2}{V^2}$ (d) $-nb$

66. At 400 K, the root mean square (rms) speed of a gas X (molar mass 40) is equal to the most probable speed of a gas Y at 60 K. The molar mass of gas Y is : **(IIT 2009)**

(a) 2 (b) 4

(c) 6 (d) 8

67. For one mole of a van der Waals' gas when $b = 0$ and $T = 300$ K, the PV *vs.* $1/V$ plot is shown below. The value of the van der Waals' constant a (atm.litre^{2}mol^{-2}) is: **(IIT 2012)**



(a) 1.0 (b) 4.5

(c) 1.5 (d) 3.0

68. For gaseous state, if most probable speed is denoted by C^*, average speed by $\overline{C}$ and mean square speed by C, then for a large number of molecules the ratios of these speeds are : **[JEE (Main) 2013]**

(a) $C^* : \overline{C} : C = 1 : 1.128 : 1.225$

(b) $C^* : \overline{C} : C = 1 : 1.225 : 1.128$

(c) $C^* : \overline{C} : C = 1.225 : 1.128 : 1$

(d) $C^* : \overline{C} : C = 1.128 : 1.225 : 1$

SOLUTIONS (One Answer Correct)

1. (c) ∵ $P' = P_T \cdot X_M$

and $V' = V_T \cdot X_M$

where X_M is mole fraction

Also $\frac{P'}{P_T}$ = Pressure fraction *i.e.*, X_P

and $\frac{V'}{V_T}$ = Volume fraction *i.e.*, X_V

∴ $X_M = X_P = X_V$

2. (a) $PV = RT$ for ideal gases.

3. (d) Temperature is mass independent.

4. (d) $Z = \frac{P_C V_C}{RT_C}$; Also, gaseous molecules showing H-bonding show maximum deviations in Z due to increase in molecular attractions (*e.g.*, Z for NH_3, H_2O, $CH_3OH \simeq 0.22$ to 0.24)

5. (d) Volume of molecules is negligible in comparison of total volume occupied by gas. About 99.9% volume of vessel is not occupied by gas molecules. The volume in which neither of the gas molecules is present $= \frac{99.9 \times 22.4}{100} = 22.3776$ litre.

6. (a)

$$Z = \frac{PV}{nRT} = 0.5$$

Now, $\left[P + \frac{n^2a}{V^2}\right][V - nb] = nRT$

$$\left[P + \frac{n^2a}{V^2}\right][V] = nRT \qquad (b \text{ is negligible})$$

$$PV^2 - nRTV + n^2a = 0$$

$$\therefore \quad V = \frac{nRT \pm \sqrt{n^2R^2T^2 - 4n^2a \times P}}{2P}$$

Since, V is constant at given P and T and thus, discriminant is = 0

$$\therefore \quad n^2R^2T^2 = 4n^2aP$$

$$\text{or} \quad a = \frac{R^2T^2}{4P} = \frac{(0.0821)^2 \times (273)^2}{4 \times 100}$$

$$= 1.256 \text{ litre}^2 \text{ mol}^{-2} \text{ atm}$$

7. (a) $\left[P + \frac{a}{V^2}\right][V - b] = RT$

$$\therefore \quad \left[P + \frac{a}{V^2}\right]V = RT \qquad (b \text{ is negligible})$$

or $V^2P - RTV + a = 0$

$$V = \frac{+RT \pm \sqrt{R^2T^2 - 4Pa}}{2P}$$

Since, V is constant at given P and T, V can have only one value or discriminant = 0.

∴ $R^2T^2 = 4Pa$

$$\text{or} \quad a = \frac{R^2T^2}{4P} = \frac{(0.0821)^2 \times (273)^2}{4 \times 34.98} = 3.59 \text{ dm}^6 \text{ atm mol}^{-2}$$

8. (b) $PV = \frac{w}{M}RT$ (for vapours of H_2O)

$P = 3.6 \times 10^3$ Pa; $V = 2 \times 10^{-3}$ m^3;

$T = 300$ K

$$\therefore \quad w_{H_2O} = \frac{3.6 \times 10^3 \times 18 \times 2 \times 10^{-3}}{8.314 \times 300}$$

$$= 0.052 \text{ kg}$$

or $w_{H_2O} = 52$ g

Since, relative humidity = 60% therefore amount of $H_2O = 52 \times 0.6 = 31.2$ g

9. (d) Molar ratio of N_2 and CO is 3 : 2

∴ Pressure ratio of N_2 and CO is 3 : 2, *i.e.*, 300 bar and 200 bar respectively

$$\frac{n_{N_2}}{n_{CO}} = \sqrt{\frac{M_{CO}}{M_{N_2}}} \times \frac{P_{N_2}}{P_{CO}} = \frac{300}{200} = \frac{3}{2}$$

10. (b)

$$Z = \frac{PV}{nRT}$$

$$\therefore \quad n = \frac{PV}{ZRT} = \frac{1 \times 1}{1.2 \times 0.0821 \times 273} = 0.037$$

∴ Number of molecules

$$= 0.037 \times 6.023 \times 10^{23} = 2.23 \times 10^{22}$$

11. (d) Ideal gas does not show cooling or heating.

12. (d) Due to H-bonding in NH_3.

13. (b) Dry ice is solid CO_2

$$\therefore \quad P \times 5 = \frac{0.44}{44} \times 0.0821 \times 300$$

$$P = 0.049 \text{ atm}$$

14. (b) $PV = \frac{w}{M}RT$

$$\therefore \quad M = \frac{w}{V \cdot P}RT = \frac{1.33 \times 0.0821 \times 423 \times 760}{764} = 46$$

molar mass of NO_2 is 46 g mol^{-1}.

15. (b) $\text{R.H.} = \frac{\text{Partial pressure of } H_2O_v}{\text{Saturated V.P. of } H_2O} \times 100$

16. (c)

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

$$\therefore \quad PM = dRT$$

$$\text{or} \quad d = \frac{PM}{RT}$$

$$Pd = \frac{P^2M}{RT}$$

$$\therefore \quad \frac{d[Pd]}{dP} = \frac{2PM}{RT} = 20$$

$$\therefore \quad T = \frac{2 \times 8.21 \times 30}{0.0821 \times 20} = 300 \text{ K}$$

17. (a)

$$\left[P + \frac{a}{V^2}\right][V - b] = RT$$

$$\therefore \quad PV + \frac{a}{V} = RT$$

$$\text{or} \quad PV^2 + a - RTV = 0$$

$$\therefore \quad V=\frac{RT\pm\sqrt{R^2T^2-4aP}}{2P}=\frac{RT}{2P}$$

(A given P and T only one value of veviat, thus discriminant is zero)

18. (b) $PV=nRT$

$$n_{\mathrm{Na}}=\frac{PV}{RT}=\frac{50\times 2}{0.0821\times 1273}=0.9568,$$

$\therefore$ No. of atoms $=0.9568\times 6.023\times 10^{23}=5.76\times 10^{23}$

19. (b) $n=\frac{PV}{RT}=\frac{PV}{kN\cdot T}\ \left(\frac{R}{N}=k\right)$

$\therefore\ n\times N=\frac{PV}{kT}=$ No. of molecules

20. (b) Let a g of Ne and b g of Ne and Ar be present respectively

$$a+b=30 \qquad \text{...(1)}$$

K.E. of mixture $=\frac{3}{2}\left[\frac{a}{20}+\frac{b}{40}\right]RT=3\times 10^3$

$$\frac{a}{20}+\frac{b}{40}=\frac{3\times 10^3\times 2}{3\times 8.314\times 250}=0.96$$

$$\therefore \quad 2a+b=38.48 \qquad \text{...(2)}$$

$$\therefore \quad a=8.48 \text{ and } b=21.52$$

$\therefore$ % b (*i.e.*, Ar) $=\frac{21.52}{30}\times 100=71.7\%$

21. (a) $\because\ u_{\mathrm{rms}}=\sqrt{\frac{3P}{d}}$

$$\therefore \quad \Delta u=\sqrt{\frac{3}{d}}\times(\sqrt{P_2}-\sqrt{P_1})$$

$$=\sqrt{\frac{3}{0.75}}\times\left[\sqrt{9\times 10^4}-\sqrt{4\times 10^4}\right]$$

$$=\sqrt{\frac{3}{0.75}}\times 100=200\,\mathrm{msec}^{-1}$$

22. (a) Monoatomic gas : $\gamma=\frac{5}{3};\ \ C_v=\frac{3}{2}R$ and $C_p=\frac{5}{2}R$

Diatomic gas : $\gamma=\frac{7}{5};\ \ C_v=\frac{5}{2}R$ and $C_p=\frac{7}{2}R$

For mixture of 1 mole each : $C_v=\frac{\left(\frac{3}{2}+\frac{5}{2}\right)R}{2}$ and

$$C_p=\frac{\left(\frac{5}{2}+\frac{7}{2}\right)R}{2}$$

$$\therefore \quad \gamma=\frac{C_p}{C_v}=\frac{6R}{4R}=\frac{3}{2}=1.5$$

23. (b) $P=\frac{d}{M}RT$

$\therefore\ \frac{d}{p}\propto\frac{1}{T}$

or $\frac{d_1}{p_1}\times\frac{p_2}{d_2}=\frac{1}{283}\times\frac{383}{1}$

$\therefore\ \frac{d_2}{p_2}=\frac{d_1}{p_1}\times\frac{283}{383}$

$\therefore\ \frac{d_2}{P_2}=\frac{283\cdot X}{383}=\frac{283X}{383}$

24. (c) 0.1 mole has 0.3 N atom of gas.

25. (a) $P'_{\mathrm{O}_2}=P_M\times$ mole fraction of O_2

$$\therefore\ \frac{P'}{P_M}=\text{mole fraction } \mathrm{O}_2=\frac{\frac{w}{32}}{\frac{w}{16}+\frac{w}{32}}=\frac{1}{3}$$

26. (b) It is definition of Boyle's temperature.

27. (b) $U_{\mathrm{rms}}=\sqrt{\frac{3RT}{M}};\ \ U_{av}=\sqrt{\frac{8RT}{\pi M}}$

$$\therefore\ \frac{u_{\mathrm{rms}}}{u_{av}}=\sqrt{\frac{3\pi}{8}}=1.086$$

28. (b) Av. K.E. $=\frac{3}{2}\frac{RT}{N}=\frac{3}{2}kT$

29. (b) $\frac{P'_{\mathrm{H}_2}}{P_M}=$ mole fraction $\mathrm{H}_2=\frac{\frac{w}{2}}{\frac{w}{2}+\frac{w}{16}}=\frac{8}{9}$

30. (c) Greater the value of 'a' *i.e.*, intermolecular forces of attraction for a gas, the more easily the gas will be liquefied.

31. (c) At a given temperature (see equilibrium exist) kinetic energy of gas liquid $=\frac{3}{2}RT$

32. (d) Graham's law of diffusion; $r\propto\sqrt{\frac{1}{M}}$

33. (a) $u_{\mathrm{AV}}=\sqrt{\frac{8RT}{\pi M}};\ \frac{u_1}{u_2}=\sqrt{\frac{T_1}{T_2}}$

$\therefore\ \frac{0.3}{u_2}=\sqrt{\frac{300}{1200}}$ or, $u_2=\sqrt{\frac{1200}{300}}\times 0.3=0.6\,\mathrm{ms}^{-1}$

34. (c) Pressure correction in gas equation by van der Waals' is $\frac{a}{V^2}$ for 1 mole. Thus $P_{\mathrm{gas}}=\left[P+\frac{a}{V^2}\right]$

35. (b) HCl diffuses at a slower rate because of its higher molar mass.

36. (b) Density of a gas, $e=\frac{PM}{RT}$; $e\propto P$ and $e\propto\frac{1}{T}$

37. (a) $\frac{r_{\mathrm{CH}_4}}{r_x}=\sqrt{\frac{M_x}{M_{\mathrm{CH}_4}}}$

Thus, $\frac{2}{1}=\sqrt{\frac{M_x}{16}}\quad\therefore M_x=4\times 16=64.$

38. (d) K.E. $=\frac{3}{2}\frac{RT}{N}$

39. (a) $PV=\frac{1}{3}mnu^2$

for one mole, $PV=\frac{1}{3}Mu^2\quad\therefore P\propto u^2$

40. (d) $\frac{P'_{\mathrm{H}_2}}{P_{\mathrm{M}}}=$ mole fraction of $\mathrm{H}_2=\frac{\frac{w}{2}}{\frac{w}{2}+\frac{w}{30}}=\frac{15}{16}$

41. (c) Due to higher molar mass of $\mathrm{C_6H_5\cdot CH_3}$.

42. (a) Due to higher repulsive forces.

43. (c) $U_{rms} = \frac{3RT}{M}$

Thus, $(U_{rms})_{H_2} = \sqrt{\frac{3 \times R \times 50}{2}}$ at 50 K ...(1)

$(U_{rms})_{O_2} = \sqrt{\frac{3 \times R \times 800}{32}}$ at 800 K ...(2)

So, $\frac{(U_{rms})_{H_2}}{(U_{rms})_{O_2}} = \sqrt{\frac{50 \times 32}{2 \times 800}} = 1$

44. (b) Use $r_0 = \frac{v}{t} \propto \sqrt{\frac{1}{M}}\,(P, T)$

$\frac{r_{H_2}}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{H_2}}},\ \frac{r_{H_2}}{r_{O_2}} = \frac{x}{5} \times \frac{t}{x} = \sqrt{\frac{32}{2}}\quad \therefore t = 20\,\text{sec}$

45. (b) $\frac{PV}{nRT} = Z$ (compressibility factor) for an ideal gas $Z = 1$.

46. (d) Dipole moment gives rise to higher value of a for H_2O inspite of low molar mass

47. (c) According to Graham's law of diffusion $r \propto P\sqrt{\frac{1}{M}}$ at constant temperature.

$\therefore\ \frac{r_A}{r_B} = \frac{P_A}{P_B}\sqrt{\frac{M_B}{M_A}} = \frac{P_A}{P_B} \times \left(\frac{M_B}{M_A}\right)^{\frac{1}{2}}$

48. (c) A gas will approach ideal behaviour at high temperature and low pressure.

49. (d) Fig. (a) represents Charles' law; Fig. (b) represents Boyle's law; Fig. (c) represents P–T law; Fig. (d) donot obey ideal gas laws as $PV = nRT$ or $\frac{P}{T} = \frac{K}{V}$. An increase in V will show decrease in $\frac{P}{T}$ like P–V curve in Boyle's law.

50. (c) Follow text.

51. (c) Let $Y = \frac{1}{V^2}$ and $X = P = \frac{K}{V}$

$\therefore\ V = \frac{1}{\sqrt{Y}}$

Also $X = K\sqrt{Y}$

$\therefore\quad Y = K^1 \cdot X^2$

i.e. curve (c).

52. (b) Let $\frac{1}{P^2} = Y$

$\therefore\ P = \frac{1}{\sqrt{Y}}$

if $X = V = \frac{K}{P} = K\sqrt{Y}$

or $X^2 = K^1 Y$ *i.e.* curve (b).

53. (a) $\frac{r_{SO_2}}{r_{CH_4}} = \sqrt{\frac{16}{64}} \times \frac{8}{64} \times \frac{16}{1} = 1$

54. (b) $T_i = \frac{2a}{Rb} = \frac{2 \times 0.244}{0.027 \times 0.0821} = 220.14$

55. (b) $Z < 1$ or $\frac{PV}{nRT} < 1$

Thus, $V_m < 22.4$ litre

56. (c) $u_{rms}\,H_2 = \sqrt{\frac{3RT_1}{2}}$ and $u_{rms}\,N_2 = \sqrt{\frac{3RT_2}{28}}$

$u_{rms}H_2 = \sqrt{7} \times u_{rms}N_2$

$u_{rms}H_2 = \sqrt{7} \times u_{rms}N_2$

or $\sqrt{\frac{3RT_1}{2}} = \sqrt{7} \times \sqrt{\frac{3RT_2}{28}}$

$\therefore\ \frac{T_1}{2} = \frac{T_2}{4}$ or $T_2 = 2T_1$ or $T_{N_2} > T_{H_2}$

57. (c) Mass of 1000 mL steam $= 1000 \times 0.0006 = 0.6\,\text{g}$

$\therefore$ Volume of liquid water $= \frac{0.6}{1} = 0.6\,\text{cm}^3$

58. (d) $u_{rms} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}}$

59. (c) Use $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

60. (b) Forces of attractions are weakened as the temperature increases.

61. (c) For positive deviations $Z > 1$, *i.e.*, the condition when repulsive forces predominates. Also, at high P, V is small and b cannot be ignored, but the factor $\frac{a}{V^2}$ can be neglected in comparison to P. Thus, $Z = 1 + \frac{Pb}{RT}$

62. (c) $u_{rms} = \sqrt{\frac{3RT}{M}}$ and $\text{KE} = \frac{3}{2}RT$

$\therefore\ u_{rms} = \sqrt{\frac{2E}{M}}$

63. (b) $\frac{r_{He}}{r_{CH_4}} = \sqrt{\frac{M_{CH_4}}{M_{He}}} = \sqrt{\frac{16}{4}} = 2$

64. (a) Let P, V be the pressure and volume of gas at temperature T.

$P_1V_1 = RT$

$P_2(V_1 + dV) = R(T + 1)$ $\quad (P_2V_2 = 1)$

$\therefore\quad P_2^2 = RT + R$ $\quad \left(\because \frac{P_2}{V_1 + dV} = 1\right)$

$\therefore\quad 2\left(\frac{\partial P_2}{\partial T}\right)_V = R$

$\therefore\quad \left(\frac{\partial P_2}{\partial T}\right) = \frac{R}{2}$

$\therefore\ C = C_v + \frac{\partial P}{\partial T} = \frac{3R}{2} + \frac{R}{2} = 2R$

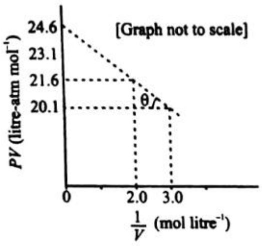
65. (b) van der Waals' equation has pressure correction term $\left[p + \frac{n^2a}{V^2}\right]$ due to attraction forces.

66. (b) $u_{rms}\ X = \sqrt{\frac{3R \times 400}{40}}$

$u_{MPY} = \sqrt{\frac{2R \times 60}{M}}$

$\therefore\quad M = 4$

67. (c)



van der Waals' equation for 1 mol of real gas is

$$\left[P+\frac{a}{V^2}\right][V-b]=RT$$

Given that $b=0$

$$\therefore \quad \left(P+\frac{a}{V^2}\right)(V)=RT$$

$$\therefore \quad PV=RT-\frac{a}{V} \qquad \ldots (i)$$

Following $y=mx+c$ for the curve PV vs $\frac{1}{V}$

Slope = $-a$

$$\text{Slope}=\frac{21.6-20.1}{2-3}=-1.5$$

$$\therefore \quad a=1.5$$

68. (b) $u_{m.p.}:u_{Av}:u_{rms}::\sqrt{\frac{2RT}{M}}:\sqrt{\frac{8RT}{\pi M}}:\sqrt{\frac{3RT}{M}}$

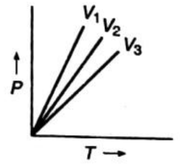
$:: 1 : 1.128 : 1.225$

Thus $C^* : \bar{C} : C :: 1 : 1.225 : 1.128$

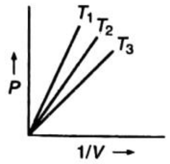
OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. For 1 mole of an ideal gas $V_1 > V_2 > V_3$ in Fig. (a), $T_1 > T_2 > T_3$ in Fig. (b), $P_1 > P_2 > P_3$ in Fig. (c) and $T_1 > T_2 > T_3$ in Fig. (d), then which curves are correct :

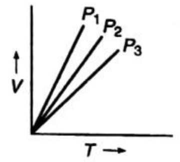
(a)



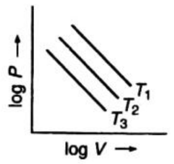
(b)



(c)



(d)



2. A mixture of SO_2 and O_2 in the molar ratio 16 : 1 is diffused through a pin hole for successive effusions three times to give a molar ratio 1 : 1 of diffused mixture. Which one are correct if diffusion is made at same P and T in each operation?

(a) Eight operations are needed to get 1 : 1 molar ratio

(b) Rate of diffusion for $SO_2 : O_2$ after 8 operations is 0.707

(c) Six operations are needed to get 2 : 1 molar ratio for SO_2 and O_2 in diffusion mixture

(d) Rate of diffusion for SO_2 and O_2 after 6 operations is 2.41

3. A graph plotted between log V and log T for 2 mole of gas at constant pressure of 0.0821 atm. V and T are in litre and K respectively. Which of the following statements are correct?

(a) The curve is straight line with slope -1

(b) The curve is straight line with slope $+1$

(c) The intercept on Y-axis is equal to 2

(d) The intercept on Y-axis is equal to 0.3010

4. A gas obeys $P(V-b)=RT$. Which of the following are correct about this gas?

(a) Isochoric curves have slope $=\frac{R}{V-b}$

(b) Isobaric curves have slope $\frac{R}{P}$ and intercept b

(c) For the gas compressibility factor $=1+\frac{Pb}{RT}$

(d) The attraction forces are overcome by repulsive forces

5. Which are correct for an ideal gas :

(a) $\left(\frac{\partial P}{\partial V_M}\right)_{T_c}=0$ (b) $\left(\frac{\partial E}{\partial V}\right)_T=0$

(c) $\left(\frac{\partial E}{\partial P}\right)_T \neq 0$ (d) $\left(\frac{\partial n}{\partial V}\right)_{P,T} \neq 0$

6. Which are correct for an ideal gas :

(a) $\left(\frac{\partial P}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial T}{\partial P}\right)_V = 0$

(b) $\left(\frac{\partial P}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial T}{\partial P}\right)_V = -1$

(c) $\left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial T}{\partial V}\right)_P \cdot \left(\frac{\partial V}{\partial P}\right)_T = -1$

(d) $\frac{\text{Thermal expansion coefficient of gas}}{\text{Isothermal compressibility constant}}=\frac{P}{T}$

7. Select the correct statements :

(a) A gas cannot be compressed below its critical temperature

(b) Critical temperature is the highest temperature at which liquid and gaseous phase can coexist

(c) The fraction of molecules having their most probable speed increases with rise in temperature

(d) Ideal gas can be liquified at high pressure

8. Select the incorrect statements :

(a) Compressibility factor for 1 mole of gas at critical conditions is 8 / 3

(b) All molecules of gas move with same speed

(c) The diameter of gaseous molecules are much smaller than the average distance travelled between collision

(d) Saturated vapours do not obey gas laws except Dalton's law

9. Select the correct statements :

(a) Greater is humidity, lesser will be rate of evaporation of water

(b) Greater is the humidity, lesser will be density of air

(c) If room temperature = dew point; relative humidity = 100%

(d) Dew point is the temperature at which the gas at given atmospheric condition becomes saturated with $H_2O(v)$

10. When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules :

(a) are above the inversion temperature

(b) exert no attractive forces on each other

(c) do work equal to loss in kinetic energy

(d) collide without loss of energy

11. If a gas is expanded at constant temperature :

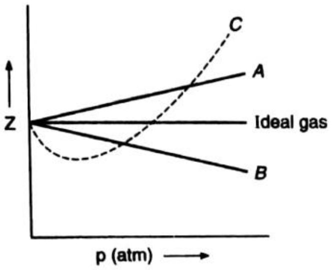
(a) the pressure decreases

(b) the kinetic energy of the molecules remains the same

(c) the kinetic energy of the molecules decreases

(d) the number of molecules of the gas increases

12. The given graph represents the variation of Z (compressibility factor) *vs.* P for three real gases A, B and C. Identify the correct statement : **(IIT 2006)**



(a) For the gas $A, a=0$ and its dependence on P is linear at all pressure

(b) For the gas $B, b=0$ and its dependence on P is linear at all pressure

(c) For the gas C, which is typical real gas for which $a \neq 1, b \neq 0$. By knowing the minima and the point of intersection with $Z \neq 1$, a and b can be calculated

(d) At high pressure, the slope is positive for all real gases

13. A gas described by van der Waals' equation : **(IIT 2008)**

(a) behaves similar to an ideal gas in the limit of large molar volumes

(b) behaves similar to an ideal gas in the limit of large pressure

(c) is characterised by van der Waals' coefficients that are dependent on the identity of gas but are independent of the temperature

(d) has the pressure that is lower than the pressure exerted by the same gas behaves ideally

14. According to kinetic theory of gases : **(IIT 2011)**

(a) Collisions are always elastic

(b) Heavier molecules transfer more momentum to the wall of the container

(c) Only a small number of molecules have very high velocity

(d) Between collisions the molecules move in straight lines with constant velocities

15. Which of the following are correct statements :

(a) Higher is $\frac{T_C}{P_C}$, larger is excluded volume

(b) Higher is V_C, larger is excluded volume

(c) Higher is $\frac{T_C}{V_C}$, more is van der Waals' constant for attraction

(d) Smaller is size of molecule, lesser will be excluded volume

16. Select the correct statements for ideal gas :

(a) Joule Thomson coefficient for ideal gas is zero

(b) Ideal gas does not have intermolecular attractions among their molecules

(c) Ideal gas can never be liquefied

(d) Gaseous phase can not exist at zero kelvin

17. Select the correct statement :

(a) Temperature does not change during phase transition equilibria

(b) Kinetic energy of liquid molecules is directly proportional to temperature

(c) Liquid phase does not exist above critical temperature

(d) The density of gas and liquid phase is equal at critical condition

18. Select the correct statements :

(a) Random molecular motion by gaseous molecules is confirmed by diffusion

(b) The boiling point of liquid N_2 is $-196°C$

(c) He is the only noble gas which does not behave ideally at any condition.

(d) Pressure of gas calculated by using van der Waals' equation is smaller than the pressure calculated by using ideal gas equation.

SOLUTIONS (More Than One Answer Correct)

1. (b,d) $PV = RT \text{ if } P_1 > P_2, V_1 < V_2.$

Also, $\log P = -\log V + \log RT$

2. (a,b,c) $(f_1)^X = \frac{n'_{SO_2}}{n'_{O_2}} \times \frac{n_{O_2}}{n_{SO_2}}$, where, n_{SO_2} and n_{O_2} are mole present initially.

or $X \log f_1 = \log \left[\frac{n'_{SO_2}}{n'_{O_2}} \times \frac{n_{O_2}}{n_{SO_2}}\right]$

$$\therefore \quad X \log \sqrt{\frac{M_{O_2}}{M_{SO_2}}} = \log \left[\frac{n'_{SO_2}}{n'_{O_2}} \times \frac{n_{O_2}}{n_{SO_2}}\right]$$

$$X \log \sqrt{\frac{32}{64}} = \log \frac{1}{1} \times \frac{1}{16} \quad \therefore \quad X = 8;$$

Also $\frac{n_1}{n_2} = \frac{r_1}{r_2} = \sqrt{\frac{32}{64}} = 0.707$

If $X = 6$ then

$$6 \log \sqrt{\frac{32}{64}} = \log \left[\frac{n'_{SO_2}}{n'_{O_2}} \times \frac{n_{O_2}}{n_{SO_2}}\right]$$

$$= \log \left[\frac{n'_{SO_2}}{n'_{O_2}} \times \frac{1}{16}\right]$$

$$\frac{n'_{SO_2}}{n'_{O_2}} = 2:1$$

Rate of diffusion is $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$, *i.e.*, 0.707 in each operation.

3. (b,d) $PV = nRT$ or $\log V = \log T + \log \frac{nR}{P}$

Slope = $\tan \theta = \tan 45° = 1$

Intercept

$$= \log \frac{nR}{P} = \log \left[\frac{2 \times 0.0821}{0.0821}\right] = 0.3010$$

4. (a,b,c,d) $P(V-b) = RT$

$$\therefore \quad P = \frac{R}{(V-b)} \cdot T \quad \text{slope} = \frac{R}{V-b}$$

$$PV - Pb = RT$$

$$V = \frac{RT}{P} + b$$

slope = $\frac{R}{P}$ and intercept b

$$Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT};$$

$Z > 1$, *i.e.*, repulsive forces predominates.

5. (a,b,d) $\left(\frac{\partial E}{\partial P}\right)_T = \text{zero}$

6. (b,c,d) Thermal expansion coefficient $\alpha = \frac{\left(\frac{\partial V}{\partial T}\right)_P}{V} = \frac{1}{T}$

(Use $PV = RT$)

Isothermal compressibility constant $= -\frac{\left(\frac{\partial V}{\partial P}\right)_T}{V} = \frac{1}{P}$

7. (b,c) Ideal gas have no forces of attractions.

8. (a,b) $Z = \frac{P_C V_C}{RT_C} = \frac{3}{8}$; each molecule move with altogether different speed.

9. (a,b,c,d) All are facts.

10. (b, d) No work is required to tear apart molecules due to the absence of attractive forces in an ideal gas. Also collision are perfectly elastic.

11. (a, b) When a gas is expanded at constant temperature, then the kinetic energy of the molecules remain the same, but the pressure decreases because $V \propto \frac{1}{P}$

12. (a,c,d) Follow Concepts of Physical Chemistry by Dr. P. Bahadur, G.R. Bathla Publications, Meerut.

13. (a,c,d) $\left[P + \frac{a}{V^2}\right] = [V - b] = RT$

If V is large $PV = RT$ $\left(\frac{a}{V^2} \text{ and } b \text{ are neglible}\right)$

14. (a,b,c,d) All are assumptions of kinetic theory of gases and Maxwell probable distribution of molecular speeds.

15. (a,b,c,d) $T_C = \frac{8a}{27b^2}; V_C = 3b; P_C = \frac{a}{27b^2}$ and excluded volume, $b = 4 \times N \times v$

16. (a,b,c,d) All are facts.

17. (a,b,c,d) —do—

18. (a,b,c,d) —do—

COMPREHENSION BASED PROBLEMS

Comprehension 1 : Gases show ideal gas behaviour in Boyle temperature range. Assume for the air this temperature range between 300 K to 900 K.

An open vessel at 27° C is heated until 3/5th of the air in it has been expelled. Assuming that the volume of the vessel remains constant,

[1] The temperature at which vessel was heated.

(a) 750 K (b) 600 K

(c) 500 K (d) 400 K

[2] The air escaped out if vessel is heated to 900 K.

(a) n (b) $\frac{n}{3}$

(c) $\frac{2n}{3}$ (d) $\frac{n}{2}$

[3] The temperature at which half of the air escapes out.

(a) 750 K (b) 600 K

(c) 500 K (d) 400 K

Comprehension 2 : Gaseous pressure is measured by barometer. The barometric tube must be exactly vertical, otherwise the pressure reading will not be accurate.

A 10 cm column of air is trapped by a column of Hg of 8 cm long. The capillary tube is horizontally fixed at 1 atm pressure. Calculate the length of air column when the tube is fixed at same temperature :

[1] The pressure of air measured when tube is held vertically with open end up is :

(a) 11.61 cm (b) 9.05 cm

(c) 11.18 cm (d) 10.18 cm

[2] The pressure of air (in cm) when tube is held vertically with open end down.

(a) 11.61 (b) 9.6

(c) 11.18 (d) 10.3

[3] The pressure of air (in cm) when tube is held at 45° from horizontal with open end up.

(a) 9.3 (b) 10.3

(c) 11.3 (d) 11.61

Comprehension 3 : An open glass bulb containing air was heated from 27° C to 227° C. Assuming ideal nature.

[1] If 200 mL of air measured at 227° C was expelled during heating, the volume of bulb in mL must be :

(a) 500 (b) 400

(c) 300 (d) 200

[2] If 200 mL of air measured at 27° C was expelled during heating, the volume of bulb in mL must be:

(a) 200 (b) 300

(c) 400 (d) 500

Comprehension 4 : Ideal gas equation is represented as $PV = nRT$. Gases present in universe were found ideal in the Boyle's temperature range only and deviated more from ideal gas behaviour at high pressure and low temperature. The deviations are explained in terms of compressibility factor Z. For ideal behaviour $Z = \frac{PV}{nRT} = 1$. The main cause to show deviations were due to wrong assumptions made about forces of attractions (which becomes significant at high pressure) and volume occupied by molecules V in $PV = nRT$ is supposed to be volume of gas or, the volume of container in which gas is placed by assuming that gaseous molecules do not have appreciable volume. Actually volume of the gas is that volume in which each molecule of a gas can move freely. If volume occupied by gaseous molecule is not negligible, then the term V should be replaced by the ideal volume which is available for free motion of each molecules of gas in 1 mole gas

V_{actual} = volume of container − volume occupied by molecules

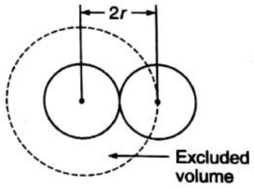
$= V - b$

where b represents the effective volume of co-volume or excluded volume occupied by molecules present in one mole of gas.

Similarly for n mole gas $V_{\text{actual}} = V - nb$

The excluded volume can be calculated by considering bimolecular collisions. The excluded volume is the volume occupied by the sphere of $2r$ for each pair of molecule.

Thus, excluded volume for one pair of molecules



$$= \frac{4}{3}\pi (2r)^3 = \frac{4 \times 8\pi r^3}{3} \quad \text{...(i)}$$

∴ excluded volume for 1 molecule

$$= \frac{2}{3} \times 8\pi r^3 \quad \text{...(ii)}$$

$$= 4 \times \left(\frac{4}{3}\pi r^3\right)$$

$= 4 \times$ volume of one molecule $= 4v$

∴ excluded volume for N molecules

$= 4Nv = b$

($b = 4Nv$, where N is Avogadro's No.)

[1] Which of the following statements are correct?

I. Larger is the value of $\frac{T_c}{P_c}$ for a gas larger would be its excluded volume.

II. Larger is the excluded volume of gas, more will be its critical volume.

III. The slope for an isochore obtained for a gas showing $P(V-b)=RT$ is $\left[\frac{R}{V-b}\right]$.

IV. The excluded volume for He is more than H_2.

(a) I, II, III (b) I, II, IV

(c) II, III, IV (d) III, IV

[2] As the pressure approaching zero *i.e.*, at very low pressure, the curves plotted between compressibility factor Z and P for n mole of gases have the following characteristics:

I. The intercept on y-axis leads to a value of unity

II. The intercept on y-axis leads to a value of 'n'

III. The curves possess same slope for different gases at same temperature

IV. The curves possess different slopes for different gases at same temperature

V. The curves possess same slope for a gas at different temperatures

(a) I, IV, V (b) II, III

(c) II, III, IV (d) II, III, V

[3] Assuming the molecules of gas as hard sphere of radius 2.0×10^{-10} m the fraction of volume occupied by the molecules to the total volume of a given mass of gas at 27°C and at 1 bar pressure and 10 bar pressure respectively are:

(a) 99.9%, 99% (b) 0.082%, 0.82%

(c) 99%, 90% (d) 1%, 10%

[4] The compressibility factor for N_2 at $-50°$C and 800 atm pressure is 1.95. The mole of N_2 required to fill up a balloon of 100 L capacity are:

(a) 2.24×10^3 L (b) 2.24×10^2 L

(c) 2.24 L (d) 22.4 L

[5] Which of the following statements are correct?

I. Rise in compressibility factor Z with increase in pressure is due to 'a'

II. Rise in compressibility factor Z with increase in pressure is due to 'b'

III. Ideal gas do not exist but is a useful concept

IV. For 1 mole of a van der Waals' gas,

$$Z=1+\frac{bP}{RT}-\frac{a}{RTV}+\frac{ab}{RTV^2}$$

(a) I, II, III, IV (b) II, III, IV

(c) I, III, IV (d) I, IV

[6] The ratio of coefficient of thermal expansion $\alpha=\frac{\left(\frac{\partial V}{\partial T}\right)_P}{V}$ and thc isothermal compressibility $K=\frac{\left(\frac{\partial V}{\partial P}\right)_T}{V}$ for an ideal gas is:

(a) $-\frac{P}{T}$ (b) $\frac{P}{T}$

(c) $\frac{T}{P}$ (d) $-\frac{T}{P}$

SOLUTIONS

Comprehension 1

[1] (a) Let initial mole of gas at 27° C are n.

On heating 3/5 mole of air are escaped out at temperature, T.

Thus, mole of air left at temperature, $T=n-\frac{3}{5}n=\frac{2n}{5}$

Now, under similar conditions of P and V

$$n_1T_1=n_2T_2$$

$$n\times300=\frac{2n}{5}\times T$$

$$\therefore \quad T=\mathbf{750\ K}$$

[2] (c) At $T_1=300$ K, No. of mole $=n$, $T_2=900$ K,

No. of mole $=n_1$

$\therefore\quad 300\times n=900\times n_1 \qquad \therefore\quad n_1=\frac{1}{3}n$

$\therefore$ No. of mole escaped out $=n-\frac{1}{3}n=\frac{2}{3}n$ **mol**

[3] (b) **When half of the air escaped out at temp. T, then $n=\frac{n}{2}$**

$$\therefore \quad n\times300=\frac{n}{2}\times T$$

$$\therefore \quad T=\mathbf{600\ K=327°C}$$

Comprehension 2

[1] (b) $P_1V_1=P_2V_2$ or $P_1l_1a=P_2l_2a$

$$\because \quad P_2=76+8=84\text{ cm}$$

$$\therefore \quad l_2=\frac{P_1l_1}{P_2}=\frac{76\times10}{84}=\mathbf{9.05\ cm}$$

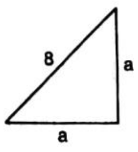
[2] (c)

$$P_1l_1a=P_2l_2a$$

$$\because \quad P_2=76-8=68\text{cm}$$

$$\therefore \quad l_2=\frac{P_1l_1}{P_2}=\frac{76\times10}{68}=\mathbf{11.18\ cm}$$

[3] (a) When the tube is held at 45° with open end up, the mass of Hg is borne partially by the gas and partially by the Hg. Vertical height of Hg is a measure of additional pressure on gas, *i.e.*,



$$l=\frac{8}{\sqrt{2}}$$

Also $P_2l_2a=P_1l_1a$

$$\therefore \qquad l_2 = \frac{P_1 l_1}{P_2} = \frac{76\times10}{76+\frac{8}{\sqrt{2}}} = \mathbf{9.3\ cm}$$

Comprehension 3

[1] (c) Let volume of bulb be V mL

$\therefore$ Volume of air at 300 K = V mL

After heating volume of air at 500 K = V + 200 mL

$$\because \qquad \frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad \text{(at constant } P\text{)}$$

$$\frac{V}{300} = \frac{V+200}{500}$$

$$\therefore \qquad V = \mathbf{300\ mL}$$

[2] (d) Let volume of bulb be V mL

Volume of air at 300 K given out = 200 mL

$$\text{or} \qquad \frac{200}{300} = \frac{V_2}{500}$$

$$\therefore \qquad V_2 = \frac{100000}{300}$$

$\therefore$ Volume of air at 500 K = $V + \frac{100000}{300}$

Therefore, $\frac{V}{300} = \frac{V+\frac{100000}{300}}{500}$; $\therefore$ $V = \mathbf{500\ mL}$

Comprehension 4

[1] (a) $V_c = 3b, T_c = \frac{8a}{27Rb}, P_c = \frac{a}{27b^2}$

Also, b for He = 0.1142 litre mol^{-1} and b for H_2 is 0.1460 litre mol^{-1}

[2] (a) $\frac{PV}{nRT} = Z$

At very low P or $P \to 0, z = 1$ since ideal gases. Also, as the temperature increases Z approaches unity.

[3] (b) At $P = 1$ bar

Volume of gas $= \frac{nRT}{P} = \frac{n\times0.0821\times300}{1} = 24.63\times n$ L

At $P = 10$ bar

Volume of gas $= \frac{n\times0.0821\times300}{10} = 2.463\times n$ L

Also, volume of molecules

$$= n \times \text{Avogadro's No.} \times \frac{4}{3}\pi r^3$$

$$= n\times6.023\times10^{23}\times\frac{4}{3}\times3.14\times(2.0\times10^{-8})^3$$

$$= 20.17\times n\ \text{cm}^3$$

$$= 0.0202\times n\ \text{L}$$

At P = 1 bar

$$\therefore \qquad \frac{V_m}{V_g} = \frac{0.0202\times n}{24.63\times n} = 8.2\times10^{-4}$$

$$\text{or} \qquad 8.2\times10^{-2}\% = 0.082\%$$

At P = 10 bar

$$\therefore \qquad \frac{V_m}{V_g} = \frac{0.0202}{2.463\times n} = 8.2\times10^{-3}$$

$$\text{or} \qquad 8.2\times10^{-1}\% = 0.82\%$$

[4] (a) $Z = \frac{PV}{nRT}$

$$\therefore \qquad n = \frac{800\times100}{1.95\times0.0821\times223} = 2.24\times10^3$$

[5] (b) There are facts.

[6] (b) $PV = RT$

$$\therefore \qquad P\partial V = R\cdot\partial T$$

$$\text{or} \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} = \frac{R\cdot V}{RT}$$

$$\text{or} \qquad \alpha = \frac{\left(\frac{\partial V}{\partial T}\right)_P}{V} = \frac{1}{T}$$

$$\text{Also,} \qquad P\cdot\partial V + V\cdot\partial P = 0$$

$$\therefore \qquad \left(\frac{\partial V}{\partial P}\right)_T = -\frac{V}{P}$$

$$\text{or} \qquad K = -\frac{\left(\frac{\partial V}{\partial P}\right)_T}{V} = \frac{1}{P}$$

STATEMENT EXPLANATION PROBLEMS

Read the following statements **(S)** and explanations **(E)**. Choose the correct answers from the codes (a), (b), (c) and (d):

(a) **S** is correct but **E** is wrong.
(b) **S** is wrong but **E** is correct.
(c) Both **S** and **E** are correct and **E** is correct explanation of **S**.
(d) Both **S** and **E** are correct but **E** is not correct explanation of **S**.

1. S : The product of pressure and volume of a fixed mass of gas is independent of temperature.
E : The product of P and V depends upon temperature.

2. S : The increase in compressibility factor with increasing pressure is due to a.
E : $Z = 1 + \frac{bP}{RT}$ for real gases can be obtained by neglecting $\frac{a}{V^2}$ term in van der Waals' equation.

3. S : A gas can be liquefied at $T = T_c$ and $P < P_c$.
E : A gas can be liquefied when $T < T_c$ and $P < P_c$.

4. S : The gas is heated, if its temperature is less than its inversion temperature in Joule-Thomson effect.
E: Heating effect in gas is noticed during Joule-Thomson effect when $T > T_i$.

5. S : It is not possible to liquefy an ideal gas.
E : There exist no forces of attraction among the molecule of ideal gas.

6. S : All molecules in a gas are moving with same speed.
E : Speed of molecules in a gas follows Maxwell's distribution law.

7. S : Average speed of molecules, if a gas in a container moving only in one dimension, will be zero.
E : The molecules of gas are not collected in one direction.

8. S : The fraction of molecules having speed in the range u and $(u + du)$ of a gas of molar mass M at temperature T is the same as that of gas of molar mass of $2M$ and temperature $T/2$.
E : The fraction of molecules having their speed within the range u to $(u + du) \propto \frac{M}{T}$.

9. S : Energy can be transferred between gaseous molecules during collisions but u_{rms} remains constant.
E : The average kinetic energy of gaseous molecules remains constant as long as temperature is constant and therefore, u_{rms} remains unchanged during collision.

10. S : The compressibility factor for H_2 and He is $\left[1 + \frac{Pb}{RT}\right]$.
E : The compressibility factor for H_2 and He can be derived from van der Waals' equation.

11. S : The numerical values of P_c, V_c, T_c are $\frac{a}{27b^2}$, $3b$ and $\frac{8a}{27Rb}$ respectively.
E : The compressibility factor Z at critical conditions is $\frac{3}{8}$.

12. S : The numerical value of a for H_2O is higher than C_6H_6.
E : H_2O shows H-bonding.

13. S : At low pressure van der Waals' equation is reduced to $\left[P + \frac{a}{V^2}\right]V = RT$.
E : The compressibility factor corresponding to low pressure is given by : $1 - \frac{RTV}{a}$.

14. S : Molar specific heat at constant volume of an ideal diatomic gas is $\left[\frac{3}{2}R + R\right]$.
E : On heating one mole of an ideal diatomic gas at constant pressure for 1°C rise in temperature, the increase in internal energy of gas is $\frac{7}{2}R$.

15. S : A vacuum is a space from which almost all gas has been removed.
E : A vacuum is produced by pumping out all the air and other gases.

16. S : Gaseous molecules are assumed to be "point masses" occupying no volume.
E : Gaseous molecules suffer no energy loss due to friction.

17. S : Compressibility factor Z according to van der Waals' equation may be written as $Z = \frac{1}{1 - \left(\frac{nb}{V}\right)} - \frac{an}{RTV}$.
E : For real gases $Z \gtrless 1$.

18. S : $P(V - b) = RTe^{-a/RTV}$ is called Dieterici equation of state.
E : Dieterici equation and van der Waals' equation both reduce to same expression of pressure at low densities.

19. S : At low temperature (say 0°C) the effect of attractive forces dominates for CO_2, CH_4 and N_2, whereas the molecular size effect dominates for H_2 and He to explain deviations.

E : $Z>1$ for H_2 and He, whereas $Z<1$ for CO_2, CH_4 and N_2.

20. S : An ideal gas is not expected to show any cooling on free expansion.

E : Ideal gas does not exist but is useful concept.

21. S : CO and N_2 have the same speed distribution at the same temperature.

E : Both have same molar mass.

22. S : Speed distribution of O_2 at T K is same as for SO_2 $2T$ K.

E : $u \propto \sqrt{\frac{T}{M}}$.

23. S : Density of argon at STP is 1.7857 g litre.

E : Specific gravity of argon at STP is 1.3842.

24. S : If the temperature of a sample of gas is increased from 25°C to 50°C, the volume of gas will increase by 100 per cent.

E : The volume of the given mass of a gas is directly proportional to absolute temperature.

25. S : The pressure of wet gas is reduced to half, if its volume is doubled.

E : Aqueous tension remains constant at constant pressure.

26. S : The value of van der Waals' constant 'a' is larger for NH_3 than for N_2.

E : NH_3 shows H-bonding.

27. S : The pressure of fixed amount of an ideal gas is proportional to its temperature.

E : Frequency of collisions and their impact both increase in proportion to the square root of temperature.

28. S : For H_2 and He, Z *vs.* P plots are linear throughout with positive slope.

E : van der Waals' constant 'a' is minimum for these gases.

29. S : Compressibility factor 'Z' for van der Waals' gases at critical conditions shows more deviations than normal conditions, *i.e.*, $Z=\frac{3}{8}$.

E : At critical conditions van der Waals' equation is not accurate.

30. S : Rise in compressibility factor with increasing pressure is due to a.

E : $Z=1+\frac{Pb}{RT}$, when $Z>1$.

31. S : The gas on subjecting to Joule-Thomson effect gets heated if its temperature is less than its inversion temperature.

E : Heating effect has Joule-Thomson coefficient −ve.

32. S : Liquefaction of a gas is a continuous process with increase in pressure below T_c.

E : Liquefaction of a gas is a discontinuous process with increase in pressure below T_c.

33. S : At STP or any identical temperature and pressure, the volume occupied by a definite mass of any gas are identical.

E : Equal mole of any monoatomic gas at same temperature have same average kinetic energy.

34. S : On heating a sample of gas collision frequency increases.

E : Heat is produced by the collision of gas molecules against each other.

35. S : The coefficient of isothermal expansion at critical point is zero.

E : $\left(\frac{\partial V_c}{\partial T_c}\right)_{P_c}=0$

36. S : Compressibility factor 'Z' for H_2 is lower than CO_2.

E : CO_2 has higher molar mass than H_2.

37. S : If two gases have same values 'b' but different values of 'a', then the gas having a larger value of 'a' will occupy lesser volume.

E : The gas with a larger value of 'a' have higher force of attraction.

38. S : If two gases have same values of 'a' but different values of 'b' then the gas having lesser value of 'b' will show higher compressibility.

E : The gas with smaller value of b will occupy lesser volume.

39. S : Poisson's ratio of atmospheric gases is approximately equal to 1.4.

E : Gases present in atmosphere are mainly diatomic.

40. S : The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero. **(IIT 2000)**

E : The volume occupied by the molecules of an ideal gas is zero.

ANSWERS (Statement Explanation Problems)

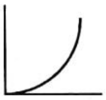
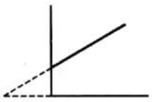
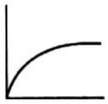
1. (b) $PV = nRT$
2. (b) At high pressure $Z = 1 + \frac{bP}{RT}$.
3. (b) At $T = T_c$, liquefaction is possible only at $P = P_c$.
4. (b) Above inversion temperature gas shows negative Joule-Thomson effect.
5. (c) Explanation is correct reason for statement.
6. (b) It is a fact, follow Maxwell distribution law.
7. (c) Explanation is correct reason for statement.
8. (b) Follow Maxwell distribution law.
9. (c) Explanation is correct reason for statement.
10. (c) $\left[P + \frac{a}{V^2}\right][V - b] = RT$; for H_2 and He, a is very small because of low molar mass Thus, $PV = RT + Pb$. Now $Z = \frac{PV}{RT} = \left[1 + \frac{Pb}{RT}\right]$.
11. (d) $\frac{RT_c}{P_c \cdot V_c} = \frac{R \times 8a \times 27b^2}{27Rb \times a \times 3b} = \frac{8}{3}$
12. (b) a is more for C_6H_6 due to high molar mass of C_6H_6.
13. (a) $$PV + \frac{a}{V} = RT$$
    $\therefore \ PV = RT - \frac{a}{V}$; Thus, $Z = \frac{PV}{RT} = \left[1 - \frac{a}{RTV}\right]$
14. (d) Average energy of diatomic moleucle is $\frac{5}{2}RT$ at constant V
    $\therefore$ Average energy of diatomic molecule $= \frac{7}{2}RT$
    $\therefore$ Increase in internal energy $= \frac{7}{2}R(T+1) - \frac{7}{2}RT = \frac{7}{2}R$
15. (c) Explanation is correct reason for statement.
16. (d) Both are facts.
17. (d) —do—
18. (d) —do—
19. (c) Explanation is correct reason for statement.
20. (d) Both are facts.
21. (c) Explanation is correct reason for statement.
22. (c) —do—
23. (d) Density at STP
    $$= \frac{\text{mass}}{V} = \frac{\text{g mol}^{-1}}{24.4 \text{ L mol}^{-1}} = \frac{40}{22.4} = 1.7857$$
    $$\text{Sp. gravity at STP} = \frac{\text{density of Ar at STP}}{\text{density of air at STP}}$$
    $$= \frac{1.7857}{1.29} = 1.3842$$
24. (b) $V \propto T$ (Kelvin)
25. (b) Saturated vapours do not obey gas laws.
26. (c) Explanation is correct reason for statement.
27. (d) Both are facts.
28. (c) Explanation is correct reason for statement.
29. (c) —do—
30. (b) The rise in compressibility factor with increase in pressure is due to b.
31. (b) If $T < T_i$ then cooling effect $\mu = +$ve
    If $T > T_i$ then heating effect $\mu = -$ve
32. (a) Follow Andrew's studies on CO_2.
33. (b) Definite mole and not definite mass.
34. (a) Collisions are perfectly elastic, however kinetic energy of molecule changes but average kinetic energy remains unchanged.
35. (c) $\alpha = \frac{\left(\frac{\partial V_c}{\partial T_c}\right)_{p,n}}{V_c}$; V_c, T_c, T_c are constant at critical conditions.
36. (b) Z for $H_2 > Z$ for CO_2.
37. (c) Explanation is correct explanation for statement.
38. (c) —do—
39. (c) Explanation is correct reason for statement $\gamma = \frac{C_p}{C_v} = 1.4$ for diatomic gases. Atmosphere mainly contains N_2 and O_2.
40. (a) $\Delta U = q - w$. For isothermal expansion, $\Delta U = 0$ and $w = 0$ because $w = P\Delta V$ (at $P = 0$)
    Volume occupied by the molecules of ideal gas is not zero but negligible.

MATCHING TYPE PROBLEMS

Type I : Only One Match Possible

1.	List-A		List-B
A.	Kinetic energy of 1 mole gas	1.	$\sqrt{2\,\text{KE}/M}$
B.	Root mean square speed	2.	$\frac{3PV}{2}$
C.	Average speed	3.	$\sqrt{\frac{8P}{\pi d}}$
D.	Most probable speed	4.	$\sqrt{4\,\text{KE}/3M}$

2.	List-A		List-B
A.	Boyle's temperature	1.	$\frac{8a}{27Rb}$
B.	Reduced temperature	2.	$\frac{a}{Rb}$
C.	Inversion temperature	3.	$\frac{2a}{Rb}$
D.	Critical temperature	4.	$\frac{T}{T_c}$

3.	List-A		List-B
A.	PT vs. T^2 plot for ideal gas at constant n and V (in K)	1.	
B.	V vs. $\frac{1}{P^2}$ graph for ideal gas at constant n and T	2.	
C.	VT vs. T^2 graph for ideal gas at constant n and P	3.	
D.	V vs. $\frac{1}{T}$ graph for ideal gas at constant P and n	4.	
E.	V vs. P graph for ideal gas at constant T and n		
F.	$\frac{1}{V^2}$ vs. P graph for ideal gas at constant T and n		

Type II : More Than One Match Are Possible

4.	List-A		List-B
A.	Vacuum technology	1.	Television tube
B.	Critical temperature	2.	Semiconductor
C.	Andrew's studies on CO_2	3.	Liquefaction of gases
D.	Dalton's law	4.	$T_c = \frac{8a}{2TRb}$
E.	Graham's law	5.	Moist gases
F.	Vacuum	6.	Aqueous tension
		7.	Effusion of gases
		8.	Diffusion of gases

5.	List-A		List-B
A.	$\left(\frac{\partial T}{\partial P}\right)_H$	1.	C_v
B.	$\left(\frac{\partial V}{\partial P}\right)_T$	2.	C_p
C.	$\left(\frac{\partial H}{\partial T}\right)_P$	3.	$\mu_{\text{J.T.}}$
D.	$\left(\frac{\partial U}{\partial V}\right)_T$	4.	Zero for ideal gas
E.	$\left(\frac{\partial U}{\partial T}\right)_V$	5.	$-\frac{V}{P}$

6.	List-A		List-B
A.	H_2 (gas) at $P = 200$ atm, $T = 273$ K	1.	$Z \neq 1$
B.	H_2 (gas) at $P \to 0$, $T = 273$ K	2.	Attractive forces predominate
C.	CO_2 gas at $P = 1$ atm, $T = 273$ K	3.	$PV = nRT$
D.	Real gas with large molar volume	4.	$P(V - nb) = nRT$

7.	List-A		List-B
A.	H_2 and He	1.	$Z > 1$
B.	CO_2	2.	$Z < 1$
C.	For a gas other than H_2 and He at T_B	3.	$Z = 1$
D.	For a gas when only repulsive forces predominates		

ANSWERS

1. A–2; B–1; C–3; D–4

2. A–2; B–4; C–3; D–1

3. A–2; B–4; C–2; D–3; E–3; F–1

4. A–1, 2; B–3, 4; C–3; D–5, 6; E–7, 8; F–1, 2, 7

5. A–3, 4; B–5; C–2; D–4; E–1

6. A–1, 4; B–3; C–1, 2; D–3

7. A–1; B–1,3; C–2; D–1

2

Mole Concept and Equivalent Concept

For Elements

$$1 \text{ g-atom} = N \text{ atoms} = 6.023 \times 10^{23} \text{ atoms}$$
$$= \text{g-atomic mass}$$

e.g., 1 g-atom of oxygen $= N$ atoms of oxygen

$$= 6.023 \times 10^{23} \text{ atoms of oxygen}$$
$$= 16 \text{ g}$$

g-atomic mass : It is the mass of Avogadro's number (N) atoms in g.

Mass of one oxygen atom $= 16$ amu

$$= 16 \times 1.66 \times 10^{-24} \text{ g}$$

$\therefore$ Mass of N oxygen atom

$$= 16 \times 1.66 \times 10^{-24} \times 6.023 \times 10^{23} \text{ g} = 16 \text{ g}$$

$$\text{g-atom of element} = \frac{\text{Mass of element}}{\text{Atomic mass of element}} \quad ...(1)$$

$$\text{No. of atoms of element} = \text{g-atom of element} \times \text{Av. No.} \quad ...(2)$$

For Compounds

$$1 \text{ g-molecule or } 1 \text{ mole} = N \text{ molecules}$$
$$= 6.023 \times 10^{23} \text{ molecules}$$
$$= \text{g molar mass}$$

$$1 \text{ mole of } O_2 = N \text{ molecules of } O_2$$
$$= 6.023 \times 10^{23} \text{ molecules of } O_2 = 32 \text{ g}$$

g-molar mass : It is the mass of Avogadro's number (N) molecules in g.

Mass of one O_2 molecule $= 32$ amu $= 32 \times 1.66 \times 10^{-24}$ g

$\therefore$ Mass of N molecules of O_2

$$= 32 \times 1.66 \times 10^{-24} \times 6.023 \times 10^{23} = 32 \text{ g}$$

$$\text{Mole} = \frac{\text{mass}}{\text{molar mass}} \quad ...(3)$$

$$\text{Molecules} = \text{mole} \times \text{Av. No.} \quad ...(4)$$

Avogadro's hypothesis : Equal volumes of gases or vapours obeying gas laws under similar conditions of P and T contain equal no. of molecules.

The statement reveals the following facts:

(1) If $P_1 = P_2, T_1 = T_2$ (for two gases)
Then at $V_1 = V_2$; $n_1 = n_2$

(2) One mole of all gases contain N molecules.

Dulong and Petits law

Atomic mass × specific heat (cal/g) ≈ 6.4 (for metals only)

Equivalent mass

Equivalent mass of a substance depends upon the nature of chemical reaction in which substance takes part. The evaluation of equivalent mass of a substance may therefore be cautiously made.

(A) Equivalent mass of an element in a redox change:

Equivalent mass of a compound

$$= \frac{\text{Molar mass}}{\text{No. of '}e\text{' lost or gained during redox change by one molecule of that compound}} \quad ...(5)$$

Equivalent mass of an element

$$= \frac{\text{Atomic mass}}{\text{No. of '}e\text{' lost or gained during redox change by one atom of that element}} \quad ...(6)$$

NOTE : (i) For details see Chapter 8.

(ii) In case of redox change, determine equivalent mass by the formulae given above and do not use any other formulae given below.

(B) Equivalent mass of an element or compound in a non redox change:

(1) Equivalent mass of an element

$$E = \frac{\text{Atomic mass of element}}{\text{Valency of element}} \quad ...(7)$$

(2) Equivalent mass of ionic compound

$$E = \frac{\text{Formula mass of ionic compound}}{\text{Total charge on cations or anions}} \quad ...(8)$$

Also Equivalent mass of an ionic compound
= Equivalent mass of I part + Equivalent mass of II part ...(9)

Eq. (9) is not valid for hydrated compounds.

e.g., (i) $E_{NaCl} = \frac{\text{F. mass of NaCl}}{1} = \frac{58.5}{1} = 58.$ By (8)

(ii) $E_{AlCl_3} = \frac{\text{F. mass of } AlCl_3}{3} = \frac{133.5}{3} = 44.5$ By (8)

$E_{AlCl_3} = \text{E. mass}_{Al} + \text{E. mass}_{Cl} = \frac{27}{3} + 35.5 = 44.5$ By (9)

(iii) $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O : E_{Alum} = \frac{M}{8}$ By (9)

(3) Equivalent mass of an acid or base:

$$\text{Eq. mass}_{\text{Acid}} = \frac{\text{Molar mass of acid}}{\text{Basicity}} \quad ...(10)$$

(Basicity is no. of H atoms replaced from one molecule of acid)

$$\text{Eq. mass}_{\text{Base}} = \frac{\text{Molar mass of base}}{\text{Acidity}} \quad ...(11)$$

(Acidity is the no. of OH groups replaced from one molecule of base)

e.g., $\underset{\text{Basicity}=2}{H_3PO_3} + \underset{\text{Acidity}=1}{2NaOH} \longrightarrow Na_2HPO_3 + 2H_2O$

$\therefore \quad E_{H_3PO_3} = \frac{M}{2} \qquad E_{NaOH} = \frac{M}{1}$

Note : However if reaction is given as:

(i) $H_3PO_3 + NaOH \longrightarrow NaH_2PO_3 + H_2O$

$E_{H_3PO_3} = \frac{M}{1}$

(ii) $Al(OH)_3 + HCl \longrightarrow Al(OH)_2Cl + H_2O$

$E_{Al(OH)_3} = \frac{M}{1}$

(4) Equivalent mass of an ion or radical :

$$\text{Eq. mass of ion or radical} = \frac{\text{Formula mass of ion or radical}}{\text{Charge on ion}} \quad ...(12)$$

(5) Equivalent mass of an acid salt :

$$E = \frac{\text{Molar mass of acid salt}}{\text{Replaceable } H \text{ atoms in acid salt}} \quad ...(13)$$

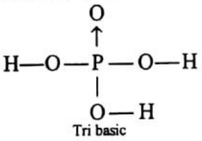
e.g. $E_{NaH_2PO_4} = \frac{M}{2}$

However if reaction is given as :

$NaH_2PO_4 + NaOH \longrightarrow Na_2HPO_4 + H_2O$

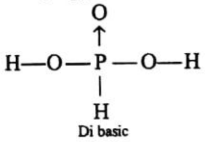
then $E_{NaH_2PO_4} = \frac{M}{1}$

An acid salt is one which has replaceable H atom, *e.g.*, $NaHCO_3, NaHSO_4, Na_2HPO_4$. However, Na_2HPO_3 is not an acid salt since it does not have replaceable H atom because H_3PO_3 is dibasic acid. In oxy acids only those H are replaceable which are attached on O atom, *e.g.*,



$$H{-}O{-}\overset{\overset{\displaystyle O}{\uparrow}}{\underset{\underset{\displaystyle O{-}H}{|}}{P}}{-}O{-}H$$

Tri basic



$$H{-}O{-}\overset{\overset{\displaystyle O}{\uparrow}}{\underset{\underset{\displaystyle H}{|}}{P}}{-}O{-}H$$

Di basic

(6) Equivalent mass of basic salt :

$$E = \frac{\text{Molar mass of basic salt}}{\text{Replaceable OH gp in basic salt}} \quad ...(14)$$

e.g. $E_{Al(OH)_2Cl} = \frac{M}{2}$

NOTE : 1. The unit of equivalent mass is $g\,eq^{-1}$.

2. However in some cases either of these formula reported does not give equivalent of the species required, *e.g.*, equivalent mass of O_3 in the reaction $2O_3 \longrightarrow 3O_2$. The equivalent mass in such cases can be determined by the concept of equivalent mass, *i.e.*, definition—Eq. mass of an species is the mass which either reacts or displaces 1 part H or 8 part O or 35.5 part Cl. For the above reaction stoichiometry suggests,

$2 \text{ mole } O_3 \equiv 3 \text{ mole } O_2$
$\equiv 96\text{ g } O_2$
$\equiv 12 \text{ eq. } O_2 \qquad (8\text{ g } O_2 = 1 \text{ eq.})$

$\therefore \quad 1 \text{ mole } O_3 \equiv 6 \text{ eq. } O_2 = 6 \text{ eq. } O_3$

or Valence factor for $O_3 = 6$

$\therefore \quad E_{O_3} = \frac{48}{6} = \mathbf{8}$

Stoichiometric concept :

	$2H_2(g)$	$+$	$O_2(g)$	$\longrightarrow$	$2H_2O(g)$
Mole ratio for reaction	2	:	1	:	2
Molecule ratio for reaction	2	:	1	:	2
Mass ratio for reaction	4	:	32	:	36
Volume ratio for reaction	2	:	1	:	2

(Volume ratio for gaseous phase reaction only at same *P*, *T*)

Percentage yield : $\% \text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$ ...(15)

Limiting reagent : The substance that is completely consumed in a reaction is called **limiting reagent** as it determines or limits, the amount of product. The other reactant present in excess is called excess reagent, *e.g.*,

	$2H_2(g) +$	$O_2(g) \longrightarrow$	$2H_2O(g)$
Mole before reaction	10	7	0
Mole after reaction	0	2	10

Thus O_2 is excess reagent and H_2 in limiting reagent

Methods for expressing concentration of solutions

1. Normality : It is defined as no. of equivalents of a solute present in one litre of solution. Its unit is eq. litre.

$$N = \frac{\text{Equivalent of solute}}{\text{Volume of solution in litre}}$$

$$= \frac{\text{Mass of solute}}{\text{Equivalent mass of solute} \times V \text{ in litre}}$$

$$N = \frac{w}{E \times V \text{ in } (l)} \qquad \text{...(16)}$$

$$= \frac{w \times 1000}{E \times V \text{ in (mL)}} \qquad \text{...(17)}$$

Also, **Equivalent** $= N \times V$ **(in L)** $= \frac{\textbf{Mass of solute}}{\textbf{Eq. mass of solute}}$ ...(18)

and **Milli equivalent** $= N \times V$ **(in L)**

$$= \frac{\textbf{Mass of solute}}{\textbf{Eq. mass of solute}} \times \mathbf{1000} \qquad \text{...(19)}$$

NOTE :
1. No doubt milli equivalent should be written as meq. (milli equivalent) but for the sake of our problems by milli equivalent, we have used Meq.
2. Eqs. (18) and (19) are commonly used in solving numericals practically in each chapter. One should be able to learn, understand and apply these equations in order to move advance to get solutions in easy and precise manner.
3. Another striking fact regarding equivalent and milli equivalent is—**Equivalent and milli equivalent of reactants reacts in equal number to give same number of equivalent or milli equivalent of products separately.**

Example. *20 mL of 0.1N* $BaCl_2$ *is mixed with 30 mL of 0.2N* $Al_2(SO_4)_3$. *How many g of* $BaSO_4$ *are formed?*

$$BaCl_2 + Al_2(SO_4)_3 \longrightarrow AlCl_3 + BaSO_4$$

Meq. before	20×0.1	30×0.2	0	0
reaction reaction			$= 2$	$= 6$
Meq. after reaction	0	4	2	2

$\therefore$ Meq. of $BaSO_4$ formed $= 2$

or $\frac{w}{E} \times 1000 = 2$

$$\therefore \quad w = \frac{2 \times E}{1000} = \frac{2 \times 233}{2 \times 1000} = \mathbf{0.233\ g}$$

2. Molarity : It is defined as the mole of solute present in one litre of solution. Its unit is mol litre^{-1}.

$$M = \frac{\text{Mole of solute}}{\text{Volume of solution in litre}}$$

$$= \frac{\text{Mass of solute}}{\text{Molar mass of solute} \times V \text{ in litre}}$$

$$= \frac{\text{Mass of solute} \times 1000}{\text{Molar masss of solute} \times V \text{ in mL}}$$

$$M = \frac{w}{m \times V\ (l)} \qquad \text{...(20)}$$

$$M = \frac{w \times 1000}{m \times V \text{ (mL)}} \qquad \text{...(21)}$$

Also, Mole of solute $= M \times V$ in l

$$= \frac{\text{mass of solute}}{\text{molar mass of solute}} \qquad \text{...(22)}$$

Milli mole of solute $= M \times V$ in mL $= \frac{w}{m} \times 1000$ ...(23)

$$\because \quad \left.\begin{aligned} \text{Molarity} &= \frac{\text{Mole}}{V \text{ in litre}} \\ \text{and} \quad \text{Normality} &= \frac{\text{Equivalent}}{V \text{ in litre}} \end{aligned}\right\} \text{for a given solution}$$

$$\therefore \quad \frac{M}{N} = \frac{\text{Mole}}{\text{Equivalent}} = \frac{w \times E}{m \times w} = \frac{E}{m} = \frac{1}{\text{Valency factor}}$$

$$\therefore \quad \text{Normality} = \text{Molarity} \times \text{Valency factor} \qquad \text{...(24)}$$

NOTE :
1. Mole and milli mole react according to stoichiometry of equation.
2. It is better to solve a numerical by equivalent or Meq. rather than using mole and milli mole. For this purpose molarity should be changed into normality by Eq. (24).
3. Equation 18, 19, 24 can be used to evaluate any problem of volumetric analysis and gravimetric analysis.
4. Problems of eudiometry can be solved in terms of stoichiometry and mole.

Example. *20 mL of 0.1M* $BaCl_2$ *in mixed with 30 mL of 0.2 M* $Al_2(SO_4)_3$. *What is the mass of* $BaSO_4$ *formed?*

By mole and milli mole : First balance it.

$$3BaCl_2 + Al_2(SO_4)_3 \longrightarrow 3BaSO_4 + 2AlCl_3$$

m mole	20×0.1	30×0.2	0	0
before reaction	$= 2$	$= 6$		
m mole after reaction	0	$\left(6 - \frac{2}{3}\right)$	2	$2 \times \frac{2}{3}$

$\because$ Reaction ratio is

$$BaCl_2 : Al_2(SO_4)_3 : BaSO_4 : AlCl_3 :: 3:1:3:2$$

$\therefore$ Milli mole of $BaSO_4 = 2$

$$\frac{w}{233} \times 1000 = 2$$

$$\therefore \quad w = \frac{2 \times 233}{1000} = 0.466\ \text{g}$$

By equivalent or Meq : No need for balancing.

$$BaCl_2 + Al_2(SO_4)_3 \longrightarrow BaSO_4 + AlCl_3$$

Meq. before reaction	$20 \times 0.1 \times 2$	$30 \times 0.2 \times 6$	0	0
[$V \times M \times$ Valency factor]	$= 4$	$= 36$		
Meq. after reaction	0	32	4	4

$\therefore$ Meq. of $BaSO_4 = 4$

$$\frac{w}{E} \times 1000 = 4$$

$$w = \frac{4 \times 233}{2 \times 1000} = 0.466\ \text{g}$$

3. Molality : Mole of solute present in one kg of solvent. Its unit is mol kg^{-1} solvent.

$$\text{Molality} = \frac{\text{mole of solute}}{\text{mass of solvent in kg}}$$

$$= \frac{\text{mass of solute}}{\text{molar mass of solute} \times \text{mass of solvent in kg}}$$

$$= \frac{\text{mass of solute} \times 1000}{\text{molar mass of solute} \times \text{mass of solvent in g}} \qquad \text{...(25)}$$

mass of solvent = mass of solution − mass of solute
mass of solution = volume of solution − specific gravity ...(26)

4. Strength of Solution : Amount of solute present in one litre solution. Its unit is g litre^{-1}.

$$S = \frac{\text{mass of solute}}{\text{volume of solution in litre}} = \frac{w}{V \text{ in } (l)} \qquad ...(27)$$

$\because$ By Eq. (15), $\quad N = \frac{w}{E} \times \frac{1}{V \text{ in } (l)}$

$\therefore \quad S = N \times E \quad (S \text{ in g litre}^{-1}) \quad ...(28)$

5. In terms of percentage :

$$\% \text{ by mass (mass/mass)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100 \qquad ...(29)$$

$$\% \text{ by strength (vol./vol.)} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100 \qquad ...(30)$$

$$\% \text{ by volume (mass/vol.)} = \frac{\text{mass of solute}}{\text{volume of solution}} \times 100 \qquad ...(31)$$

Example. A solution is 35% by ...... means
35% by mass : 100 g solution contains 35 g solute
by strength : 100 mL solution contains 35 mL solute
by volume : 100 mL solution contains 35 g solute

6. Mole fraction :

Mole fraction of solute

$$(X_A) = \frac{\text{mole of solute}}{\text{mole of solute + mole of solvent}} = \frac{n}{n+N} \qquad ...(32)$$

Mole fraction of solvent

$$(X_B) = \frac{\text{mole of solvent}}{\text{mole of solute + mole of solvent}} = \frac{N}{n+N} \qquad ...(33)$$

By Eqs. (31) and (32),

$$\therefore \quad X_A + X_B = \frac{n}{n+N} + \frac{N}{n+N} = 1 \qquad ...(34)$$

$$\text{Also,} \quad \frac{X_A}{X_B} = \frac{n}{N} \qquad ...(35)$$

NOTE :
1. Molality, % by mass, mole fractions are independent of temperature since these involve masses.
2. Rest all, *i.e.*, normality, molarity, % by vol., % by strength and strength are temperature dependent, normally decrease with increase in temperature since volume of solution increases with *T*.
3. Sometimes term formality is used in place of molarity.
4. Normal, molar solution means for solutions having normality 1*N* and molarity 1*M* respectively.
5. Standard solution is one whose *N* or *M* are known.
6. On diluting a solution, eq, milli equivalent mole or milli mole of solute do not change however *N* and *M* change.

Use of specific gravity

(1) Specific gravity of solution (mass of 1 mL solution)

$$= \frac{\text{mass of solution}}{\text{volume of solution}} \qquad ...(36)$$

(2) It is commonly used to obtain either mass of solution or volume of solution as desired.

7. Formality : Since molar mass of ionic solids is not determined accurately experimentally due to their dissociation nature and therefore molar mass of ionic solid is often referred as formula mass and molarity as formality.

$$\text{Formality} = \frac{\text{mass of solute}}{\text{Formula mass} \times V_l \text{ (in } l)} \qquad ...(37)$$

NOTE : For all practically purposes formality is molarity.

8. Ionic strength : Ionic strength (μ) of a solution is given by:

$$\mu = \frac{1}{2} \Sigma c Z^2 \qquad ...(38)$$

where *c* is concentration (in mole litre^{-1}) of ion and *Z* is its valence.

Some general points :

(1) Under similar conditions of *P* and *T*, combination of gases may be made in terms of volume ratio since mole of gas $\propto$ volume of gas at constant *P* and *T*.

(2) Acidic oxides such as CO_2, oxides of N(NO_2, N_2O_3, N_2O_5), oxides of P, Si, halogens are absorbed by alkalines, *e.g.*, NaOH, KOH, CaO etc.

(3) Basic oxides such as Na_2O, CuO, ... etc., are absorbed by acids.

Hardness of water :

(1) The hardness of water is due to the presence of bicarbonates, chlorides and sulphates of Ca and Mg.

(2) The hardness is temporary due to bicarbonates and permanent due to chlorides and sulphates of Ca and Mg.

(3) The extent of hardness is known as degree of hardness defined as the no. of parts by mass of $CaCO_3$ present per million parts by mass of water or 10^6 parts by mass or volume of water since $d_{H_2O} = 1$

$$\text{Hardness (in ppm) of water} = \frac{\text{mass of } CaCO_3}{\text{mass of water}} \times 10^6$$

$$= \frac{\text{mass of } CaCO_3}{\text{Volume of water (in mL)}} \times 10^6 \qquad ...(39)$$

NOTE : 1. Equivalent and Meq. of reactants react in equal amount to give same no. of equivalent or Meq. of products separately.

(i) *e.g.*, In a given reaction,

$$\alpha A + bB \longrightarrow mM + nN$$

Meq.of *A* = Meq. of *B* = Meq. of *M* = Meq. of *N*

(ii) In a compound $M_x N_y$

Meq. of $M_x N_y$ = Meq. of *M* = Meq. of *N*

or Eq. of $M_x N_y$ = Meq. of *M* = Meq. of *N*

(iii) In a series of reaction for complete reaction,

$$\alpha A + bB \longrightarrow cC \xrightarrow[\text{excess}]{dD} eE \xrightarrow[\text{excess}]{fF} gG$$

Meq. of *A* used = Meq. of *B* used = Meq. of *C* formed = Meq. of *D* used = Meq. of *E* formed = Meq. of *F* used = Meq. of *G* formed

2. Mole and millimole react according to equation.
3. Molarity × Valency factor = Normality
4. On diluting a solution, mole, *mM*, Equivalents and Meq. of solute do not change.
5. For reporting concentration of H_2O_2, direct conversions can be made as :
   (i) % strength of
   $$H_2O_2 = \frac{17}{56} \times \text{Volume strength of } H_2O_2$$
   (ii) Volume strength of
   $$H_2O_2 = 5.6 \times \text{Normality of } H_2O_2$$
   (iii) Volume strength of
   $$H_2O_2 = 11.2 \times \text{Molarity of } H_2O_2$$

Use of double indicator: In the titration of alkali mixtures *e.g.*, $(NaOH + Na_2CO_3)$ or $(Na_2CO_3 + NaHCO_3)$ two indicators phenolphthalein and methyl orange are used. The indicator phenolphthalein is a weak organic acid and gives end point between pH 8 to 10, while methyl orange, a weak base indicates end point sharply between pH 3.1 to 4.4. Following points are to be remembered therefore,

1. Phenolphthalein is not a good indicator for weak alkali titrations.
2. Methyl orange is not a good indicator for weak acid titrations.
3. Titration in between strong acid and strong base using phenolphthalein or methyl orange as indicator gives reading for complete neutralization, *i.e.*, Meq. of acid = Meq. of base.
4. Titration between strong acid and strong base such as Na_2CO_3 using phenolphthalein as indicator, the Meq. of acid are utilized only for the end point upto $NaHCO_3$ state.

$$\frac{224.4}{63.5} : \overset{3.5}{\frac{\cancel{2244}}{\cancel{635}}}$$

$$Na_2CO_3 + H^+ \longrightarrow \underset{\text{weak}}{NaHCO_3} + Na^+$$

i.e., $\text{Meq. of Acid} = \frac{1}{2}\text{Meq. of } Na_2CO_3$

(if Eq. mass of Na_2CO_3 is taken as $M/2$)

or $\text{Meq. of Acid Meq. of } Na_2CO_3$

(if Eq. mass of Na_2CO_3 is taken as $M/1$ since one H is replaced)

However, in titration with methyl orange as indicator, the Meq. of acid corresponds to total Meq. of alkali present at that time in mixture.

5. It is to be clearly noted that methyl orange is used as indicator in titration for fresh mixture or in continuation of phenolphthalein *e.g.*,

Na_2CO_3 + NaOH mixture *Vs* HCl

Case I. I end point is determined using phenolphthalein as indicator and then methyl orange is used to get II end point in continuation.

I end point : Meq. of Acid

$$= \text{Meq. of NaOH} + \frac{1}{2}\text{Meq. of } Na_2CO_3$$

II end point : $\text{Meq. of Acid} = \frac{1}{2}\text{Meq. of } Na_2CO_3$

Case II. End point is determined using phenolphthalein as indicator. Next time end point is determined by taking another (fresh) same volume of mixture using methyl orange as indicator.

For phenolphthalein:

$\text{Meq. of Acid} = \text{Meq. of NaOH} + \frac{1}{2}\text{Meq. of } Na_2CO_3$

For methyl orange:

$\text{Meq. of Acid} = \text{Meq. of NaOH} + \text{Meq. of } Na_2CO_3$

Representation of % of oleum: $(100 + a)\%$ m oleum means a g H_2O reacts with equivalent amount of free SO_3 dissolved in H_2SO_4 *i.e.* oleum.

• NUMERICAL PROBLEMS •

1. How many g-atom and no. of atoms are there in (a) 60 g 5 $5N_A$ carbon, (b) 224.4 g Cu? 3·5 N_A 3·5
   Given atomic masss of C and Cu are 12 and 63.5 respectively. Avogadro's no. $= 6.02 \times 10^{23}$.
2. Find the no. of g-atoms and mass of an element having 2×10^{23} atoms. Atomic mass of elemment is 32.
3. In 4 g-atoms of Ag. Calculate :
   (a) mass of Ag
   (b) mass of one atom of Ag; atomic mass of Ag $= 108$.
4. How many g-atoms are there in one atom?
5. If the diameter of a carbon atom is 0.15 nm, calculate the mass of carbon when atoms of carbon are placed side by side across the line of length 10^4 km.
6. Calculate mass of 1 atom of hydrogen.
7. Calculate the no. of atoms and volume of 1 g He gas at NTP.
8. How many mole and molecules of O_2 are there in 64 g O_2? What is the mass of one molecule of O_2?
9. How many year it would take to spend Avogadro's number of rupees at the rate of 10 lac rupees per second?
10. From 200 mg of CO_2, 10^{21} molecules are removed. How many g and mole of CO_2 are left?
11. Mass of one atom of an element is 6.644×10^{-23} g. Calculate g-atom of element in 40 kg.
12. How many g-atom of S are present in 49 g H_2SO_4 ?
13. The density of O_2 at NTP is 1.429 g/L. Calculate the standard molar volume of gas.
14. The measured density at NTP of He is 0.1784 g/L. What is the mass of one mole of He?
15. How many g of S are required to produce 100 mole and 100 g H_2SO_4 separately?
16. An alloy has Fe, Co and Mo equal to 71%, 12% and 17% respectively. How many cobalt atoms are there in a cylinder of radius 2.50 cm and a length of 10.0 cm? The density of alloy is 8.20 g/mL. Atomic mass of cobalt $= 58.9$.
17. Calculate the number of Cl^- and Ca^{2+} ions in 222 g anhydrous $CaCl_2$.
18. The dot at the end of this sentence has a mass of about one microgram. Assuming that black stuff is carbon, calculate approximate atoms of carbon needed to make such a dot.
19. Calculate the mole of water in 488 g $BaCl_2 \cdot 2H_2O$.
20. What is the molar mass of a substance, each molecule of which contains 9 carbon atoms, 13 hydrogen atoms and 2.33×10^{-23} g of other component?
21. A plant virus is found to consist of uniform cylindrical particles of 150 Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm^3/g. If the virus is considered to be a single particle, find its molar mass. **(IIT 1999)**
22. K-40 is a naturally occurring radioactive isotope having natural abundance 0.012% of potassium isotopes. How many K-40 atoms do you ingest by drinking one cup of whole milk containing 370 mg K?
23. The vapour density of a mixture containing NO_2 and N_2O_4 is 38.3 at 27°C. Calculate the mole of NO_2 in 100g mixture.
24. The vapour density of a mixture containing NO_2 and N_2O_4 is 38.3 at 27°C. Calculate the mole of NO_2 in 100 mole mixture.
25. Calculate molecules of methane, C and H atoms in 25 g methane.
26. Calculate no. of oxalic acid molecules in 100 mL of 0.02N oxalic acid. **(Roorkee 1992)**
27. Calculate the number of atoms of oxygen present in 88 g CO_2. What would be the mass of CO having the same no. of oxygen atoms?
28. A compound contains 28% N and 72% of a metal by mass. Three atoms of metal combine with two atoms of N. Find the atomic mass of metal.
29. Insulin contains 3.4% sulphur. Calculate minimum molar mass of insulin.
30. Haemoglobin contains 0.25% iron by mass. The molar mass of Haemoglobin is 89600. Calculate the no. of iron atom per molecule of Haemoglobin.
31. P and Q are two elements which forms P_2Q_3 and PQ_2. If 0.15 mole of P_2Q_3 weighs 15.9 g and 0.15 mole of PQ_2 weighs 9.3 g, what are atomic masses of P and Q?
32. Calculate the residue obtained on strongly heating 2.76g Ag_2CO_3.
33. By heating 10 g $CaCO_3$, 5.6 g CaO is formed. What is the mass of CO_2 obtained in this reaction?
34. On heating 1.763 g of hydrated $BaCl_2$ to dryness, 1.505 g of anhydrous salt remained. What is the formula of hydrate?
35. Calculate the mass of iron which will be converted into its oxide by the action of 18 g of steam.
36. Copper forms two oxides. For the same amount of copper, twice as much oxygen was used to form first oxide than to form second one. What is the ratio of the valencies of copper in first and second oxides?
37. Calculate the volume of O_2 and volume of air needed for combustion of 1 kg carbon at STP.
38. Nitrogen content in a sample of urea is 42.5%. What is the percentage purity of urea in urea sample?

39. Calculate the mass of lime (CaO) obtained by heating 200 kg of 95% pure limestone ($CaCO_3$).

40. 4.125 g of a metallic carbonate was heated and the CO_2 evolved was found to measure 1336 mL at 27°C and 700 mm pressure. What is equivalent mass of metal?

41. From the following reaction sequence

$$Cl_2 + 2KOH \longrightarrow KCl + KClO + H_2O$$
$$3KClO \longrightarrow 2KCl + KClO_3$$
$$4KClO_3 \longrightarrow 3KClO_4 + KCl$$

Calculate the mass of chlorine needed to produce 100 g of $KClO_4$.

42. Potassium selenate is isomorphous with potassium sulphate and contains 45.42% selenium by mass. Calculate the atomic mass of selenium. Also report the equivalent mass of potassium selenate.

43. A hydrocarbon contains 10.5 g of carbon per g of H. One litre vapours of hydrocarbon at 127°C and 1 atm pressure weighs 2.8 g. Find molecular formula of hydrocarbon.

44. The reaction, $2C + O_2 \longrightarrow 2CO$ is carried out by taking 24 g of carbon and 96 g O_2, find out:

(a) Which reactant is left in excess?

(b) How much of it is left?

(c) How many mole of CO are formed?

(d) How many g of other reactant should be taken so that nothing is left at the end of reaction?

45. Calculate the mass of FeO produced from 2 g VO and 5.75 g of Fe_2O_3. Also report the limiting reagent.

$$VO + Fe_2O_3 \longrightarrow FeO + V_2O_5$$

46. A polystyrene, having formula $Br_3C_6H_3(C_8H_8)_n$ was prepared by heating styrene with tribromobenzoyl peroxide in the absence of air. If it was found to contain 10.46% bromine by mass, find the value of *n*.

47. One litre of a mixture of CO and CO_2 is passed through red hot charcoal in tube. The new volume becomes 1.4 litre Find out % composition of mixture by volume. All measurements are made at same *P* and *T*.

48. One litre of CO_2 is passed over hot coke. The volume becomes 1.4 litre. Find the composition of products, assuming measurements at NTP.

49. 5 mL of a gaseous hydrocarbon was exposed to 30 mL of O_2. The resultant gas, on cooling is found to measure 25 mL of which 10 mL are absorbed by NaOH and the remainder by pyrogallol. Determine molecular formula of hydrocarbon. All measurements are made at constant pressure and temperature.

50. When a mixture of 10 mole of SO_2, 15 mole of O_2 was passed over catalyst, 8 mole of SO_3 was formed. How many mole of SO_2 and O_2 did not enter into combination?

51. A mixture of 20 mL of CO, CH_4 and N_2 was burnt in excess of O_2 resulting in reduction of 13 mL of volume. The residual gas was then treated with KOH solution to show a contraction of 14 mL in volume. Calculate volume of CO, CH_4 and N_2 in mixture. All measurements are made at constant pressure and temperature. **(IIT 1995)**

52. 50 mL of dry ammonia gas was sparked for a long time in an eudiometer tube over mercury. After sparking, the volume becomes 97 mL. After washing the gas with water and drying, the volume becomes 49 mL. This was mixed with 60.5 mL of oxygen and the mixture was burnt. After the completion of the combustion of H_2, the volume of the residual gas was 48.75 mL. Derive molecular formula of ammonia.

53. The percentage by volume of C_3H_8 in a mixture of C_3H_8, CH_4 and CO is 36.5. Calculate the volume of CO_2 produced when 100 mL of the mixture is burnt in excess of O_2.

54. 100 mL of any gas at NTP was heated with Tin. Tin converted into stannous sulphide and hydrogen was left. This hydrogen when passed over hot CuO, produced 0.081 g of water. If the vapour density of the gas is 17, find its formula.

55. A gaseous alkane is exploded with oxygen. The volume of O_2 for complete combustion to CO_2 formed is in the ratio of 7 : 4. Deduce molecular formula of alkane.

56. 40 mL ammonia gas taken in an eudiometer tube was subjected to sparks till the volume did not further change. The volume was found to increase by 40 mL. 40 mL of oxygen was then mixed and the mixture was further exploded. The gases remained were 30 mL. Deduce formula of ammonia. All measurements are made at constant *P* and *T*. Assume H_2O in liquid phase.

57. The mass of one litre sample of ozonised oxygen at NTP was found to be 1.5 g. When 100 mL of this mixture at NTP were treated with terpentine oil, the volume was reduced to 90 mL. Hence calculate the molar mass of ozone.

58. 60 mL of a mixture of nitrous oxide and nitric oxide was exploded with excess of hydrogen. If 38 mL of N_2 was formed, calculate the volume of each gas in mixture. All measurements are made at constant *P* and *T*. Assume H_2O in liquid phase.

59. 50 mL of pure and dry oxygen was subjected to a silent electric discharge and on cooling to the original temperature, the volume of ozonised oxygen was found to be 47 mL. The gas was then brought into contact with terpentine oil, when after the absorption of ozone, the remaining gas occupied a volume of 41 mL. Find molecular formula of ozone. All measurements are made at constant *P* and *T*.

60. A sample of gaseous hydrocarbon occupying 1.12 litre at NTP, when completely burnt in air produced 2.2 g CO_2 and 1.8 g H_2O. Calculate the mass of hydrocarbon taken and the volume of O_2 at NTP required for its combustion.

61. 16 mL of a gaseous aliphatic compound $C_nH_{3n}O_n$ was mixed with 60 mL O_2 and sparked. The gas mixture on cooling occupied 44 mL. After treatment with KOH solution, the volume of gas remaining was 12 mL. Deduce the formula of compound. All measurements are made at constant pressure and room temperature.

62. A 5.0 g sample of a natural gas consisting of CH_4, C_2H_4 was burnt in excess of oxygen yielding 14.5 g CO_2 and some H_2O as products. What is mass percentage of CH_4 and C_2H_4 in mixture?

63. 4 g C_3H_8 and 14 g O_2 are allowed to react to the maximum possible extent to form only CO and H_2O. Find the mass of CO formed.

64. Assume that the nucleus of the F atom is a sphere of radius 5×10^{-13} cm. Calculate the density of matter in F nucleus.

65. A metal *M* of atomic mass 54.94 has a density of $7.42\,g/cm^3$. Calculate the volume occupied and the radius of the atom of this metal assuming it to be sphere.

66. A granulated sample of aircraft alloy (Al, Mg, Cu) weighing 8.72 g was first treated with alkali and then with very dilute HCl, leaving a residue. The residue after alkali boiling weigh 2.10 g and the acid insoluble residue weigh 0.69 g. What is the composition of the alloy?

67. Calculate the mass of CaO required to remove the hardness of 10^6 litre of water containing 1.62 g of calcium bicarbonate per litre.

68. One litre of sample of hard water contains 1 mg of $CaCl_2$ and 1 mg of $MgCl_2$. Find the total hardness of water in terms of $CaCO_3$ per 10^6 parts of water by mass.

69. 1.60 g of a metal were dissolved in HNO_3 to prepare its nitrate. The nitrate was strongly heated to give 2 g oxide. Calculate equivalent mass of metal.

70. 1.0 g of metal nitrate gave 0.86 g of metal sulphate. Calculate equivalent mass of metal.

71. 1.35 g of pure Ca metal was quantitatively converted into 1.88 g of pure CaO. What is atomic mass of Ca?

72. 2 g of a metal in H_2SO_4 gives 4.51 g of the metal sulphate. The specific heat of metal is 0.057 cal/g. Calculate the valency and atomic mass of metal.

73. 1.878 g of MBr_x, when heated in a stream of HCl gas, was completely, converted to chloride MCl_x, which weighed 1.0 g. The specific heat of metal is 0.14 cal/g. Calculate molar mass of metal bromide.

74. A hydrated sulphate of metal contained 8.1% metal and 43.2% SO_4^{-2} by mass. The specific heat of metal is 0.24 cal / g. What is hydrated sulphate?

75. Find the milli equivalent of :

(a) $Ca(OH)_2$ in 74 g.

(b) NaOH in 20 g.

(c) H_2SO_4 in 2.45 g.

76. Find the mass of NaOH in its 50 milli equivalents.

77. Find the normality of H_2SO_4 having 50 milli equivalents in 2 litre.

78. 1.2048 g sample of impure Na_2CO_3 is dissolved and allowed to react with a solution of $CaCl_2$. The resulting $CaCO_3$, after precipitation, filtration and drying was found to mass 1.0362 g. Assuming impurities do not contribute to the mass of precipitate, calculate per cent purity of Na_2CO_3.

79. Calculate normality and molarity of the following :

(a) 0.74 g of a $Ca(OH)_2$ in 5 mL of solution.

(b) 3.65 g of HCl in 200 mL of solution.

(c) 1/10 mole of H_2SO_4 in 500 mL of solution.

80. Find the mass of H_2SO_4 in 1200 mL of a solution of 0.2 *N* strength.

81. Calculate the mass of calcium oxide required when it reacts with 852 g of P_4O_{10}. **(IIT 2005)**

82. What mass of Na_2CO_3 of 95% purity would be required to neutralize 45.6 mL of 0.235 *N* acid?

83. How many millilitre of 0.5 *M* H_2SO_4 are needed to dissolve 0.5 g of copper II carbonate? **(IIT 1999)**

84. What is the strength in g per litre of a solution of H_2SO_4, 12 mL of which neutralized 15 mL of *N*/10 NaOH solution?

85. The formula mass of an acid is 82.0. 100 cm^3 of a solution of this acid containing 39.0 g of the acid per litre were completely neutralized by 95.0 cm^3 of aqueous NaOH containing 40.0g of NaOH per litre. What is the basicity of the acid? **(Roorkee 2000)**

86. Calculate the normality of the resulting solution made by adding 2 drops (0.1 mL) of 0.1*N* H_2SO_4 in 1 litre of distilled water.

87. What volume at NTP of ammonia gas weill be required to be passed into 30 mL of *N* H_2SO_4 solution to bring down the acid normality to 0.2*N*?

88. Two litre of NH_3 at 30°C and 0.20 atmosphere is neutralized by 134 mL of a solution of H_2SO_4. Calculate normality of H_2SO_4.

89. One g of calcium was burnt in excess of O_2 and the oxide was dissolved in water to make up one litre solution. Calculate normality of alkaline solution.

90. 1.82 g of a metal required 32.5 mL of *N* HCl to dissolve it. What is equivalent mass of metal?

91. Calculate normality of mixture obtained by mixing:
(a) 100 mL of 0.1 N HCl + 50 mL of 0.25 N NaOH.
(b) 100 mL of 0.2 M H_2SO_4 + 200 mL of 0.2 M HCl.
(c) 100 mL of 0.2 M H_2SO_4 + 100 mL of 0.2 M NaOH.
(d) 1 g-equivalent of NaOH + 100 mL of 0.1 N HCl.

92. In what ratio should you mix 0.2 M $NaNO_3$ and 0.1 M $Ca(NO_3)_2$ solution so that in resulting solution, the concentration of −*ve* ion is 50% greater than the concentration of +*ve* ion?

93. Calculate the mass of KOH required to neutralize 15 Meq. of the following:
(a) HCl, (b) $KHSO_4$, (c) N_2O_5, (d) CO_2.

94. What volume of water is required to make 0.20N solution from 1600 mL of 0.2050N solution?

95. How much $BaCl_2 \cdot 2H_2O$ and pure water are to be mixed to prepare 50 g of 12.0% (by mass) $BaCl_2$ solution?

96. What volume of a solution of hydrochloric acid containing 73 g of acid per litre would suffice for the exact neutralization of sodium hydroxide obtained by allowing 0.46 g of metallic sodium to act upon water?

97. 20 mL of 0.2M $Al_2(SO_4)_3$ is mixed with 20 mL of 0.6 M $BaCl_2$. Calculate the concentration of each ion in solution.

98. Find out equivalent mass of H_3PO_4 in the reaction.

$$Ca(OH)_2 + H_3PO_4 \longrightarrow CaHPO_4 + 2H_2O$$

99. What volume of 0.20 M H_2SO_4 is required to produce 34.0 g of H_2S by the reaction?

$$8KI + 5H_2SO_4 \longrightarrow 4K_2SO_4 + 4I_2 + H_2S + 4H_2O$$

100. How much AgCl will be formed by adding 200 mL of 5N HCl to a solution containing 1.7g $AgNO_3$?

101. What mass of AgCl will be precipitated when a solution containing 4.77 g NaCl is added to a solution of 5.77 g of $AgNO_3$?

102. How much $BaCl_2$ would be needed to make 250 mL of a solution having same concentration of Cl^- as the one containing 3.78 g of NaCl per 100 mL?

103. Upon mixing 45.0 mL of 0.25 M lead nitrate solution with 25 mL of 0.10M chromtic sulphate, precipitation of lead sulphate takes place. How many mole of lead sulphate are formed? Also calculate the molar concentrations of the species left behind in final solution. Assume that lead sulphate is completely insoluble. **(IIT 1993)**

104. What is the normality and nature of a mixture obtained by mixing 0.62 g of $Na_2CO_3.H_2O$ to 100 mL of 0.1N H_2SO_4?

105. A sample of an alloy weighing 0.50 g and containing 90% Ag was dissolved in conc. HNO_3. Ag was analysed by Volhard method in which 25 mL of KCNS were required for complete neutralization. Determine normality of KCNS.

106. What is the purity of conc. H_2SO_4 solution (specific gravity 1.8 g/mL), if 5.0 mL of this solution is neutralized by 84.6 mL of 2.0 N NaOH?

107. A sample of H_2SO_4 (density 1.787 g mL^{-1}) is labeled as 86% by mass. What is molarity of acid? What volume of acid has to be used to make 1 litre of 0.2 M H_2SO_4?

108. A piece of Al weighing 2.7 g is titrated with 75.0 mL of H_2SO_4 (sp. gr. 1.18 g mL^{-1} and 24.7% H_2SO_4 by mass). After the metal is completely dissolved, the solution is diluted to 400 mL. Calculate molarity of free H_2SO_4 in solution.

109. A 6.90M solution of KOH in water has 30% by mass of KOH. Calculate density of solution.

110. Mole fraction of I_2 in C_6H_6 is 0.2. Calcualte molality of I_2 in C_6H_6.

111. A drop (0.05 mL) of 12 M HCl is spread over a thin sheet of aluminium foil (thickness 0.10 mm and density of Al = 2.70 g /mL). Assuming whole of the HCl is used to dissolve Al, what will be the maximum area of hole produced in foil?

112. Calculate the volume of NH_3 in a solution (density 0.99 g /cm^3 and 2.3% by mass) which will be required to precipitate $Fe(OH)_3$ from a sample of 0.70 g of 25% Fe_2O_3 purity.

113. Calculate molality of 1 litre solution of 93% H_2SO_4 by volume. The density of solution is 1.84 g mL^{-1}. **(IIT 1990)**

114. The gases produced when 18 g carbon reacts with 5 litre of oxygen at 18°C and 5 atm pressure are treated with 0.5 litre of 2 M NaOH. Calculate the concentration of sodium carbonate and sodium bicarbonate produced by the reaction of CO_2 with NaOH.CO has no reaction under these conditions.

115. What would be the molality of a solution obtained by mixing equal volumes of 30% by mass H_2SO_4 (d = 1.218 g mL^{-1}) and 70% by mass H_2SO_4 (d = 1.610 g mL^{-1})? If the resulting solution has density 1.425 g/mL, calculate its molarity.

116. Calculate molarity of water, if its density is 1000 kg /m^3. **(IIT 2003)**

117. To 50 litre of 0.2 N NaOH, 5 litre of 1N HCl and 15 litre of 0.1N $FeCl_3$ solution are added. What mass of Fe_2O_3 can be obtained from the precipitate? Also report the normality of NaOH left in the resultant solution.

118. The molar mass of an organic acid was determined by the study of its barium salt. 4.290 g of salt was quantitatively converted to free acid by the reaction with 21.64mL of 0.477 M H_2SO_4. The barium salt was found to have two mole of water of hydration per Ba^{2+} ion and the acid is monobasic. What is the molar mass of anhydrous acid?

119. A solution is 0.5 *M* in $MgSO_4$, 0.1 *M* in $AlCl_3$ and 0.2 *M* in $(NH_4)_2SO_4$. What is the total ionic strength?

120. What volume of 0.010 *M* NaOH (aq.) is required to react completely with 30 g of an aqueous acetic acid solution in which mole fraction of acetic acid is 0.15?

121. A solution contains 1 mol of total amount of solute and solvent. The mole fraction of solute being X_1 and that of solvent being X_2, prove :

(a) $X_1 = \frac{MM_2}{\rho + M(M_2 - M_1)}$ where M_1 and M_2 are molar masses of solute and solvent respectively and *M* is molarity of solution; ρ is density of solution in g /dm^3.

(b) $M = \frac{X_1\rho}{M_2}$ for dilute solution; ρ is density of solvent.

122. A mixture of Al and Zn weighing 1.67 g was completely dissolved in acid and evolved 1.69 litre of H_2 at NTP. What was the mass of Al in original mixture?

123. A mixture of HCOOH and $H_2C_2O_4$ is heated with conc. H_2SO_4. The gas produced is collected and on treating with KOH solution the volume of the gas decreases by $\frac{1}{6}$ *th*. Calculate molar ratio of two acids in original mixture. **(Roorkee 1990)**

124. A sample of Mg was burnt in air to give a mixture of MgO and Mg_3N_2. The ash was dissolved in 60 Meq. of HCl and the resulting solution was back titrated with NaOH. 12 Meq. of NaOH were required to reach the end point. An excess of NaOH was then added and the solution distilled. The ammonia released was then trapped in 10 Meq. of second acid solution. Back titration of this solution required 6 Meq. of the base. Calculate the percentage of Mg burnt to the nitride. **(Roorkee 1998)**

125. For the reaction, $N_2O_5(g) \rightleftharpoons 2NO_2(g) + 0.5O_2(g)$, calculate the mole fraction of $N_2O_5(g)$ decomposed at a constant volume and temperature, if the initial pressure is 600 mm Hg and the pressure at any time is 960 mm Hg. Assume ideal gas behaviour.

126. A gas mixture of 3 litre of propane (C_3H_8) and butane (C_4H_{10}) on complete combustion at 25°C produced 10 litre CO_2. Find out the composition of gas mixture.

127. 8.0575×10^{-2} kg of Glauber's salt is dissolved in water to obtain 1 dm^3 of a solution of density 1077.2 kg m^{-3}. Calculate the molarity, molality and mole fraction of Na_2SO_4 in solution. **(IIT 1994)**

128. A solid mixture 5 g consists of lead nitrate and sodium nitrate was heated below 600° C until mass of residue was constant. If the loss in mass is 28%, find the mass of lead nitrate and sodium nitrate in mixture. **(IIT 1990)**

129. A mixture of ethane (C_2H_6) and ethene (C_2H_4) occupies 40 litre at 1.00 atm and at 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O. Assuming ideal gas behaviour, calculate the mole fractions of C_2H_4 and C_2H_6 in the mixture. **(IIT 1995)**

130. A sample of hard water contains 96 ppm of SO_4^{2-} and 183 ppm of HCO_3^-, with Ca^{2+} as the only cation. How many mole of CaO will be required to remove HCO_3^- from 1000 kg of this water? If 1000 kg of this water is treated with the mass of CaO calculated above, what will be the concentration (in ppm) of residual Ca^{2+} ions (Assume $CaCO_3$ to be completely insoluble in water)? If the Ca^{2+} ions in one litre of the treated water are completely exchanged with hydrogen ions, what will be its pH (One ppm means one part of the substance in one million part of water, mass/mass)? **(IIT May 1997)**

131. 1.20 g sample of Na_2CO_3 and K_2CO_3 was dissolved in water to form 100 mL of a solution. 20 mL of this solution required 40 mL of 0.1 *N* HCl for complete neutralization. Calculate the mass of Na_2CO_3 in mixture. If another 20 mL of this solution is treated with excess of $BaCl_2$, what will be the mass of precipitate? **(Roorkee 1997)**

132. 25 mL of a solution of Na_2CO_3 having a specific gravity of 1.25 g mL^{-1} required 32.9 mL of a solution of HCl containing 109.5 g of the acid per litre for complete neutralization. Calculate the volume of 0.84 *N* H_2SO_4 that will be completely neutralized by 125 g of Na_2CO_3 solution.

133. 200 mL of *a M* solution of HCl is mixed with 500 mL of *b M* solution of HCl. The mixture is diluted to 2 litre to obtain the solution of molarity 1.5 *M*. If *a* : *b* : : 5 : 4, what are the values of *a* and *b*?

134. Calculate the % of free SO_3 in oleum that is labelled as 106%.

SOLUTIONS (Numerical Problems)

1. $\because$ g-atom $= \dfrac{\text{mass}}{\text{atomic mass}}$ and No. of atoms $= \dfrac{\text{mass} \times \text{Av. No.}}{\text{atomic mass}}$

(a) $\therefore$ **For 60 g C :** g-atom $= \dfrac{60}{12} = \mathbf{5}$

No. of atoms $= \dfrac{60 \times 6.02 \times 10^{23}}{12} = \mathbf{30.1 \times 10^{23}}$

(b) **For 224.4 g Cu :** g-atom $= \dfrac{224.4}{63.6} = \mathbf{3.53}$

No. of atoms $= \dfrac{224.4 \times 6.02 \times 10^{23}}{63.6} = \mathbf{21.24 \times 10^{23}}$

2. $\because$ N atoms have 1 g-atom

$\therefore$ 2×10^{23} atoms have $= \dfrac{2 \times 10^{23}}{6.023 \times 10^{23}} = \mathbf{0.33}$ **g atom**

$\because$ N atoms of element weigh 32g

$\because$ 2×10^{23} atoms of element weigh

$= \dfrac{32 \times 2 \times 10^{23}}{6.023 \times 10^{23}} = \mathbf{10.63}$ **g**

3. (a) $\because$ 1 g-atom of Ag weighs 108 g

4g-atom of Ag weighs $108 \times 4 = \mathbf{432}$ **g**

(b) $\because$ N atoms of Ag weigh 108 g

$\therefore$ 1 atom of Ag weighs $\dfrac{108}{6.023 \times 10^{23}} = \mathbf{17.93 \times 10^{-23}}$ **g**

4. $\because$ N atom has 1 g-atom

$\therefore$ 1 atom has $\dfrac{1}{6.023 \times 10^{23}} = \mathbf{1.66 \times 10^{-24}}$ **g atom**

5. Carbon atoms occupies the distance

$= 10^4 \text{ km} = 10^4 \times 10^3 \text{ m}$

$= 10^4 \times 10^3 \times 10^2 \text{ cm} = 10^9 \text{ cm}$

$\therefore$ No. of carbon atoms placed across the line

$= \dfrac{10^9}{0.15 \times 10^{-7}} = 6.67 \times 10^{16}$

Mass of these carbon atoms $= \dfrac{12 \times 6.67 \times 10^{16}}{6.023 \times 10^{23}}$

$= 1.328 \times 10^{-6} \text{ g} = \mathbf{1.328\ \mu g}$

6. $\because$ N atom of H weigh 1 g

$\therefore$ 1 atom of H weigh $\dfrac{1}{6.023 \times 10^{23}} = \mathbf{1.66 \times 10^{-24}}$ **g**

7. $\because$ 4 g He has 6.023×10^{23} atoms

$\therefore$ 1 g He has $\dfrac{6.023 \times 10^{23}}{4}$ atoms $= \mathbf{1.506 \times 10^{23}}$ **atoms**

Also, $\because$ 4 g He $\equiv$ 22.4 L at NTP

$\therefore$ 1 g He $\equiv \dfrac{22.4}{4} \equiv$ **5.6 litre at NTP**

8. $\because$ 32 g O_2 has mole = 1

$\therefore$ 64 g O_2 has mole $= \dfrac{64 \times 1}{32} = \mathbf{2}$ **mol**

$\because$ 32 g O_2 contain 6.023×10^{23} molecules

$\therefore$ 64 g O_2 contain $\dfrac{6.023 \times 10^{23} \times 64}{32}$

$= \mathbf{12.04 \times 10^{23}}$ **molecules**

$\therefore$ N molecules of O_2 weigh 32 g

$\therefore$ 1 molecule of O_2 weighs

$= \dfrac{32}{6.023 \times 10^{23}} = \mathbf{5.313 \times 10^{-23}}$ **g**

9. Total rupees to be expanded $= 6.023 \times 10^{23}$

Rupees spent per second $= 10^6$

$\therefore$ Rupees spent per year $= 10^6 \times 60 \times 60 \times 24 \times 365$

$\because$ $10^6 \times 60 \times 60 \times 24 \times 365$ Rupees are spent in 1 year

$\therefore$ 6.023×10^{23} Rupees are spent

$= \dfrac{6.023 \times 10^{23}}{10^6 \times 60 \times 60 \times 24 \times 365}$ year

$= \mathbf{1.9099 \times 10^{10}}$ **year**

10. $\because$ 6.023×10^{23} molecules of $CO_2 \equiv 44$ g

$\therefore$ 10^{21} molecules of $CO_2 \equiv \dfrac{44 \times 10^{21}}{6.023 \times 10^{23}}$ g

$= 7.31 \times 10^{-2} \text{ g} = 73.1 \text{ mg}$

$\therefore$ CO_2 left $\equiv 200 - 73.1 = \mathbf{126.9}$ **mg**

Also, Mole of CO_2 left $= \dfrac{\text{mass}}{\text{molar mass}} = \dfrac{126.9 \times 10^{-3}}{44}$

$= \mathbf{2.88 \times 10^{-3}}$

11. Mass of 1 atom of element $= 6.644 \times 10^{-23}$ g

$\therefore$ Mass of N atom of element

$= 6.644 \times 10^{-23} \times 6.023 \times 10^{23} = 40$

$\because$ 40g of element has a 1 g atom

$\therefore$ 40×10^3 g of element $= \dfrac{40 \times 10^3}{40} = \mathbf{10^3}$ **g atom**

12. $\because$ $98 \text{ g } H_2SO_4 \equiv 32 \text{ g S} \equiv 1 \text{ g atom S}$

$\therefore$ $49 \text{ g } H_2SO_4 \equiv \dfrac{1 \times 49}{98}$ g atom S = **0.5 g atom of S**

13. Standard molar volume is the volume occupied by 1 mole of gas at NTP.

$\because$ 1.429 g of $O_2 \equiv$ 1 litre at NTP

$\therefore$ 32 g of $O_2 \equiv \dfrac{32}{1.429}$ litre at NTP = 22.39 litre at NTP

$\therefore$ Molar volume = **22.39 litre mol^{-1}**

14. One mole of He occupies 22.4 litre volume

$\because$ 1 litre volume weigh = 0.1784g

$\therefore$ 22.4 litre volume weigh $= 0.1784 \times 22.4 = \mathbf{4}$ **g mol^{-1}**

15. $\because$ 1 mole of $H_2SO_4 \equiv 32$ g S

$\therefore$ 100 mole $H_2SO_4 \equiv 32 \times 100 \equiv \mathbf{3200}$ **g S**

$\because$ 98 g $H_2SO_4 \equiv 32$ g S

$\therefore$ 100 g $H_2SO_4 \equiv \dfrac{32 \times 100}{98} = \mathbf{32.65}$ **g S**

16. Mass of alloy cylinder $= \text{Volume} \times \text{density} = \pi r^2 h \times d$

$$= \frac{22}{7} \times (2.5)^2 \times 10 \times 8.20 = 1610.7\,\text{g}$$

Mass of cobalt in alloy $= \frac{1610.7 \times 12}{100} = 193.3\,\text{g}$

$\because$ 58.9 g cobalt has atoms $= 6.023 \times 10^{23}$

$\therefore$ 193.3 g cobalt has atoms

$$= \frac{6.023 \times 10^{23} \times 193.3}{58.9} = \mathbf{19.8 \times 10^{23}}$$

17. Molar mass $CaCl_2 = 111\,\text{g}$

$\because$ 111g $CaCl_2 \equiv$ N ions of Ca $\equiv$ N ions of Ca^{2+}

$\therefore$ 222 g $CaCl_2 \equiv \frac{N \times 222}{111} = \mathbf{2\ N\ ions\ of\ Ca^{2+}}$

$\because$ 111 g $CaCl_2 \equiv$ 2 N ions of Cl^-

$\therefore$ 222 g $CaCl_2 \equiv \frac{2 \times N \times 222}{111}$ ions of Cl^-

$= \mathbf{4\ N\ ions\ of\ Cl^-}$

18. Mass of carbon in dot $= 1 \times 10^{-6}$ g

$\because$ 12 g C $\equiv 6.023 \times 10^{23}$ atoms

$\therefore$ 1×10^{-6} g C $\equiv \frac{6.023 \times 10^{23} \times 1 \times 10^{-6}}{12}$

$= \mathbf{5 \times 10^{16}}$ **atoms of C**

19. Molar mass of $BaCl_2 \cdot 2H_2O = 244$ g

$\because$ 244 g $BaCl_2 \cdot 2H_2O \equiv 36$ g $H_2O = 2$ mole

$\therefore$ 488 $BaCl_2 \cdot 2H_2O \equiv \frac{2 \times 488}{244} = \mathbf{4\ mole\ H_2O}$

20. Molecule has C, H and other component

$\therefore$ Mass of 9 C atoms $= 12 \times 9 = 108$ amu

$\because$ Mass of 13 H atoms $= 13 \times 1 = 13$ amu

Mass of 2.33×10^{-23} g of other atom

$$= \frac{2.33 \times 10^{-23}}{1.66 \times 10^{-24}} = 14.04\ \text{amu}$$

$\therefore$ Total mass of one molecule

$= 108 + 13 + 14.04 = \mathbf{135.04\ amu}$

$\therefore$ molar mass $= \mathbf{135.04\ g}$

21. Volume of virus

$$= \pi r^2 l = \frac{22}{7} \times \frac{150}{2} \times \frac{150}{2} \times 10^{-16} \times 5000 \times 10^{-8}$$

$= 0.884 \times 10^{-16}\ \text{cm}^3$

$\therefore$ Mass of one virus

$$= \frac{0.884 \times 10^{-16}}{0.75}\ \text{g} = 1.178 \times 10^{-16}\ \text{g}$$

$\therefore$ molar mass of virus

$= 1.178 \times 10^{-16} \times 6.023 \times 10^{23} = \mathbf{7.095 \times 10^7}$

22. Mass of K-40 in 370 mg K

$$= \frac{370 \times 0.012}{100}\ \text{mg} = 0.0444\ \text{mg}$$

$\therefore$ 40 g K-40 has atoms of K-40 $= 6.023 \times 10^{23}$

$\therefore$ 0.0444×10^{-3} g K-40 has atoms

$$= \frac{6.023 \times 10^{23} \times 0.0444 \times 10^{-3}}{40}$$

$= \mathbf{6.69 \times 10^{17}}$ **atoms**

23. Molar mass of mixture of NO_2 and $N_2O_4 = 38.3 \times 2 = 76.6$

Let a g of NO_2 present in 100 g mixture

$\therefore$ Mole of NO_2 + Mole of N_2O_4 = Mole of mixture

$$\frac{a}{46} + \frac{100 - a}{92} = \frac{100}{76.6}$$

$$a = 20.10\,\text{g}$$

$\therefore$ Mole of NO_2 in mixture $= \frac{20.10}{46} = \mathbf{0.437}$

24. Molar mass of mixture of NO_2 and $N_2O_4 = 38.3 \times 2 = 76.6$

Let a mole of NO_2 are present in mixture

g of NO_2 + g of N_2O_4 = Total g of mixture

$$a \times 46 + (100 - a)92 = 100 \times 76.6$$

$$a = \mathbf{33.48\ mol}$$

25. Molar mass of $CH_4 = 16$

$\because$ 16 g $CH_4 \equiv N$ molecules

$\therefore$ 25 g $CH_4 \equiv \frac{6.023 \times 10^{23} \times 25}{16}$ molecules

$= \mathbf{9.41 \times 10^{23}}$ **molecules**

16g $CH_4 \equiv N$ atom of C

$\therefore$ 25 g $CH_4 \equiv \frac{6.023 \times 10^{23} \times 25}{16}$ atoms of C

$= \mathbf{9.41 \times 10^{23}}$ **atoms of C**

16g $CH_4 \equiv 4N$ atoms of H

$\therefore$ 25 g $CH_4 \equiv \frac{4 \times 25 \times 6.023 \times 10^{23}}{16}$ atoms of H

$= \mathbf{3.764 \times 10^{24}}$ **atoms of H**

26. Normality $= 0.02$

$\therefore$ Molarity $= \frac{0.02}{2}$ ($\because$ valency factor $= 2$)

$\therefore$ Mole of oxalic acid $= \frac{0.02}{2} \times \frac{100}{1000}$ [$\because$ mole $= M \times V\ (l)$]

$\therefore$ No. of molecules of oxalic acid

$= 0.001 \times 6.023 \times 10^{23} = \mathbf{6.023 \times 10^{20}}$

27. $\because$ Molar mass of $CO_2 = 44$ and it has 32 g O_2 and one molecule of O_2 has 2 atoms.

$\because$ 44 g $CO_2 \equiv 2N$ atoms of O

$\therefore$ 88 g $CO_2 \equiv \frac{2 \times 6.023 \times 10^{23} \times 88}{44}$ atoms of O

$= 24.092 \times 10^{23}$ atoms of Oxygen

Also molar mass of CO = 28 and it has 16 g O and one atom of O in one molecule of CO.

$\because$ N atoms of O are present in = 28 g CO

$\therefore$ 24.092×10^{23} atoms of O are present in

$$= \frac{28 \times 24.092 \times 10^{23}}{6.023 \times 10^{23}} = \mathbf{112\ g\ CO}$$

28. Given that, $3M + 2\text{N} \longrightarrow M_3\text{N}_2$

Let a is atomic mass of metal

$\because \quad (3a+28)\text{g } M_3\text{N}_2$ has metal $= 3a$

$\therefore \quad 100 \text{ g } M_3\text{N}_2$ has metal $= \dfrac{3a \times 100}{(3a+28)}$

$$\because \quad \frac{3a \times 100}{(3a+28)} = 72$$

$$\therefore \quad a = \mathbf{24}$$

29. For minimum molar mass, insulin must have at least one S atom in its one molecule.

$\because$ 3.4 g S then molar mass of insulin = 100

$\therefore$ 32 g S then molar mass of insulin $= \dfrac{100 \times 32}{3.4} = 941.176$

$\therefore$ Minimum molar mass of insulin = **941.176**

30. $\because$ 100 g Haemoglobin has = 0.25 g Fe

$\therefore$ 89600 g Haemoglobin has

$$= \frac{0.25 \times 89600}{100} \text{ g Fe} = 224 \text{ g Fe}$$

i.e., 1 mole or N molecules of Haemoglobin has

$$= \frac{224}{56} \text{ g atom Fe} = 4\text{g atom Fe}$$

$\therefore$ **1 molecule of Haemoglobin has 4 atom of Fe.**

31. Let atomic mass of P and Q are a and b respectively.

$\therefore$ molar mass of $P_2Q_3 = 2a + 3b$

and molar mass of $PQ_2 = a + 2b$

Now given that 0.15 mole of P_2Q_3 mass 15.9 g

$$(2a+3b) = \frac{15.9}{0.15} \qquad \left(\because \frac{\text{mass}}{\text{molar mass}} = \text{mole}\right)$$

Similarly, $(a+2b) = \dfrac{9.3}{0.15}$

Solving these two equation $b = \mathbf{18}$

$a = \mathbf{26}$

32.
$$\text{Ag}_2\text{CO}_3 \xrightarrow{\Delta} 2\text{Ag} + \text{CO}_2 + \frac{1}{2}\text{O}_2$$

and molar mass of $\text{Ag}_2\text{CO}_3 = 276$

atomic mass of Ag = 108

$\because$ 276 g Ag_2CO_3 gives Ag = 216 g

$\therefore$ 2.76 g Ag_2CO_3 gives Ag = **2.16 g**

33.
$$\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$$

molar mass 100 56 44

$\because$ 100 g CaCO_3 gives 56 g CaO and 44 g CO_2

$\therefore$ **10 g CaCO_3 gives 5.6 g CaO and 4.4 g CO_2**

34.
$$\text{BaCl}_2 \cdot n\text{H}_2\text{O} \xrightarrow[208]{\Delta} \text{BaCl}_2 + n\text{H}_2\text{O}$$

molar mass $(208 + 18n)$

$\because$ $(208 + 18n)$ g $\text{BaCl}_2 \cdot n\text{H}_2\text{O}$ gives = 208 g BaCl_2

$\because$ 1.763 g $\text{BaCl}_2 \cdot n\text{H}_2\text{O} = \dfrac{208 \times 1.763}{208 + 18n}$ g BaCl_2

$$\therefore \quad \frac{208 \times 1.763}{208 + 18n} = 1.505$$

$$n = 1.98 \approx 2$$

$\therefore$ **Formula is $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$**

35. The reaction occurs as :

$$3\text{Fe} + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$$

Mole ratio of reaction suggests:

$$\frac{\text{Mole of Fe}}{\text{Mole of H}_2\text{O}} = \frac{3}{4}$$

$$\therefore \quad \text{Mole of Fe} = \frac{18}{18} \times \frac{3}{4} = \frac{3}{4}$$

$$\therefore \quad \text{Mass of Fe} = \frac{3}{4} \times 56 = \mathbf{42\ g}$$

36. Let valencies of Cu in two oxides be x and y, then

I oxide is Cu_2O_x

II oxide is Cu_2O_y

In I oxide : Equivalent of Cu = Equivalent of oxygen

$$\frac{w}{A/x} = \frac{a}{8} \qquad \text{...(1)}$$

where w, A, x_1 and a are mass of Cu, atomic mass of Cu, valency of Cu and mass of oxygen.

In II oxide :
$$\frac{w}{A/y} = \frac{a}{2 \times 8} \qquad \text{...(2)}$$

($\because$ Oxygen used half of I)

By Eqs. (1) and (2) $\dfrac{x}{y} = \dfrac{2}{1}$

$\therefore$ Valency of Cu in I and II oxides are in the ratio **2 : 1.**

37.
$$\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$$

$\because$ 12 g C requires O_2 = 22.4 litre = 1 mole = 32g

$\therefore$ 1000 g C requires

$$\text{O}_2 = \frac{22.4 \times 1000}{12} \text{ litre} = 1866.67 \text{ litre O}_2$$

$$\therefore \quad V_{\text{air}} = 5 \times V_{\text{O}_2} = 5 \times 1866.67 = \mathbf{9333.35\ litre}$$

38. Urea is NH_2CONH_2, having molar mass = 60 and nitrogen in it is 28.

$\because$ 28g nitrogen ≡ 60g urea

$\therefore$ 42.5 g nitrogen $\equiv \dfrac{60 \times 42.5}{28} = $ **91.07 g urea**

Since, 42.5 g nitrogen is present in 100 g sample, therefore, percentage of urea in sample = 91.07%

39. 100 kg impure sample has CaCO_3 = 95 kg

$\therefore$ 200 kg impure sample has $\text{CaCO}_3 = \dfrac{95 \times 200}{100} = 190$ kg

Now $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$

M. mass 100 g 56 g 44 g

$\because$ 100 kg CaCO_3 gives CaO = 56 kg

$\therefore$ 190 kg CaCO_3 gives CaO $= \dfrac{56 \times 190}{100} = $ **106.4 kg**

40.
$$PV = \frac{w}{m} RT \qquad \text{(for CO}_2\text{ gas)}$$

$$\frac{700}{760} \times \frac{1336}{1000} = \frac{w}{44} \times 0.0821 \times 300$$

$$\therefore \quad w_{\text{CO}_2} = 2.20 \text{ g}$$

Let carbonate be $M_2(\text{CO}_3)_n$ and atomic mass of metal be a

$$M_2(\text{CO}_3)_n \longrightarrow M_2O_n + n\text{CO}_2$$

$\because$ $(2a + 60n)$g $M_2(\text{CO}_3)_n$ gives $44n$ g CO_2

$\therefore$ 4.215 g $M_2(CO_3)_n$ gives $\frac{44n \times 4.215}{(2a+60n)}$ g CO_2

$$\therefore \qquad \frac{44n \times 4.215}{2a+60n} = 2.20$$

$$\therefore \qquad \text{Eq. mass} = \frac{a}{n} = \mathbf{12.15}$$

41. Taking the given reactions

$$\begin{array}{rl} & 4KClO_3 \longrightarrow 3KClO_4 + KCl \\ & 12KClO \longrightarrow 8KCl + 4KClO_3 \\ & \underline{12Cl_2 + 24KOH \longrightarrow 12KClO + 12H_2O + 12KCl} \\ \text{Adding} & 12Cl_2 + 24KOH \longrightarrow 3KClO_4 + 21KCl + 12H_2O \end{array}$$

molar mass of $KClO_4 = 138.5$

$\because$ 3×138.5 g $KClO_4$ is formed by $= 12 \times 71$ g Cl_2

$\therefore$ 100g $KClO_4$ will be formed

$$= \frac{12 \times 71 \times 100}{3 \times 138.5} = \mathbf{205.05\ g}$$

42. Potassium selenate is isomorphous to K_2SO_4 and thus its molecular formula is K_2SeO_4.

Now molar mass of $K_2SeO_4 = (39 \times 2 + a + 4 \times 16)$
$= (142 + a)$

where a is atomic mass of Se.

$(142+a)$g K_2SeO_4 has Se $= a$g

100 g K_2SeO_4 has Se $= \frac{a \times 100}{142+a}$

$$\therefore \qquad \% \text{ of Se} = 45.42$$

$$\therefore \qquad \frac{a \times 100}{142+a} = 45.42$$

$$\therefore \qquad a = \mathbf{118.168 \approx 118.2}$$

Also Eq. mass of $K_2SeO_4 = \frac{\text{Molar mass}}{2}$

$$= \frac{2 \times 39 + 118.2 + 64}{2} = \mathbf{130.1}$$

43. Given,

C	: H	
10.5	1	$\therefore$ Total = 11.5

Now from $PV = \frac{w}{M} RT$ for vapours of compound

$$1 \times 1 = \frac{2.8}{M} \times 0.0821 \times 400$$

$\therefore$ Molar mass of compound = 92

$\because$ 11.5 g has 1 g H

$\therefore$ 92 g has $\frac{92 \times 1}{11.5} = 8$ g H = 8 g atom of H

and thus, 92 g has 84 g carbon = 7 g atom carbon

$\therefore$ Molecular formula $= \mathbf{C_7H_8}$

44.

$$2C + O_2 \longrightarrow 2CO$$

	$2C$	O_2	$2CO$	
Mole before reaction	$\frac{24}{12}$	$\frac{96}{32}$		
	$= 2$	$= 3$	0	$\because$ mole ratio of
Mole after reaction	0	2	2	$C : O_2 : CO :: 2 : 1 : 2$

(a) $\therefore$ $\mathbf{O_2}$ is left in excess.

(b) **2 mole of O_2** or 64 g O_2 is left.

(c) **2 mole of CO** or 56 g CO is formed.

(d) To use O_2 completely total 6 mole of carbon or **72 g** carbon is needed.

45. Balancing the given equation

$$2VO + 3Fe_2O_3 \longrightarrow 6FeO + V_2O_5$$

	$2VO$	$3Fe_2O_3$	$6FeO$	V_2O_5
Mole before reaction	$\frac{2}{67}$	$\frac{5.75}{160}$		
	$= 0.0298$	0.0359	0	0
Mole after reaction	$\left(0.0298 - \frac{0.0359 \times 2}{3}\right)$	0	0.0359×2	$0.0359 \times \frac{1}{3}$

$\therefore$ Mole of FeO formed $= 0.0359 \times 2$

$\therefore$ Mass of FeO formed $= 0.0359 \times 2 \times 72 = \mathbf{5.17\ g}$

The limiting reagent is one which is used completely, *i.e.*, Fe_2O_3 here.

46. Let the mass of polystyrene prepared by 100 g.

$\therefore$ No. of mole of Br in 100 g of polystyrene

$$= \frac{10.46}{80} = 0.1308 \text{ mole}$$

From the formula of polystyrene, we have,

No. of mole of Br $= 3 \times$ mole of $Br_3C_6H_3(C_8H_8)_n$

$$0.1308 = 3 \times \frac{\text{mass}}{\text{molar mass}} = \frac{3 \times 100}{315 + 104n}$$

$$n = \mathbf{19}$$

47. On passing through charcoal only CO_2 reduces to CO.

$$CO + C \longrightarrow \text{No reaction}$$

Volume a

$$CO_2 + C \longrightarrow 2CO$$

	CO_2	$2CO$
Volume before reaction	b	0
Volume after reaction	0	$2b$

As given $a + b = 1$ and $a + 2b = 1.4$

$\therefore$ $b = \mathbf{0.4\ litre}$ $\therefore$ % of $b = \frac{0.4}{1} \times 100 = \mathbf{40\%}$

$\therefore$ $a = \mathbf{0.6\ litre}$ $\therefore$ % of $a = \frac{0.6}{1} \times 100 = \mathbf{60\%}$

48.

$$CO_2 + C \longrightarrow 2CO$$

	CO_2	$2CO$
Initial volume	1	0
Final volume	$(1-a)$	$2a$

Given $1 - a + 2a = 1.4$

$$\therefore \qquad a = 0.4 \text{ litre}$$

$$\therefore \qquad CO_2 = 1 - 0.4 = \mathbf{0.6\ litre}$$

and $CO = 2 \times 0.4 = \mathbf{0.8\ litre}$

49. Let formula of hydrocarbon be C_aH_b

$$\therefore \qquad C_aH_b + \left[a + \frac{b}{4}\right] O_2 \longrightarrow aCO_2 + \frac{b}{2} H_2O(l)$$

	C_aH_b	O_2	aCO_2	$H_2O(l)$
Volume taken	5 mL	30 mL	0	—
Volume left	0	$30 - 5\left[a + \frac{b}{4}\right]$	$5a$	—

Also given

Volume absorbed by NaOH is of CO_2 formed = 10 mL

Volume absorbed by pyrogallol is of O_2 left = 15 mL

Volume of O_2 used = 30 − 15 = 15 mL

$\therefore$ $5a = 10$ or $a = 2$

$\therefore$ $5\left(a+\frac{b}{4}\right) = 15$ or $5\left(2+\frac{b}{4}\right) = 15$

$\therefore$ $b = 4$

$\therefore$ Hydrocarbon is $\mathbf{C_2H_4}$.

50.

$$\begin{array}{lccc} & 2SO_2 & + \quad O_2 & \longrightarrow \quad 2SO_3 \\ \text{Initial mole} & 10 & 15 & 0 \\ \text{Final mole} & (10-2x) & (15-x) & 2x \end{array}$$

Given $2x = 8$

$\therefore$ $x = 4$

$\therefore$ Mole of SO_2 left $= 10 - 2\times 4 = \mathbf{2}$

Mole of O_2 left $= 15 - 4 = \mathbf{11}$

51. Let a mL CO, b mL CH_4 and c mL N_2 be present in mixture, Then

$$a+b+c = 20 \qquad ...(1)$$

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2$$

$\because$ Volume of CO $= a$; $\therefore$ Volume of $CO_2 = a$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O(l)$$

$\because$ Volume of $CH_4 = b$; $\therefore$ Volume of $CO_2 = b$

$$N_2 + O_2 \longrightarrow \text{No reaction}$$

Volume of CO_2 formed = Volume absorbed by KOH

$$a+b = 14 \text{ mL} \qquad ...(2)$$

Now Initial volume of CO + CH_4 + N_2 + vol. of O_2 taken − volume of CO_2 formed − volume of N_2 − volume of O_2 left = 13 (the contraction)

$\therefore a+b+c+$ vol O_2 taken − vol. of O_2 left − (a + b) − c = 13

$\therefore$ Vol. of O_2 used = 13

$$\therefore \quad \frac{a}{2} + 2b = 13 \qquad ...(3)$$

$$\left(\because \text{volume of } O_2 \text{ used} = \frac{a}{2} + 2b\right)$$

Solving Eqs. (1), (2) and (3), we get

$\mathbf{a = 10}$ **mL;** $\mathbf{b = 4}$ **mL;** $\mathbf{c = 6}$ **mL**

52. Let formula of ammonia be N_aH_b

$$\begin{array}{lccc} & N_aH_b & \rightleftharpoons \frac{a}{2}N_2 & + \quad \frac{b}{2}H_2 \\ \text{Initial volume} & 50 & 0 & 0 \\ \text{Final volume} & (50-x) & \frac{a\cdot x}{2} & \frac{b\cdot x}{2} \end{array}$$

$$\therefore \quad (50-x) + \frac{ax}{2} + \frac{bx}{2} = 97$$

Washing of gas dissolves NH_3 and therefore, since washing reduces the volume by 3 mL, thus

$$50 - x = 3$$

$$\therefore \quad x = 47 \text{ mL}$$

Thus, $N_2 = \frac{47a}{2}$ mL; $H_2 = \frac{47b}{2}$ mL

Also, $\frac{47a}{2} + \frac{47b}{2} = 94$

$$\therefore \quad a+b = 4 \qquad ...(1)$$

Also,

$$\begin{array}{ccc} H_2 & + \quad \frac{1}{2}O_2 & \longrightarrow H_2O \\ \frac{47b}{2} & 60.5 & (H_2 \text{ is completely oxidized}) \\ 0 & \left(60.5 - \frac{47b}{4}\right) & \end{array}$$

$\therefore$ Residual gases after combustion $= N_2 + O_2$ left

$$48.75 = \frac{47a}{2} + 60.5 - \frac{47b}{4} \qquad ...(2)$$

By Eqs. (1) and (2), $a = 1$ and $b = 3$

$\therefore$ Formula is $\mathbf{NH_3}$

53.

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O(l)$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O(l)$$

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2$$

Let a mL, b mL and c mL be volumes of C_3H_8, CH_4 and CO respectively in 100 mL given sample, then

$$a+b+c = 100$$

and $a = 36.5$

Now CO_2 is formed as a result of combustion of mixture.

$\therefore$ Vol. of CO_2 formed

$$= 3a+b+c \begin{pmatrix} \because 1 \text{ vol. } C_3H_8 \text{ gives 3 vol. } CO_2 \\ 1 \text{ vol. } CH_4 \text{ gives 1 vol. } CO_2 \\ 1 \text{ vol. CO gives 1 vol. } CO_2 \end{pmatrix}$$

$$= 3\times 36.5 + (100-36.5) = \mathbf{173 \text{ mL}}$$

54. Tin is converted into sulphide and hydrogen is left, this gas contains H and S say H_aS_b

$$H_aS_b + bSn \longrightarrow bSnS + \frac{a}{2}H_2 \xrightarrow{CuO} \frac{a}{2}H_2O$$

The reaction suggests that

$\because$ Mole of H_2 : mole of H_2O formed :: 1 : 1

and Mole of H_aS_b : mole of H_2 :: 1 : $a/2$

$$\therefore \quad \frac{100}{22400} = \frac{0.081}{18} \times \frac{2}{a}$$

$$\therefore \quad a = 2$$

$\because$ Molar mass of H_aS_b = V.D. × 2 = 17 × 2 = 34

$$\therefore \quad 1\times a + 32\times b = 34$$

$$1\times 2 + 32\times b = 34$$

$$\therefore \quad b = 1$$

Thus gas is $\mathbf{H_2S}$.

55. Let formula of alkane be C_nH_{2n+2}

$$C_nH_{2n+2} + \left[n + \frac{n+1}{2}\right]O_2 \longrightarrow nCO_2 + (n+1)H_2O(l)$$

Given $\frac{\text{Volume of } O_2 \text{ used}}{\text{Volume of } CO_2 \text{ formed}} = \frac{7}{4}$

$$\therefore \quad \frac{n + (n+1)/2}{n} = \frac{7}{4}$$

$$\therefore \quad n = 2$$

$\therefore$ Alkane is $\mathbf{C_2H_6}$.

56. Let formula of ammonia be N_aH_b

$$N_aH_b \longrightarrow \frac{a}{2}N_2 + \frac{b}{2}H_2$$

Volume before reaction	40	0	0
Volume after reaction	0	$20a$	$20b$

$\therefore$ $20a+20b=40+40=80$

($\because$ an increase in volume occurs by 40 mL)

or $a+b=4$ ...(1)

Now 40 mL O_2 is added,

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O(l)$$

Volume before combination	$20b$	40
Volume after combination	0	$\left(40-\frac{20b}{2}\right)$

Gases left after the end of reaction = 30 mL

$\therefore$ Volume of O_2 left + Volume of N_2 left = 30 mL

$40-10b+20a=30$

$\therefore$ $b-2a=1$ ...(2)

By Eqs. (1) and (2) $a=1$ and $b=3$

$\therefore$ Molecular formula of ammonia is $\mathbf{NH_3}$.

57. Volume absorbed by terpentine oil = 10 mL

$\therefore$ Volume of ozone = 10 mL (terpentine oil absorbs O_3)

$\therefore$ Volume of $O_2 = 100-10=90$

Molar mass of ozonised oxygen

$$=\frac{WRT}{PV}=\frac{1.5\times 0.0821\times 273}{1\times 1}=33.62$$

Volume or mole ratio of O_2 and O_3 is 900 : 100

$\therefore$ Molar mass of ozonised oxygen $=\frac{900\times 32+100\times a}{1000}$

or $33.62=\frac{900\times 32+100\times a}{1000}$ or $a=48.2$

$\therefore$ molar mass of ozone = **48.2**

58. Let the volume of NO and N_2O be a and b mL respectively, then,

$a+b=60$ ...(1)

$$NO + N_2O + H_2 \longrightarrow \frac{3}{2}N_2 + H_2O(l)$$

Volume before reaction	a mL	b m L	excess	0	0
Volume after reaction	0	0		38 mL	

$\because$ 1 mole or 1 vol. NO gives $\frac{1}{2}$ vol. N_2

and 1 mole or 1 vol. N_2O gives 1 vol. N_2

$\therefore$ $\frac{a}{2}+b=38$ ...(2)

By Eqs. (1) and (2), $\mathbf{a=44}$ **mL**

$\mathbf{b=16}$ **mL**

59.

$$nO_2 \longrightarrow 2O_n$$

Volume before reaction	50 mL	0
Volume after reaction	$(50-a)$ mL	$\frac{2a}{n}$ mL

(Let a mL of O_2 forms O_n)

$\therefore$ Volume of O_2 left $=(50-a)$

or $41=50-a$

$\therefore$ $a=9$

Also Volume of O_3 formed $=47-41=6$ mL

$\therefore$ $\frac{2a}{n}=6$ or $n=3$

$\therefore$ Molecular formula of ozone is $\mathbf{O_3}$.

60. Formula of hydrocarbon be C_aH_b

$\therefore$ $C_aH_b+\left(a+\frac{b}{4}\right)O_2 \longrightarrow aCO_2+\frac{b}{2}H_2O(l)$

$\because$ 22.4 litre C_aH_b gives $44a$ g CO_2

$\therefore$ 1.12 litre C_aH_b gives $=\frac{44a\times 1.12}{22.4}$ g CO_2

$\therefore$ $\frac{44a\times 1.12}{22.4}=2.2$

$\therefore$ $a=1$

$\because$ 22.4 litre or 1 mole C_aH_b gives $\frac{b}{2}\times 18$ g H_2O

$\therefore$ 1.12 litre C_aH_b gives $\frac{b}{2}\times\frac{18\times 1.12}{22.4}$ g H_2O

$\therefore$ $\frac{b\times 18\times 1.12}{2\times 22.4}=1.8$

$b=4$

$\therefore$ Hydrocarbon is $\mathbf{CH_4}$

$\therefore$ Mass of 1.12 litre CH_4 at NTP $=\frac{16\times 1.12}{22.4}=\mathbf{0.8\ g}$

Also, volume of O_2 used in combustion for 22.4 litre CH_4

$$=a+\frac{b}{4}=1+1=2\text{ mole}$$

$\because$ 22.4 litre CH_4 requires 2 mole O_2 or 2×22.4 litre O_2

$\therefore$ 1.12 litre CH_4 requires 2 mole O_2

$$=\frac{2\times 22.4\times 1.12}{22.4}=\mathbf{2.24\ litre\ O_2}$$

61. $C_nH_{3n}O_m+\left(n+\frac{3n}{4}-\frac{m}{2}\right)O_2 \longrightarrow nCO_2+\frac{3n}{2}H_2O(l)$

Volume taken	16	60	0	0
Volume left	—	$60-16\left(n+\frac{3n}{4}-\frac{m}{2}\right)$	$16n$	—

$\therefore$ Volume of $CO_2=16n$ = volume absorbed by KOH

$16n=44-12=32$

$\therefore$ $n=2$

Volume of O_2 left = 12

$\therefore$ Volume of O_2 used $=60-12=48$

$16\left(n+\frac{3n}{4}-\frac{m}{2}\right)=48$ $\because$ $m=1$

$\therefore$ Formula of Compound = $\mathbf{C_2H_6O}$

62. Mole of CO_2 formed $=\frac{14.5}{44}=0.330$

$$\underset{a\text{ mole}}{CH_4} + 2O_2 \longrightarrow CO_2+2H_2O;$$

$$\underset{b\text{ mole}}{C_2H_4} + 3O_2 \longrightarrow 2CO_2+2H_2O$$

$\therefore$ CO_2 formed $=a+2b=0.330$ ...(1)

Also $a\times 16+b\times 28=5.0$ ...(2)

By Eqs. (1) and (2) $b=0.07$

$a=0.19$

$\therefore$ $w_{CH_4}=0.19\times 16=3.04$

$$w_{C_2H_4} = 0.07 \times 28 = 1.96$$

$$\therefore \quad \%C_2H_4 = \frac{1.96}{5} \times 100 = \mathbf{39.2}$$

$$\%CH_4 = \frac{3.04}{5} \times 100 = \mathbf{60.8}$$

63.	C_3H_8	+	$\frac{7}{2}O_2 \longrightarrow$	$3CO$	+ $4H_2O(l)$
Mole before reaction	$\frac{4}{44}$		$\frac{14}{32}$		
Mole after reaction	0		$\left(\frac{14}{32} - \frac{4}{44} \times \frac{7}{2}\right)$	$\frac{3 \times 4}{44}$	

$$\therefore \quad \text{Mole of CO formed} = \frac{3 \times 4}{44}$$

$$\therefore \quad \text{Mass of CO formed} = \frac{3 \times 4}{44} \times 28\,\text{g} = \mathbf{7.636\ g}$$

64. For spherical shape of nucleus, since whole mass of atom is in nucleus and therefore,

$$\text{Mass of one nucleus} = \text{Volume of nucleus} \times \text{density}$$

$$\frac{\text{Atomic mass}}{\text{Avogadro's no.}} = \frac{4}{3}\pi r^3 \times d$$

For F nucleus

$$\therefore \quad \frac{19}{6.023 \times 10^{23}} = \frac{4}{3}\pi(5 \times 10^{-13})^3 \times d$$

$$\therefore \quad d = \mathbf{6.02 \times 10^{13}\ g\ mL^{-1}}$$

65.
$$\frac{\text{Atomic mass}}{\text{Av. No.}} = \text{volume of atom} \times \text{density}$$

$$\frac{54.94}{6.023 \times 10^{23}} = \frac{4}{3}\pi r^3 \times 7.42$$

$$\therefore \quad r = \mathbf{1.432 \times 10^{-8}\ cm}$$

and $\text{Volume} = \frac{4}{3}\pi r^3 = \mathbf{1.23 \times 10^{-23}\ cm^3}$

66. Let Al, Mg and Cu be a, b, c g respectively.

$$2Al + 2NaOH \xrightarrow{2H_2O} 2NaAlO_2 + 3H_2$$

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$

$$Cu + HCl \longrightarrow \text{No reaction}$$

i.e., only Al reacts with NaOH and then only Mg reacts with HCl

$\therefore \quad a + b + c = 8.72$

$b + c = 2.10$ (Residue left after alkali treatment)

$c = 0.69$ (Residue left after acid treatment)

$\therefore \quad b = 1.41\text{g}$

and $\quad a = 6.62\text{g}$

$$\therefore \quad \%\text{ of Al} = \frac{6.62}{8.72} \times 100 = \mathbf{75.9}$$

$$\%\text{ of Mg} = \frac{1.41}{8.72} \times 100 = \mathbf{16.2}$$

$$\%\text{ of Cu} = \frac{0.69}{8.72} \times 100 = \mathbf{7.9}$$

67. The reaction,

$$CaO + Ca(HCO_3)_2 \longrightarrow 2CaCO_3 + H_2O$$

$\because$ Eq. of $Ca(HCO_3)_2$ present in hard water (1 litre)

$$\frac{1.62}{162/2} = 0.02$$

$\therefore$ Eq. of CaO required to remove $Ca(HCO_3)_2$ in 1 litre $= 0.02$

$\therefore$ Eq. of CaO required to remove $Ca(HCO_3)_2$ in 10^6 litre $= 0.02 \times 10^6$

$\therefore$ Mass of $CaO = 0.02 \times 10^6 \times \frac{56}{2}\,\text{g} = \mathbf{5.6 \times 10^5\ g}$

68. $\text{mM of } MgCl_2 = \frac{1 \times 10^{-3} \times 10^3}{95} = \frac{1}{95}$

$$\left(\text{milli mole} = \frac{\text{mass}}{\text{Molar mass}} \times 1000\right)$$

$\text{mM of } CaCl_2 = \frac{1 \times 10^{-3} \times 10^3}{111} = \frac{1}{111}$

$\therefore$ mM of $CaCO_3$ if $MgCl_2$ and $CaCl_2$ are taken in form of $CaCO_3$

$$= \frac{1}{95} + \frac{1}{111} = \frac{106}{111 \times 95}$$

($\because$ Ca, Mg are both bivalent $\therefore$ mole ratio is 1 : 1)

$\therefore$ Mass of $CaCO_3$ in 1000 mL $= \frac{206}{111 \times 95} \times \frac{100}{1000}$ g

$\therefore$ Hardness in ppm (part per million)

$$= \frac{\text{g of } CaCO_3}{10^6 \text{ g of } H_2O} = \frac{206 \times 100 \times 10^6}{111 \times 95 \times 1000 \times 1000} = \mathbf{1.953}$$

$\therefore$ **Hardness = 1.953 ppm**

69.
$$M \xrightarrow{HNO_3} M(NO_3)_n \xrightarrow{\Delta} M_2O_n$$

where n is valency of metal

$\therefore$ Eq. of metal = Eq. of nitrate = Eq. of metal oxide = Eq. of oxygen

$$\frac{w_{\text{metal}}}{E_{\text{metal}}} = \frac{w_{\text{oxygen}}}{E_{\text{oxygen}}}$$

$$\frac{1.60}{E} = \frac{2 - 1.6}{8}$$

$$\therefore \quad E = \mathbf{32}$$

70.
$$M(NO_3)_n \longrightarrow M_2(SO_4)_n$$

$\therefore$ Eq. of $M(NO_3)_n$ = Eq. of $M_2(SO_4)_n$

$$\frac{1}{\frac{a}{n} + \frac{62}{1}} = \frac{0.86}{\frac{a}{n} + \frac{96}{2}}$$

where, a is atomic mass of metal and n is its valency

$$\therefore \quad \frac{a}{n} = E$$

$$\frac{1}{E + 62} = \frac{0.86}{E + 48}$$

$$\therefore \quad E = \mathbf{38}$$

71. Let Eq. mass of Ca be E

$$Ca + \frac{1}{2}O_2 \longrightarrow CaO$$

Equivalent of Ca = Equivalent of CaO

$$\frac{1.35}{E} = \frac{1.88}{E + 8}$$

$\therefore$ Eq. mass of Ca = 20.375

$\therefore$ atomic mass of Ca $= 20.375 \times 2 = \mathbf{40.75}$

72. Atomic mass × specific heat = 6.4

$$a \times 0.057 = 6.4$$

$$a = 112.28$$

Now Equivalent of metal = Equivalent of metal sulphate

$$\frac{2}{E} = \frac{4.51}{E+48} \quad (\because \text{Eq. mass of } SO_4^{-2} = 48)$$

$\therefore \quad E = 38.24$

$\therefore$ Valency of metal $= \frac{\text{Atomic mass}}{\text{Eq. mass}} = \frac{112.28}{38.24} = 2.93$

$\approx 3 \quad (\because$ Valency is integer)

$\therefore$ Exact atomic mass of metal = Eq. mass × Valency

$= 38.24 \times 3 = \mathbf{114.72}$

73. $MBr_x + xHCl \longrightarrow MCl_x + xHBr$

Mass of $MBr_x = 1.878\,g$

Mass of $MCl_x = 1.0\,g$

For the reaction, Equivalent of MBr_x = Equivalent of MCl_x

$$\frac{1.878}{E+80} = \frac{1.0}{E+35.5}$$

$\therefore \quad E = 15.18$

$\because$ atomic mass × sp. heat = 6.4

$\therefore$ atomic mass of metal $M = \frac{6.4}{0.14} = 45.71$

$\therefore$ Valency of metal $= \frac{\text{Atomic mass}}{\text{Eq. mass}} = \frac{45.71}{15.18} \approx 3.01 = 3$

(integer)

$\therefore$ Exact atomic mass of metal $= 15.18 \times 3 = 45.54$

$\therefore$ Molar mass of $MBr_x = 45.54 + 80 \times 3 = \mathbf{285.54}$

74. Let hydrated sulphate be $M_2(SO_4)_n \cdot mH_2O$

where n is valency of metal

Also, atomic mass × specific heat = 6.4

$\therefore$ atomic mass of metal $= \frac{6.4}{0.24} = 26.67$

Now, Eq. of metal = Equivalent of SO_4^{-2}

$$\frac{8.1}{a/n} = \frac{43.2}{96/2}$$

$$\therefore \quad n = \frac{43.2 \times 2 \times a}{96 \times 8.1} = \frac{43.2 \times 2 \times 26.67}{96 \times 8.1} = 2.96$$

$$n \approx 3$$

$\therefore$ Exact atomic mass of metal $= 9 \times 3 = 27$

$$M_2(SO_4)_3 \cdot mH_2O$$

$\therefore$ M. mass $= 2 \times 27 + 96 \times 3 + 18m = 342 + 18m$

$\because$ $(342 + 18m)$g $M_2(SO_4)_3 \cdot mH_2O$ has $18m$ g H_2O

$\therefore$ 100 g $M_2(SO_4)_3 \cdot mH_2O$ has $= \frac{18m \times 100}{342 + 18m}$ g H_2O

$\therefore \quad \frac{18m \times 100}{342 + 18m} = \%$ of $H_2O = 100 - 8.1 - 43.2 = 48.7$

$\therefore \quad m = 18$

$\therefore$ **Formula of hydrated sulphate $M_2(SO_4)_3 \cdot 18H_2O$**

Since, metal has atomic mass 27, it will be Al. Thus, sulphate is $Al_2(SO_4)_3 \cdot 18H_2O$.

75. Meq. of $Ca(OH)_2 = \frac{w}{E} \times 1000 = \frac{74}{74/2} \times 1000 = \mathbf{2000}$

Meq. of NaOH $= \frac{20}{40} \times 1000 = \mathbf{500} \quad (\because E_{NaOH} = 40)$

Meq. of $H_2SO_4 = \frac{2.45}{49} \times 1000 = \mathbf{50} \quad (\because E_{H_2SO_4} = 49)$

76. $\because \quad$ Meq. $= \frac{W}{E} \times 1000$

$\therefore \quad 50 = \frac{w}{40} \times 1000$

$\therefore \quad w = \mathbf{2\ g}$

77. $\because \quad N \times V$ (in l) = Equivalent

$\therefore \quad N \times 2 = \frac{50}{1000}$

$\therefore \quad N = \mathbf{0.025}$

78. $Na_2CO_3 \xrightarrow{CaCl_2} CaCO_3$

Meq. of Na_2CO_3 = Meq. of $CaCO_3$

$$\frac{w}{106/2} \times 1000 = \frac{1.0362 \times 1000}{100/2}$$

$\therefore \quad w_{Na_2CO_3} = 1.0984\,g$

$\therefore \quad \%$ purity $= \frac{1.0984}{1.2048} \times 100 = \mathbf{91.16\%}$

79. (a) $\because$ Eq. of $Ca(OH)_2 = \frac{0.74}{74/2} \quad \left(\text{Eq.} = \frac{w}{E}\right)$

Volume of solution = 5/1000 litre

$$\therefore \quad N = \frac{0.74 \times 1000 \times 2}{74 \times 5}$$

$$N = \mathbf{4} \quad \therefore \quad M = \frac{N}{\text{Valency}} = \frac{4}{2} = \mathbf{2}$$

(b) $\because$ Eq. of HCl $= \frac{3.65}{36.5}$

and Volume of solution = 200/1000 litre

$$\therefore \quad N = \frac{3.65 \times 1000}{36.5 \times 200} = \mathbf{0.5}$$

$$\text{and} \quad M = \frac{N}{\text{Valency}} = \frac{0.5}{1} = \mathbf{0.5}$$

(c) Eq. of $H_2SO_4 = \frac{1}{10} \times 2 \quad (\because$ Eq. = mole × valency)

Volume of solution = 500/1000 litre

$$\therefore \quad N = \frac{2 \times 1000}{10 \times 500} = \mathbf{0.4} \quad \text{and} \quad M = \frac{0.4}{2} = \mathbf{0.2}$$

80. Meq. of $H_2SO_4 = 0.2 \times 1200 \quad (\because$ Meq. $= N \times V$ in mL)

$\therefore \quad \frac{w}{49} \times 1000 = 240$

$\therefore \quad w = \mathbf{11.76\ g}$

81.

$$\underset{\text{Base}}{6CaO} + \underset{\text{Acid}}{P_4O_{10}} \longrightarrow \underset{\text{Salt}}{2Ca_3(PO_4)_2}$$

Mole ratio of reactant $= \frac{CaO}{P_4O_{10}} = \frac{6}{1}$

Molar mass of $P_4O_{10} = 284$

$\therefore$ Mole of CaO required $= 6 \times$ mole of $P_4O_{10} = 6 \times \frac{852}{284}$

$\therefore$ Mass of CaO required $= \frac{6 \times 852}{284} \times 56 = \mathbf{1008\ g}$

82. $\because \quad$ Meq. of Na_2CO_3 = Meq. of H_2SO_4

(for complete neutralization)

Meq. of $Na_2CO_3 = 45.6 \times 0.235$

$\therefore \quad \frac{w}{106/2} \times 1000 = 45.6 \times 0.235$

$\therefore \quad w = 0.5679\,g$

$\because$ 95 g pure Na_2CO_3 is to be taken then weighed sample $= 100\,g$

$\therefore$ 0.5679 g pure Na_2CO_3 is to be taken, weighed sample

$$= \frac{100 \times 0.5679}{95} = \mathbf{0.5978\ g}$$

83. Meq. of H_2SO_4 = Meq. of $CuCO_3$

$$\left(\text{Eq. mass of } CuCO_3 = \frac{M}{2}\right)$$

$$0.5 \times 2 \times V = \frac{0.5 \times 2 \times 1000}{123.5}$$

$$\therefore \quad V = \mathbf{8.097\ mL}$$

84. Meq. of H_2SO_4 = Meq. of NaOH $(\because \text{Meq.} = N \times V \text{ in mL})$

$$N \times 12 = 15 \times \frac{1}{10}$$

$$N = \frac{15}{10 \times 12}$$

$$\therefore \quad \text{Strength} = \frac{15}{10 \times 12} \times 49 \qquad (\because S = N \times E)$$

$$= \mathbf{6.125\ g / litre}$$

85. Normality of acid $= \frac{39}{82 / n \times 1}$ (*n* is basicity of acid)

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

Now, Meq. of acid = Meq. of NaOH

$$\frac{39n}{82} \times 100 = 1 \times 95$$

$\therefore$ $n = 2$; *i.e.*, acid is dibasic.

86. $\because$ Meq. of solute does not change on dilution

Meq. of H_2SO_4 (conc.) = Meq. of H_2SO_4 (dil.)

$$0.1 \times 0.1 = N \times 1000$$

$$(\because \text{Meq.} = N \times V \text{ in mL})$$

$$n = \mathbf{10^{-5}}$$

87. Meq. of original $H_2SO_4 = 30 \times 1 = 30$

Meq. of H_2SO_4 after passing $NH_3 = 30 \times 0.2 = 6$

$\therefore$ Meq. of H_2SO_4 lost $= 30 - 6 = 24$

$\therefore$ Meq. of NH_3 passed = Meq. of H_2SO_4 lost

$$\because \quad \frac{w}{17} \times 1000 = 24$$

$$\therefore \quad w_{NH_3} = 0.408\,g$$

$\therefore$ Volume of NH_3 at STP $= \frac{22.4 \times 0.408}{17} = 0.5376$ litre

$$= \mathbf{537.6\ mL}$$

88. For NH_3, $PV = \frac{w}{m} RT$

$$\therefore \quad \frac{w}{m} = \frac{PV}{RT} = \frac{0.2 \times 2}{0.0821 \times 303} = 0.01608$$

$\therefore$ Mole of NH_3 = Equivalent of $NH_3 = 0.01608$

$\therefore$ Meq. of $NH_3 = 16.08$

Now Meq. of H_2SO_4 = Meq. of NH_3

$$N \times 134 = 16.08$$

$$\therefore \quad N = \mathbf{0.12}$$

89.

$$Ca + \frac{1}{2}O_2 \longrightarrow CaO$$

Equivalent taken 1/20 excess

Equivalent after reaction 0 — 1/20 $(\because \text{Eq.} = w/E)$

$$\therefore \quad N_{CaO} = \frac{1}{20 \times 1} = \mathbf{0.05} \qquad \left(\because N = \frac{\text{Eq.}}{V \text{ in litre}}\right)$$

90. $\because$ Meq. of metal = Meq. of HCl

$$\frac{1.82}{E} \times 1000 = 32.5 \times 1$$

$$\therefore \quad E = \mathbf{56}$$

91. (a) Meq. of HCl $= 100 \times 0.1 = 10$

Meq. of NaOH $= 50 \times 0.25 = 12.5$

$\because$ HCl and NaOH neutralize each other with equal equivalent

Meq. of NaOH left $= 12.5 - 10 = 2.5$

Volume of new solution $= 100 + 50 = 150$ mL

$$\therefore \quad N_{NaOH} \text{ left} = \frac{2.5}{150} = \mathbf{0.0167}$$

(b) Meq. of $H_2SO_4 = 100 \times 0.2 \times 2 = 40$

$(\because N = M \times \text{Valency})$

Meq. of HCl $= 200 \times 0.2 \times 1 = 40$

$\therefore$ Total Meq. of acid $= 40 + 40 = 80$

Total volume of solution = 300 mL

$$\therefore \quad N_{\text{Acid Solution}} = \frac{80}{300} = \mathbf{0.267}$$

(c) Meq. of $H_2SO_4 = 100 \times 0.2 \times 2 = 40$

Meq. of NaOH $= 100 \times 0.2 \times 1 = 20$

$\therefore$ Meq. of H_2SO_4 left after reaction $= 40 - 20 = 20$

Total volume of solution $= 100 + 100 = 200$ mL

$$\therefore \quad N_{H_2SO_4} \text{ left} = \frac{20}{200} = \mathbf{0.1}$$

(d) Meq. of NaOH $= 1 \times 1000 = 1000$

Meq. of HCl $= 100 \times 0.1 = 10$

$\therefore$ Meq. of NaOH left after reaction $= 1000 - 10 = 990$

Total volume of solution = 100 mL

$$\therefore \quad N_{NaOH} \text{ left} = \frac{990}{100} = \mathbf{9.9}$$

92. Let V_1 mL of $NaNO_3$ is mixed with V_2 mL of $Ca(NO_3)_2$

mM of $NaNO_3$ mixed $= 0.2 \times V_1$

mM of $Ca(NO_3)_2$ mixed $= 0.1 \times V_2$

$\because$ Mole ratio of $Ca^{2+} : NO_3^-$ in $Ca(NO_3)_2$ is 1 : 2

$\therefore$ Molarity of NO_3^- in mixture

$$= [NO_3^-] \text{ of } NaNO_3 + [NO_3^-] \text{ of } Ca(NO_3)_2$$

$$= \frac{0.2 \times V_1}{(V_1 + V_2)} + \frac{0.1 \times 2 \times V_2}{(V_1 + V_2)}$$

$$= \frac{(0.2V_1 + 0.2V_2)}{V_1 + V_2}$$

Similarly, Molarity of Na^+ and Ca^{2+} in mixture

$$= \frac{0.2 \times V_1}{V_1 + V_2} + \frac{0.1 \times V_2}{V_1 + V_2}$$

$$=\frac{(0.2V_1+0.1V_2)}{(V_1+V_2)}$$

Now, given that, Molarity of NO_3^-

$$=\frac{3}{2}\text{Molarity of } Na^+ \text{ and } Ca^{2+}$$

$$\therefore \quad \frac{0.2V_1+0.2V_2}{(V_1+V_2)}=\frac{3}{2}\left[\frac{(0.2V_1+0.1V_2)}{(V_1+V_2)}\right]$$

$$\therefore \quad \frac{V_1}{V_2}=\frac{\mathbf{1}}{\mathbf{2}}$$

93. $\because$ 15 Meq. of each separately react with KOH and therefore only 15 Meq. of KOH are required every time.

$\therefore$ Meq. of KOH required = 15

$$\frac{w}{56}\times1000=15$$

$$\therefore \quad w=\mathbf{0.84\ g}$$

94. Meq. of conc. solution $=1600\times0.2050=328$

Let after dilution volume becomes V mL

Meq. of dil. solution $=0.20\times V$

$$\therefore \quad 328=0.20\times V$$

$$\therefore \quad V=1640\text{ mL}$$

Thus, volume of water used to preapare 1640 mL of 0.20N solution

$$=1640-1600=\mathbf{40\ mL}$$

95. $w=12\text{ g } BaCl_2$; $W=100\text{ g}$ solution

$\therefore$ **For 50 g solution:** $w_{BaCl_2}=6\text{g}$; $W_{\text{solution}}=50\text{g}$

$$\therefore \quad w_{BaCl_2\cdot2H_2O}=\frac{6\times244}{208}=\mathbf{7.038\ g}$$

$$\therefore \quad w_{H_2O}=50-7.038=\mathbf{42.962\ g}$$

96.

$$Na+H_2O\longrightarrow NaOH+\frac{1}{2}H_2$$

$$NaOH+HCl\longrightarrow NaCl+H_2O$$

Thus, Meq. of Na = Meq. of NaOH formed = Meq. of HCl used

$$\frac{0.46}{23}\times1000=\frac{73}{36.5}\times V \quad (\text{Meq. of HCl}=N\times V)$$

$$\therefore \quad V=\mathbf{10\ mL}$$

97.

	$Al_2(SO_4)_3$ +	$BaCl_2$ ⟶	$BaSO_4\downarrow$ +	$AlCl_3$
Meq. before mixing	$20\times0.2\times6$ $=24$	$20\times0.6\times2$ $=24$	0	0
Meq. after mixing	0	0	24	24

(Meq.$=N\times V$ in mL $=M\times$ valency $\times V$ in mL)

$$\therefore \quad [Al^{3+}]=\frac{24}{40\times3}=\mathbf{0.2}\ M$$

$$[Cl^-]=\frac{24}{40}=\mathbf{0.6}\ M$$

No concentration of Ba^{2+} or SO_4^{2-} in solution since $BaSO_4$ gets precipitated.

98. The reaction shows two H atoms replaced from H_3PO_4

$\therefore$ Basicity of $H_3PO_4=2$

$$\therefore \quad \text{Eq. mass } H_3PO_4=\frac{M}{2}=\frac{98}{2}=\mathbf{49}$$

99. 1 mole of $H_2S\equiv5$ mole of H_2SO_4

$$\therefore \quad \frac{34}{34}=1\text{ mole of } H_2S\equiv5\text{ mole of } H_2SO_4$$

$$\therefore \quad 0.20\times V=5$$

$$\therefore \quad V=\frac{5}{0.20}=\mathbf{25\ litre}$$

100.

	$AgNO_3$ +	HCl ⟶	$AgCl$ +	HNO_3
Meq. mixed	$\frac{1.7}{170}\times1000$ $=10$	200×5 $=1000$	0	0
Meq. after reaction	0	990	10	10

$\therefore$ Meq. of AgCl formed = 10

$$\therefore \quad \frac{w}{143.5}\times1000=10$$

$$\therefore \quad w_{AgCl}=\mathbf{1.435\ g}$$

101.

	$AgNO_3$ +	$NaCl$ ⟶	$AgCl$ +	$NaNO_3$
Meq. mixed	$\frac{5.77}{170}\times1000$ $=33.94$	$\frac{4.77}{58.5}\times1000$ $=81.54$	0	0
Meq. left	0	47.60	33.94	33.94

$\therefore$ Meq. of AgCl formed = 33.94

$$\frac{w}{143.5}\times1000=33.94$$

$$\therefore \quad w_{AgCl}=\mathbf{4.87\ g}$$

102.

$$N_{NaCl}=\frac{3.78}{58.5\times100/1000}=0.646 \quad \left(\because N=\frac{\text{Eq.}}{V\text{ in litre}}\right)$$

Let w g of $BaCl_2$ is dissolved in 250 mL then

$$N_{BaCl_2}=\frac{w}{\frac{208}{2}\times\frac{250}{1000}}=0.0385w$$

$\therefore$ $[Cl^-]$ in both is same.

$$\therefore \quad N_{NaCl}=N_{BaCl_2}$$

$$\therefore \quad 0.646=0.0385w$$

$$\therefore \quad w=\mathbf{16.80\ g}$$

103. Given,

	$3Pb(NO_3)_2$ +	$Cr_2(SO_4)_3$ ⟶	$3PbSO_4\downarrow$ +	$2Cr(NO_3)_3$
Meq. before reaction	$45\times0.25\times2$ $=22.5$	$25\times0.1\times6$ $=15$	0	0
Meq. after reaction	7.5	0	15	15

$\therefore$ Meq. of $PbSO_4$ precipitated = 15

$\therefore$ mM of $PbSO_4$ precipitated $=\frac{15}{2}$

$\therefore$ Mole of $PbSO_4$ precipitated $=\frac{15}{2}\times\frac{1}{1000}=\mathbf{0.0075}$

$$\because \quad [\text{Normality}]=\frac{\text{Meq.}}{\text{total volume}\times\text{valency}}$$

Also,

$$[Pb^{2+}]=\frac{7.5}{70\times2}=\mathbf{0.0536}\ M$$

$$[NO_3^-]=\frac{7.5+15}{70\times1}=\mathbf{0.32}\ M$$

$$[Cr^{3+}]=\frac{15}{70\times3}=\mathbf{0.0714}\ M$$

104. Meq. of $Na_2CO_3 \cdot H_2O = \frac{0.62}{62} \times 1000$ $\left(\frac{w}{E} \times 1000 = \text{Meq.}\right)$

$= 10$

Meq. of $H_2SO_4 = 100 \times 0.1 = 10$

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2 \uparrow$$

Meq. added	10	10	0	0	0
Meq. left	0	0	10	10	10

$\therefore$ $N_{Na_2SO_4} = \frac{10}{100} = \mathbf{0.1}$

Solution becomes neutral since both acid and base are used up and Na_2SO_4 does not show hydrolysis.

105. Mass of Ag $= \frac{90 \times 0.5}{100} = 0.45$

$\therefore$ Meq. of Ag $= \frac{0.45}{108} \times 1000 = 4.17$

Now, $Ag \xrightarrow{HNO_3} AgNO_3 \xrightarrow{KCNS} AgCNS$

$\because$ Equal Meq. reacts and therefore,

Meq. of KCNS = Meq. of $AgNO_3$

= Meq. of HNO_3 = Meq. of Ag

$\therefore$ $N \times 25 = 4.17$

$\therefore$ $N = \mathbf{0.167}$

106. Meq. of H_2SO_4 = Meq. of NaOH

$N \times 5 = 84.6 \times 2$

$\therefore$ $N = \frac{84.6 \times 2}{5} = 33.84$ eq. litre^{-1}

$\therefore$ Mass of H_2SO_4 in 1 litre $= 33.84 \times 49$

$\therefore$ Density or mass of H_2SO_4 in 1 mL

$= \frac{33.84 \times 49}{1000} = 1.658$ g / mL

$\therefore$ Purity $= \frac{1.658}{1.8} \times 100 = \mathbf{92.12\%}$

107. H_2SO_4 is 86% by mass.

$\therefore$ Mass of $H_2SO_4 = 86$g

Mass of solution = 100g

$\therefore$ Volume of solution $= \frac{100}{1.787}$ mL $= \frac{100}{1.787 \times 1000}$ litre

$\therefore$ $M_{H_2SO_4} = \frac{86}{98 \times \frac{100}{1.787 \times 1000}} = \mathbf{15.68}$

Let V mL of this H_2SO_4 are used to prepare 1 litre of 0.2M H_2SO_4

$\therefore$ mM of H_2SO_4 conc. = mM of H_2SO_4 dilute

$V \times 15.68 = 1000 \times 0.2$

$\therefore$ $V = \mathbf{12.75\ mL}$

108. Given, Mass of Al = 2.7 g

$\therefore$ Equivalent of Al $= \frac{2.7}{9} = 0.3$

$\therefore$ Meq. of Al $= 0.3 \times 1000 = 300$

For H_2SO_4 given that solution is 24.7% by mass

$\therefore$ Mass of $H_2SO_4 = 24.7$ g

and Mass of solution = 100 g

$\therefore$ Volume of solution $= \frac{100}{1.18}$ mL = 84.75 mL

$N_{H_2SO_4} = \frac{24.7}{49 \times \frac{100}{1.18 \times 1000}} = 5.95$

Now, Meq. of H_2SO_4 in 75 mL $5.95 \times 75 = 446.25$

and Meq. of Al added = 300

$\therefore$ Meq. of H_2SO_4 left after reaction

$= 446.25 - 300 = 146.25$

$\because$ Solution is diluted to 400 mL

$\therefore$ $N_{H_2SO_4}$ left $= \frac{146.25}{400} = \mathbf{0.367}$

$\therefore$ $M_{H_2SO_4}$ left $= \frac{0.367}{2} = \mathbf{0.183}$

109. KOH solution is 30% by mass.

$\therefore$ Mass of KOH = 30 g

and Mass of solution = 100 g

$\therefore$ Volume of solution $= \frac{100}{d}$

(where d is density of solution)

$\therefore$ Molarity $= 6.90 = \frac{30}{56 \times \frac{100}{1000 \times d}}$

$d = \mathbf{1.288\ g\ mL^{-1}}$

110. Given mole fraction of $I_2 = 0.2$

$\therefore$ $\frac{n}{n+N} = 0.2$ ...(1)

Also mole fraction of $C_6H_6 = 1 - 0.2 = 0.8$

$\therefore$ $\frac{N}{n+N} = 0.8$ ...(2)

where n and N are mole of I_2 and C_6H_6 respectively.

By Eqs. (1) and (2) $\frac{n}{N} = \frac{0.2}{0.8} = \frac{1}{4}$

or $\frac{n \times M_{C_6H_6}}{w_{C_6H_6}} = \frac{1}{4}$ or $\frac{n}{w_{C_6H_6}} = \frac{1}{4 \times 78}$

or $\frac{n}{w_{C_6H_6}} \times 1000 = \frac{1000}{4 \times 78}$

or Molality $= \frac{1000}{4 \times 78} = \mathbf{3.205}$

111. Meq. of Al = Meq. of HCl $= 12 \times 0.05 = 0.6$

$\therefore$ Mass of Al $= \frac{0.6 \times 9}{1000} = 0.0054$ g

$\therefore$ Volume of Al foil $= \frac{0.0054}{2.7}$ mL or cm^3 $= 0.002$ cm^3

Now, Area × thickness = Volume

$\therefore$ Area $= \frac{0.002}{0.01} = \mathbf{0.2\ cm^2}$

(thickness = 0.01 cm)

Note : The maximum area is possible when 0.01 cm foil of Al is completely attacked.

112. Mass of $Fe_2O_3 = \frac{0.70 \times 25}{100}$

$\therefore$ mole of $Fe_2O_3 = \frac{0.70 \times 25}{100 \times 160}$

$\therefore$ mole of $Fe^{3+} = \frac{2 \times 0.70 \times 25}{100 \times 160} = 2.1875 \times 10^{-3}$

$\therefore$ Eq. of $Fe^{3+} = 2.1875 \times 10^{-3} \times 3 = 6.5625 \times 10^{-3}$

Also, Normality of NH_3 (aq.) $= \frac{2.3 \times 0.99 \times 1000}{17 \times 100} = 1.34$

$$\text{Eq. of } NH_3 = \text{Eq. of } Fe^{3+}$$

$$1.34 \times V = 6.5625 \times 10^{-3}$$

$$\therefore \quad V = 4.9 \times 10^{-3} \text{ litre} = \mathbf{4.9\ mL}$$

113. Given, H_2SO_4 is 93% by volume.

$\therefore$ Mass of $H_2SO_4 = 93\,g$

Volume of solution $= 100\,mL$

$\therefore$ Mass of solution $= 100 \times 1.84 = 184\,g$

$\therefore$ Mass of water $= 184 - 93 = 91\,g$

$$\therefore \quad \text{Molality} = \frac{\text{Mole}}{\text{Mass of water in kg}} = \frac{93}{98 \times \frac{91}{1000}} = \mathbf{10.42}$$

114.

$$C + \frac{1}{2}O_2 \longrightarrow CO \qquad ...(1)$$

$$C + O_2 \longrightarrow CO_2 \qquad ...(2)$$

Let *a* mole of C reacts according to Eq. (1) and *b* mole of C reacts according to Eq. (2).

Then, $a + b = \frac{18}{12} = 1.5$ ...(3)

Also, Mole of O_2 used $= \frac{a}{2} + b = \frac{5 \times 5}{0.0821 \times 291}$ $\left(n = \frac{PV}{RT}\right)$

or $\frac{a}{2} + b = 1.046$ ...(4)

By Eqs. (3) and (4), $a = 0.908$

$b = 0.592$

$\therefore$ CO_2 formed $= 0.592$ mole

m mole of NaOH given $= 2 \times 500 = 1000$

m mole of CO_2 formed $= 592$

Now the reaction of CO_2 with NaOH will occur as :

	$2NaOH$ +	$CO_2 \longrightarrow$	$Na_2CO_3 + H_2O$
m mole before reaction	1000	592	0
m mole after reaction	0	92	500

	Na_2CO_3 +	$CO_2 + H_2O \longrightarrow$	$2NaHCO_3$
m mole before reaction	500	92	0
m mole after reaction	408	0	$2 \times 92 = 184$

$$\therefore \quad M_{Na_2CO_3} = \frac{408}{500} = \mathbf{0.816\ M}$$

$$M_{NaHCO_3} = \frac{184}{500} = \mathbf{0.368\ M}$$

115. Let V mL of each are mixed

For I solution. H_2SO_4 is 30% by mass.

$\therefore$ Mass of $H_2SO_4 = 30\,g$

and Mass of solution $= 100\,g$

$\therefore$ Volume of solution $= \frac{100}{1.218}$ mL

i.e., $\frac{100}{1.218}$ mL contains 30 g H_2SO_4

$\therefore$ V mL contains $\frac{30 \times V \times 1.218}{100}$ g H_2SO_4

For II solution. H_2SO_4 is 70% by mass.

$\therefore$ **Mass of $H_2SO_4 = 70\,g$**

Mass of solution $= 100\,g$

$\therefore$ Volume of solution $= \frac{100}{1.610}$ mL

i.e., $\frac{100}{1.610}$ mL contains 70 g H_2SO_4

$\therefore$ V mL contains $\frac{70 \times V \times 1.610}{100}$ g H_2SO_4

On mixing these two, total mass of H_2SO_4

$$= \left[\frac{30 \times 1.218}{100} + \frac{70 \times 1.610}{100}\right] V\,g = 1.4924\,V\,g$$

Total volume of solution $= 2V$ mL

$$\therefore \quad \text{Molarity of solution} = \frac{1.4924V}{98 \times \frac{2V}{1000}} = \mathbf{7.61}$$

Now, Mass of total solution $= 2V \times 1.425\,g = 2.85V\,g$

$\therefore$ Mass of water $= (2.85V - 1.4924V)\,g = 1.3576V\,g$

$$\therefore \quad \text{Molality of solution} = \frac{1.4924V}{98 \times \frac{1.3576V}{1000}} = \mathbf{11.22}$$

116. Consider one litre water or 10^{-3} m^3 of water

$\therefore$ Volume of water $= 1$ litre $= 10^{-3}$ m^3 $= 1000$ mL

$\therefore$ 1 m^3 H_2O weigh 10^3 kg $H_2O = 10^6$ g H_2O

$\therefore$ 10^{-3} m^3 H_2O weigh $= 10^6 \times 10^{-3}$ g $H_2O = 10^3$ g H_2O

$$\therefore \quad \text{Mole of water} = \frac{10^3}{18}$$

$$\text{Molarity} = \frac{1000}{18 \times 1}$$

$$\text{Molarity} = \mathbf{55.6}$$

117. Eq. of NaOH $= 50 \times 0.2 = 10$

Eq. of HCl $= 5 \times 1 = 5$

$\therefore$ Eq. of NaOH left after reaction with HCl $= 10 - 5 = 5$

Also NaOH reacts with $FeCl_3$ to give $Fe(OH)_3$ which on ignition gives Fe_2O_3.

$\therefore$ Eq. of NaOH used for $FeCl_3$ = Eq. of $Fe(OH)_3$

$= $ Eq. of $Fe_2O_3 = 15 \times 0.1 = 1.5$

$\therefore$ Eq. of NaOH left finally $= 5 - 1.5 = 3.5$

$$\therefore \quad N_{NaOH} \text{ left} = \frac{3.5}{70} = \mathbf{0.05\ N}$$

$\because$ Total volume $= 70$ litre

Also, Eq. of $Fe_2O_3 = 1.5$

$$\therefore \quad \frac{w}{M/6} = 1.5$$

$$\therefore \quad w_{Fe_2O_3} = \frac{1.5 \times 160}{6} = \mathbf{40\ g}$$

118. Meq. of barium salt = Meq. of acid

$$\frac{4.290}{M/2} \times 1000 = 21.64 \times 0.477 \times 2$$

Molar mass of salt $= 415.61$

$$\text{Molar mass of anion} = \frac{415.61 - 137 - 36}{2} = 121.31$$

$\therefore$ Molar mass of acid $= 121.31 + 1 = \mathbf{122.31}$

119. The ionic strength (μ) of a solution is given by

$$\mu = \frac{1}{2}\Sigma cZ^2$$

where, c is the concentration of ion and Z is its valency.

$$\mu = \frac{1}{2}[0.5\times 2^2 + 0.5\times 2^2 + 0.1\times 3^2 + 0.3\times 1^2 + 0.4\times 1^2 + 0.2\times 2^2]$$

$$= 3.2$$

120. $$\frac{n_{AA}}{n_{AA} + n_{H_2O}} = 0.15$$

$$\therefore \quad \frac{n_{H_2O}}{n_{AA} + n_{H_2O}} = 0.85$$

$$\therefore \quad \frac{n_{AA}}{n_{H_2O}} = \frac{15}{85} \text{ or } \frac{\frac{w_{AA}}{60}}{\frac{w_{H_2O}}{18}} = \frac{15}{85}$$

$$\therefore \quad \frac{w_{AA}}{w_{H_2O}} = \frac{15}{85}\times\frac{60}{18} = 0.59 \qquad ...(i)$$

Also, $$w_{AA} + w_{H_2O} = 30 \qquad ...(ii)$$

$$\therefore \quad w_{AA} = 11.13\,\text{g}$$

$\therefore$ Meq. of acetic acid = Meq. of NaOH

$$\frac{11.13}{60}\times 1000 = 0.01\times V_{\text{mL}}$$

$$\therefore \quad V = 18550\,\text{mL} = \textbf{18.55 litre}$$

121. Let n_1 mole of solute and n_2 mole of solvent be present in solution.

Given, $n_1 + n_2 = 1$

$$\because \quad X_1 = \frac{n_1}{n_1+n_2} \text{ and } X_2 = \frac{n_2}{n_1+n_2}$$

and thus, $X_1 + X_2 = 1$ and $\frac{X_1}{X_2} = \frac{n_1}{n_2}$

(a) $\therefore$ Mole of solute, $n_1 \propto$ mole fraction of solute, X_1

mole of solvent, $n_2 \propto$ mole fraction of solvent, X_2

$\therefore$ Total mass of solution = $(X_1 \cdot M_1 + X_2 \cdot M_2)$

$\therefore$ Total volume of solution = $\left[\frac{X_1M_1 + X_2M_2}{\rho}\right]$ litre

$$\therefore \text{ Molarity } M = \frac{X_1}{(X_1M_1 + X_2M_2)/\rho}$$

$$= \frac{X_1\rho}{(X_1M_1 + X_2M_2)} \qquad ...(i)$$

$$\therefore \quad MX_1M_1 + MX_2M_2 = X_1\rho$$

$$\text{or} \quad MX_1M_1 + MM_2(1 - X_1) = X_1\rho$$

$$\text{or} \quad X_1(\rho - MM_1 + MM_2) = MM_2$$

$$\therefore \quad \boldsymbol{X_1 = \frac{MM_2}{\rho + M(M_2 - M_1)}}$$

(b) For a dilute solution $X_1M_1 << X_2M_2$;

$X_2 \longrightarrow$ unity, *i.e.*, 1

and $\rho_{\text{solution}} = \rho_{\text{solvent}}$

Thus from Eq. (i), $$M = \frac{X_1\rho}{M_2}$$

Thus molarity, M of a dilute solution is directly proportional to mole fraction of solute, *i.e.*, $M \propto X_1$.

122. Let a and b g are masses of Al and Zn in mixture.

$$\therefore \quad a + b = 1.67 \qquad ...(1)$$

$$Al + 3HCl \longrightarrow AlCl_3 + \frac{3}{2}H_2$$

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

$\because$ 27 g Al gives $\frac{3}{2}\times 22.4$ litre H_2

a g Al gives $\frac{3\times 22.4\times a}{2\times 27}$ litre H_2 ($\because$ atomic mass of Al = 27)

Similarly 65 g Zn gives 22.4 litre H_2 ($\because$ atomic mass of Zn = 65)

$\therefore$ b g Zn gives $\frac{22.4\times b}{65}$ litre H_2

$$\therefore \quad \frac{3\times 22.4\times a}{2\times 27} + \frac{22.4\times b}{65} = 1.69 \qquad ...(2)$$

Solving Eqs. (1) and (2) $\quad a = \textbf{1.25 g}$

$b = \textbf{0.42 g}$

Alternate solution

$$a + b = 1.67 \qquad ...(1)$$

Meq. of Al + Meq. of Zn = Meq. of H_2

$$\frac{a}{27/3}\times 1000 + \frac{b}{65/2}\times 1000 = \frac{1.69}{22.4/2}\times 1000 \qquad ...(2)$$

Solve Eqs. (1) and (2) to get a and b.

123. $$HCOOH \xrightarrow[\Delta]{H_2SO_4} H_2O + CO$$

$$H_2C_2O_4 \xrightarrow[\Delta]{H_2SO_4} H_2O + CO + CO_2$$

Let a mole of HCOOH and b mole of $H_2C_2O_4$ are present in original mixture.

$$\therefore \text{ Mole of CO formed} = \underset{\text{from HCOOH}}{a} + \underset{\text{from } H_2C_2O_4}{b}$$

$$\text{Mole of } CO_2 \text{ formed} = \underset{\text{from } H_2C_2O_4}{b}$$

Total mole of gases = $a + b + b = a + 2b$

$\because$ CO_2 is absorbed by KOH and volume reduces by $\frac{1}{6}$

$$\therefore \quad \text{Mole of } CO_2 = \frac{1}{6}(a + 2b)$$

$$b = \frac{1}{6}(a + 2b)$$

$$\therefore \quad a/b = 4$$

$$\therefore \quad a : b :: \mathbf{4 : 1}$$

124. Let total millimole of Mg used for MgO and Mg_3N_2 be a and b respectively.

	$2Mg + O_2 \longrightarrow$	$2MgO$
Before reaction	a	0
After reaction	0	a

	$3Mg + N_2 \longrightarrow$	Mg_3N_2
Before reaction	b	0
After reaction	0	$b/3$

Now, $\left(a + \frac{b}{3}\right)$ millimole of MgO and Mg_3N_2 are present in the mixture.

$$MgO + 2HCl \longrightarrow MgCl_2 + H_2O;$$

$$Mg_3N_2 + 8HCl \longrightarrow 3MgCl_2 + 2NH_4Cl$$

or the solution contains a millimole of $MgCl_2$ from MgO and b millimole of $MgCl_2$ and $\frac{2b}{3}$ millimole of NH_4Cl from Mg_3N_2.

Also, millimole of HCl used for this purpose

$$= \underset{\text{for MgO}}{2a} + \underset{\text{for } Mg_3N_2}{\frac{8b}{3}}$$

Now, millimole of HCl or Meq. of HCl (monobasic acid) $= 60 - 12 = 48$

$$2a + \frac{8b}{3} = 48 \qquad \text{...(1)}$$

Further, millimole of NH_4Cl formed = millimole of NH_3 liberated = millimole of HCl used for absorbing NH_3

$$\therefore \quad \frac{2b}{3} = 4 \quad \text{or} \quad b = 6 \qquad \text{...(2)}$$

From Eq. (1) $\quad 2a + \frac{8 \times 6}{3} = 48 \quad \text{or} \quad a = 16$

Thus, % of Mg used for $Mg_3N_2 = \frac{6}{(6+16)} \times 100 = \mathbf{27.27\%}$

125. $$N_2O_5 \rightleftharpoons 2NO(g) + \frac{1}{2}O_2(g)$$

Initial pressure	600	0	0	
Final pressure	$600 - P$	$2P$	$P/2$	[$P \propto$ mole if V, T are constant (where mole equivalent] to pressure P are decomposed)

Thus, $\quad 600 - P + 2P + P/2 = 960 \quad \text{or} \quad P = 240 \text{ mm Hg}$

Thus, $\quad$ mole fraction of N_2O_5 decomposed $= \frac{240}{600} = \mathbf{0.4}$

126. $$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O(l)$$

$$C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O(l)$$

Let a litre of C_3H_8 and b litre of C_4H_{10} be present in mixture.

$$\therefore \qquad a + b = 3 \qquad \text{...(1)}$$

Also volume of CO_2 formed $= 10 = CO_2$ formed by C_3H_8 + CO_2 formed by C_4H_{10}

$$10 = 3a + 4b \qquad \text{...(2)}$$

Solving Eqs. (1) and (2) $\quad b = \mathbf{1\ litre}$

127. Glauber's salt is $Na_2SO_4 \cdot 10H_2O$ having molar mass = 322 g mol^{-1}

$\because$ Mass of Na_2SO_4 in 8.0575×10^{-2} kg glauber salt

$$= \frac{142 \times 8.0575 \times 10^{-2}}{322} = 3.5533 \times 10^{-2} \text{ kg}$$

$$\therefore \text{ Molarity '}M\text{' of } Na_2SO_4 = \frac{3.5533 \times 10^{-2}}{142 \times 10^{-3} \times 1}$$

$$\left(\because M = \frac{\text{mole}}{\text{volume in litre}}\right)$$

$$= \mathbf{0.2502\ M}$$

$\because$ Mass of solution $= 1077.2 \times 10^{-3}$ kg

$$= 1077.2 \times 10^{-3} \times 10^3 \text{ g} = 1077.2 \text{ g}$$

Mass of $Na_2SO_4 = 3.5533 \times 10^{-2} \times 10^3 \text{ g} = 35.533 \text{ g}$

$\therefore$ Mass of water $= 1077.2 - 35.533 = 1041.667$ g

$$\because \text{ Molality of } Na_2SO_4 = \frac{\text{Mole of } Na_2SO_4}{\text{Mass of water in kg}}$$

$$= \frac{3.5533 \times 10^{-2}}{142 \times 10^{-3} \times \frac{1041.667}{10^3}} = \mathbf{0.24\ m}$$

Also, $\quad$ Mole fraction of Na_2SO_4

$$= \frac{\text{Mole of } Na_2SO_4}{\text{Mole of } Na_2SO_4 + \text{Mole of } H_2O}$$

$$= \frac{\frac{3.5533 \times 10^{-2}}{142 \times 10^{-3}}}{\frac{3.5533 \times 10^{-2}}{142 \times 10^{-3}} + \frac{1041.667}{18}} = \mathbf{4.3 \times 10^{-3}}$$

128. $$\underset{a\ g}{Pb(NO_3)_2} \longrightarrow PbO + 2NO_2\uparrow + \frac{1}{2}O_2\uparrow$$

$$\underset{b\ g}{NaNO_3} \longrightarrow NaNO_2 + \frac{1}{2}O_2\uparrow$$

$$\therefore \qquad a + b = 5 \qquad \text{...(1)}$$

The loss in mass for 5 g mixture $= 5 \times \frac{28}{100} = 1.4$ g

$\therefore \qquad$ Residue left $= 5 - 1.4 = 3.6$g

The residue contains PbO + $NaNO_2$

$\because \qquad 331$g $Pb(NO_3)_2$ gives = 223 g PbO

$\therefore \qquad a$ g $Pb(NO_3)_2$ gives $= \frac{223 \times a}{331}$ g PbO

Similarly,

$\because \qquad 85$ g $NaNO_3$ gives = 69 g $NaNO_2$

$\therefore \qquad b$ g $NaNO_3$ gives $= \frac{69 \times b}{85}$ g $NaNO_2$

$$\therefore \qquad \frac{223 \times a}{331} + \frac{69 \times b}{85} = 3.6 \qquad \text{...(2)}$$

Solving Eqs. (1) and (2),

$$\therefore \qquad a = \mathbf{3.32\ g}$$

$$b = \mathbf{1.68\ g}$$

129. For a gaseous mixture of C_2H_6 and C_2H_4

$$PV = nRT$$

$$\therefore \qquad 1 \times 40 = n \times 0.082 \times 400$$

$\therefore$ Total mole of $(C_2H_6 + C_2H_4) = 1.2195$

Let mole of C_2H_6 and C_2H_4 be a, b respectively

$$a + b = 1.2195 \qquad \text{...(1)}$$

$$C_2H_6 + (7/2)O_2 \longrightarrow 2CO_2 + 3H_2O$$

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

$\therefore$ Mole of O_2 needed for complete reaction of mixture $= 7a/2 + 3b$

$$\therefore \qquad \frac{7a}{2} + 3b = \frac{130}{32} \qquad \text{...(2)}$$

By Eqs. (1) and (2), $\quad a = 0.808$

$$b = 0.4115$$

$\therefore \qquad$ Mole fraction of $C_2H_6 = 0.808/1.2195 = \mathbf{0.66}$

and $\qquad$ Mole fraction of $C_2H_4 = \mathbf{0.34}$

130. Sample of hard water contains 96 ppm SO_4^{2-} and 40 ppm Ca^{2+} ($CaSO_4$). Also it contains 183 ppm HCO_3^- and 60 ppm Ca^{2+} [$Ca(HCO_3)_2$].

To remove $Ca(HCO_3)_2$ from 10^3 kg or 10^6 g sample of hard water which contains 243 g $Ca(HCO_3)_2$ or 3/2 mole of $Ca(HCO_3)_2$, CaO required is 3/2 mole.

$$Ca(HCO_3)_2 + CaO \longrightarrow 2CaCO_3 + H_2O$$

Thus, mole of CaO required = 3/2 or 1.5

Also, Ca^{2+} ions left in solution are of $CaSO_4$ *i.e.*, **40 ppm**

Now, 1 litre water contains Ca^{2+} after removal of $Ca(HCO_3)_2$

$$= \frac{40 \times 10^3}{10^6} = 40 \times 10^{-3} \text{ g}$$

or $$[Ca^{2+}] = \frac{40 \times 10^{-3}}{40} = 10^{-3}$$

If these Ca^{2+} are exchanged with H^+, then $[H^+]$ in solution $= 2 \times 10^{-3}$

$\therefore$ $$pH = -\log 2 \times 10^{-3} = \mathbf{2.6989}$$

131. Mass of $Na_2CO_3 = a$ g

Mass of $K_2CO_3 = b$ g

$\therefore$ $$a + b = 1.20 \qquad \text{...(1)}$$

For neutralization reaction 100 mL solution

Meq. of Na_2CO_3 + Meq. of K_2CO_3 = Meq. of HCl

$$\frac{a}{106/2} \times 1000 + \frac{b}{138/2} \times 1000 = \frac{40 \times 0.1 \times 100}{20}$$

$\therefore$ $$69a + 53b = 73.14 \qquad \text{...(2)}$$

By Eqs. (1) and (2), $a = \mathbf{0.5962\ g}$

$b = \mathbf{0.6038\ g}$

Further, solution of $Na_2CO_3 + K_2CO_3$ gives ppt of $BaCO_3$ with $BaCl_2$.

Meq. of $BaCO_3$ = Meq. of Na_2CO_3 + Meq. of K_2CO_3 (in 20 mL)

= Meq. of HCl for 20 mL mixture

$= 40 \times 0.1 = 4$

$\therefore$ $$\frac{w}{197/2} \times 1000 = 4$$

$\therefore$ Mass of $BaCO_3$ = **0.394 g**

132. $$N_{HCl} = \frac{109.5}{36.5 \times 1} = 3$$

Since, Na_2CO_3 is completely neutralized by HCl

$\therefore$ Meq. of Na_2CO_3 = Meq. of HCl

$$N \times 25 = 32.9 \times 3$$

$\therefore$ $$N_{Na_2CO_3} = 3.948$$

Now, Na_2CO_3 fresh solution reacts with H_2SO_4

Mass of Na_2CO_3 solution = 125 g

$\therefore$ Volume of Na_2CO_3 solution $= \frac{125}{1.25} = 100$ mL

$\therefore$ Meq. of H_2SO_4 = Meq. of Na_2CO_3

$$0.84 \times V = 100 \times 3.948$$

$\therefore$ Volume of H_2SO_4 required = **470 mL**

133. m M of HCl $= 200 \times a + 500 \times b$

$\therefore$ Molarity after diluting to 2 litre $= \frac{200 \times a + 500 \times b}{2000}$

Thus $$1.5 = \frac{200a + 500b}{2000}$$

Also $$\frac{a}{b} = \frac{5}{4}$$

$\therefore$ $$1.5 \times 2000 = 200 \times \frac{5}{4} b + 500b$$

$\therefore$ **b = 4 and a = 5**

134. $H_2O + SO_3 \longrightarrow H_2SO_4$

$\because$ 18 g H_2O reacts with 80 g SO_3

$\therefore$ 6 g H_2O reacts with $\frac{80 \times 6}{18} = 26.67$g

$\therefore$ % of free SO_3 = **26.67 g**

• SINGLE INTEGER ANSWER PROBLEMS •

1. The number of mole of N_2O_4 in 276 g N_2O_4 are ......
2. 10 mL of 'a' M solution of HCl is mixed with 40 mL of 1M HCl to produce a mixture of 2M. The value of a is ......
3. Molar ratio in a mixture of water and absolute alcohol is 0.2. The mole fraction ratio of alcohol and water is ......
4. 6 g of H_2 reacts with 14 g N_2 to form NH_3 till the reaction completely consumes the limiting reagent. The mass of other reactant (in g) left are ......
5. 1 g of titanium (atomic mass 48) reacts with Cl_2 to give 3.21875 g compound. The valence of titanium is ......
6. A reaction requires two atoms of P for five atoms of O. The amount in g of O_2 required for 3.10 g P :
7. A mixture of C_2H_4 and H_2 (in excess) has a pressure of 60 cm Hg. The mixture on passing over Ni catalyst gives : $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$. The resultant pressure of mixture after completion of reaction at same T and V is 40 cm Hg. The ratio of mole fraction of H_2 and C_2H_4 in original mixture are ......
8. Haemoglobin contains 0.25% iron by mass. The molar mass of haemoglobin is 89600. Number of iron atoms present in one mole of haemoglobin are ......
9. A gaseous alkane C_nH_{2n+2} an explosion with O_2 gives CO_2. The volume of O_2 required for complete combustion of alkane to CO_2 formed is 7 : 4. The value of n is ......
10. Compound S_4N_4 decompose completely into $S_X(g)$ and $N_2(g)$. If all measurements are made of same P and T each volume of S_4N_4 gives 4.0 volume of gaseous product. The value of X is ......
11. 0.98 g of a polybasic acid (molar mass 98) requires 30 mL of 0.5 M $Ba(OH)_2$ for complete neutralisation. The basicity of acid is ......
12. A solution of H_2O_2 has normality $\frac{N}{1.7}$. Its % strength is ......
13. Number of water molecules attached on Cu^{2+} ion in $CuSO_4 \cdot 5H_2O$ is ......
14. Number of water molecules present in Mohr's salt is ......
15. 'n' factor for potash alum is ......
16. 100 mL solution of an acid (molar mass 82) containing 39 g acid per litre was completely neutralised by 95.0 mL of aqueous NaOH solution containing 40 g NaOH per litre. The basicity of acid is ......
17. The acidity of acid salt $BaHPO_4$ is ......
18. The basicity of acid salt $BaHPO_4$ is ......
19. 3 mole of $BaCl_2$ are mixed with 5 mole of Na_3PO_4 in 1000 mL water. The maximum number of mole of $Ba_3(PO_4)_2$ formed are.....
20. A gaseous alkane C_nH_{2n+2} is exploded with oxygen. The volume of oxygen for complete combustion of alkane to CO_2 formed is in the ratio 7 : 4. The value of n is :
21. In what volume ratio 0.1M $Ca(NO_3)_2$ and 0.2 M $NaNO_3$ solutions should be mixed, so that the concentration of negative ion is 50% greater than the concentration of +ve ions.
22. The molality of 49% by volume of H_2SO_4 solution having density 1.49 g/mL is....
23. The ratio of mole of H_2 and CH_4 in a mixture having equal masss of both is....
24. A mixture of C_2H_4 and excess of H_2 has a pressure of 60 cm Hg. The mixture on passing over catalyst forms ethane. The pressure of resultant mixture under identical conditions is 40 cm of Hg. The mole ratio of H_2 and C_2H_4 in the mixture is....
25. Two acid solutions A and B are titrated separately each with 25 mL of 1N Na_2CO_3 solution. The volume of each acid used for titration is 10 mL and 40 mL respectively for the complete neutralisation. The volume ratio of V_B and V_A which is mixed to prepare one mL 1N solution is...
26. The oxidation of toluene with $KMnO_4$ gives potassium benzoate yield of 76.66%. The amount to closest integer value of toluene to obtain 12g potassium benzoate required is....
27. 500 mL of aM and 500 mL of bM solution of a solute are mixed and diluted to 2 litre to prepare a solution of 1.5 M. If a and b are in the ratio 2 : 1, then value of a is....
28. A sample of crystalline $Ba(OH)_2 \cdot X\,H_2O$ weighing 1.578 g was dissolved in water. The solution required 40 mL of 0.25N HNO_3 for complete reaction. Determine the number of molecules of water of crystallisation in base.
29. The specific gravity of a solution of 1.8 g mL^{-1} having 62% by mass of acid. It is to be diluted to specific gravity of 1.2 g mL^{-1}. What volume of water (in litre) should be added to 1 litre of this solution?
30. A mixture of Xe and F_2 was heated and the white solid so formed reacted with H_2 to give 81 mL of Xe at STP and HF. The HF formed required 68.43 mL of 0.3172 M NaOH for complete neutralization. The empirical formula of white solid is XeF_n. The value of n is....
31. 100 g HCl solution having density 1.20 g/mL contains 36.5 g HCl. How much volume in litre of this HCl is required to neutralise exactly 36 litre of N NaOH solution.
32. An element A forms a thiocyanate of formula $A(CNS)_m \cdot nH_2O$. Analysis shows that compound

contains 19.7% of *A* and 19% water. If atomic mass of *A* is 55.96, the value of *m* is....

33. In the above problem14 value of *n* is....

34. A certain metal *M* forms an insoluble oxalate $M_4O_3(C_2O_4)_3 \cdot 12H_2O$. If 61.87g of the complex are formed from *n* g oxalic acid ($H_2C_2O_4$). The atomic mass of metal is 100. The value of *n* is......

35. 1 g dry algae absorbs 7.4×10^{-3} mole of CO_2 per sec by photosynthesis. If the fixed carbon atoms were all stored after the photosynthesis as starch $(C_6H_{10}O_5)_m$, the time required in sec for absorption of CO_2 by algae to double its own mass.

36. One litre of milk mass 1.035 kg. The density of butter fat and fat free skimmed milk are 875 kg m^{-3} and 1042 kg m^{-3}. The vol/vol per cent of butter fat in milk is...

37. Chloride samples are prepared for analysis by using NaCl, KCl and NH_4Cl separately or as mixture. What minimum volume of 5% by mass $AgNO_3$ solution (sp. gravity 1.19 g/mL) must be added to a sample of 0.1498 g in order to ensure precipitation of chloride in every possible case?

38. Valence factor of potash alum is....

39. Valence factor of S in SO_2 is four and in SO_3 is six. Valence factor of S in $2SO_2 + O_2 \longrightarrow 2SO_3$ is....

40. 2×10^{10} atoms of carbon are arranged in a straight line occupying 2.4 cm putting side by side. The radius of carbon atom in nm is....

41. 23.1 mL of 0.115 *M* solution of NaOH is required for the end point using bromocresol green for 25 mL of 0.107 H_3PO_4. If the indicator phenolphthalein is used then 46.2 mL of same NaOH requires 25 mL of 0.107 *M* H_3PO_4. What is the ratio of replaceable H-atom in phenolphthalein and bromocresol indicators titrations?

42. Number of equivalents of oxygen in 1*M* $K_2Cr_2O_7$ acting as oxidant in presence of acid are....

43. 1 mL of 12*M* HCl is spread over a thin Al foil of thickness 0.1 mm and density 2.70 g/mL. Assuming area covered by HCl dissolves Al only, the area in cm^2 of hole produced in Al foil is....

44. A hydrated salt $MSO_4 \cdot nH_2O$ undergoes 43.9% loss in mass on heating and becomes anhydrous. If atomic mass of metal is 65, the value of *n* is....

45. The volume strength of H_2O_2 solution is 11.2. What is its normality?

46. Mole of 400 g $CaCO_3$ is ......

47. A mixture of HCOOH and $H_2C_2O_4$ is heated with conc. H_2SO_4. The gaseous mixture on passing through KOH shows a reduction of $\frac{1}{6}$ in volume at same *P* and *T*. The mole ratio of HCOOH and $H_2C_2O_4$ in mixture is.

48. Atomicity of sulphur in vapour state is ......

49. An aqueous solution of 6.3 g oxalic acid $(H_2C_2O_4 \cdot 2H_2O)$ is dissolved in water to prepare 250 mL solution. The volume of 1 N NaOH required to neutralise 10 mL solution of oxalic acid is ......

50. Equal masses of hydrogen and methane are taken in a container under identical conditions of *P* and *T*. The mole ratio of H_2 and CH_4 is.

51. An inorganic compound $ZnCr_2O_x$, 9.81 g Zn, 1.8×10^{23} atoms of Cr and 0.6 g-atom of O. The value of *x* is ......

52. The equilibrium molarity of OH^- is 0.08 *M* in a solution of 0.1 $M(OH)_2$. The % of dissociation of $Ca(OH)_2$ is ......

53. The normality of 0.5 *M* H_3PO_3 solution is ......

54. How much of the following have equilibrium molality of $[H^+] = 0.6\,M$

0.3 *M* H_2SO_4, 0.3 *M* H_3PO_3, 0.6 *M* HI, 0.2 *M* H_3PO_4, 0.6 *M* HNO_3.

55. How much of the following are temperature independent in case of solution.

Meq. of solute, mole of solute, % by mass, mole fraction, molarity, normality, % by strength, strength, molality.

56. How much of the following are dilution independent in case of solution. Meq. of solute, mole of solute, % by mass, mole fraction, molarity, molality % by strength, strength, molality.

57. 245 g impure $KClO_3$ decomposes to give 2.4 g O_2. The % yield of product O_2 is ......

58. Equilibrium molarity of 196 g H_2SO_4 present in 1 litre solution is ......

59. Ionic strength of Ba^{2+} present in a solution obtained by mixing 30 mL 0.1 *N* $BaCl_2$ with 40 mL of 0.2 *N* $Al_2(SO_4)_3$ is ......

60. A student performs a titration with different burettes and finds titre value of 25.2 mL, 25.25 mL, 25.0 mL. The number of significant figures in the average titre value is ...... **(IIT 2010)**

61. The volume (in mL) of 0.10 M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of $[Cr(H_2O)_5Cl]Cl_2$ as silver chloride is close to ...... **(IIT 2011)**

62. 29.2% (mass/mass) HCl stock solution has a density of 1.25 g mL^{-1}. The molar mass of HCl is 36.5 g mol^{-1}. The volume (mL) of stock solution required to prepare a 200 mL solution of 0.4 *M* HCl is: **(IIT 2012)**

ANSWERS

1. Three **2.** Six **3.** Five **4.** Three **5.** Three **6.** Four **7.** Two **8.** Four **9.** Two **10.** Two **11.** Three **12.** One
13. Four **14.** Six **15.** Eight **16.** Two **17.** Two **18.** One **19.** One **20.** Two **21.** Two **22.** Five **23.** Eight **24.** Two
25. Four **26.** Nine **27.** Four **28.** Eight **29.** Three **30.** Six **31.** Three **32.** Three **33.** Three **34.** Two **35.** Five **36.** Four
37. Eight **38.** Eight **39.** Two **40.** Six **41.** Two **42.** Six **43.** Four **44.** Seven **45.** Two **46.** Four **47.** Four **48.** Two
49. Four **50.** Eight **51.** Four **52.** Four **53.** One **54.** Three **55.** Five **56.** Two **57.** Five **58.** Zero **59.** Zero **60.** Three
61. Six **62.** Eight

OBJECTIVE PROBLEMS (One Answer Correct)

1. A sample contains 9.81 g Zn (atomic mass 65), 1.8×10^{23} atoms of Cr and 0.6 g-atoms of Cr. The simple formula of this compound is :
(a) $ZnCrO_4$ (b) $ZnCr_2O_4$
(c) Zn_2CrO_4 (d) $ZnCrO_3$

2. The number of H^+ ions present in 100 mL of 0.001 M H_2SO_4 solution is :
(a) 1.2×10^{20} (b) 6×10^{19}
(c) 2.4×10^{20} (d) 1.2×10^{23}

3. The atomic masses of two elements A and B are 30 and 90 respectively. If 'a' g of element A contains 'b' atoms, then number of atoms of B in $2a$ g is :
(a) $2b/3$ (b) $b/3$
(c) $b/4$ (d) $b/2$

4. A nugget of gold and quartz weighs 100 g. Specific gravity of gold, quartz and nugget are 20.0, 4.0 and 5.0 g mL^{-1} respectively. The mass of gold in nugget is:
(a) 30 g (b) 35 g
(c) 25 g (d) 20 g

5. The mass of wet NaOH containing 20% water required to neutralise 6 litre of 0.5 M H_2SO_4 solution is:
(a) 3 kg (b) 1.5 kg
(c) 0.3 kg (d) 0.15 kg

6. 1 g of an acid (molar mass 146) is completely neutralised by 0.768 g KOH. The number of neutralisable protons in acid are :
(a) 1 (b) 3
(c) 2 (d) 4

7. The volume ratio of 6 N and 2 N HCl required to prepare 100 mL of 5 N HCl is :
(a) 3 : 1 (b) 1 : 3
(c) 4 : 1 (d) 1 : 4

8. 105 mL of pure water at 4°C is saturated with NH_3 producing a solution of 30% by mass of NH_3. The total mass of solution after saturation becomes :
(a) 105 g (b) 130 g
(c) 150 g (d) 160 g

9. The total ionic strength of solution on mixing 10 mL of 1 N $AgNO_3$ and 90 mL of 1 N $BaCl_2$ solution is :
(a) 2.8 (b) 2.6
(c) 1.35 (d) 1.2

10. The mass of 5 litre C_6H_6 is maximum at :
(a) 10°C (b) 20°C
(c) 30°C (d) 40°C

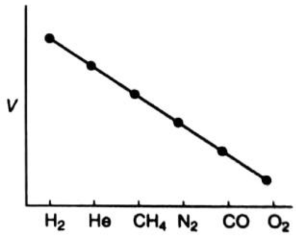
11. An aqueous solution of glucose is 10% by mass/mass of solution. The percentage by mass/mass of solvent is : (assume $d_{H_2O} = 1$)
(a) 11.11% (b) 15%
(c) 20.22% (d) 22.22%

12. The equivalent mass of a metal is double that of oxygen. The ratio of masses of metal oxide and mass of the metal is :
(a) 2 (b) 1.5
(c) 2.5 (d) 3.0

13. The volume and radius of 1 molecule of water is : (assume $d_{H_2O} = 1\text{ g / mL}$)
(a) 3.0×10^{-20}, 19.25 Å (b) 6.0×10^{-23}, 2.42 Å
(c) 3.0×10^{-23}, 1.925 Å (d) 6.0×10^{-23}, 1.925 Å

14. If $a = 49\text{ g } H_2SO_4 + (3\times10^{23}\text{ molecule } H_2SO_4) - (0.02\ N\ H_2SO_4)$, then the value of a is :
(a) 0.9 mol (b) 0.99 mol
(c) 0.8 mol (d) 0.88 mol

15. Which of the following gases does not show correct variation in figure where volume *vs.* gas plots are made. Each gas is taken in equal mol at STP ?



(a) He and H_2 (b) CH_4 and He
(c) CO and N_2 (d) O_2 and CO

16. A solution requires $[OH^-] = 2\ M$. If degree of dissociation of $Mg(OH)_2$ is α, what analytical molarity solution of $Mg(OH)_2$ needed is equal to:
(a) α (b) 2α
(c) $\frac{1}{\alpha}$ (d) $\frac{1}{2\alpha}$

17. Hardness of water is 400 ppm. The molarity of $CaCO_3$ in this water is :
(a) $4\times10^{-6}\ M$ (b) $4\times10^{-2}\ M$
(c) $4\times10^{-3}\ M$ (d) $4\times10^{-1}\ M$

18. The volume strength of 1.5 N H_2O_2 solution is :
(a) 4.8 (b) 8.4
(c) 3.0 (d) 8.0

19. The normality of 0.3 M phosphorous acid :
(a) 0.1 (b) 0.9
(c) 0.3 (d) 0.6

20. How many g of KCl would have to be dissolved in 60 g H_2O to give 20% by mass of solution:
(a) 1.5 g (b) 15 g
(c) 25 g (d) 12 g

21. 10 mL of oxygen and 60 mL of H_2 is sparked till reaction is complete to form $H_2O_{(l)}$. After attaining the initial condition of *P* and *T*, the reduction in volume (in mL) of gases after reaction is:
(a) 30 (b) 40
(c) 20 (d) 10

22. 10 mL of CH_4 was burnt in limited supply of oxygen forming CO_2 and CO in the ratio 99 : 1 along with water vapours. The volume of oxygen needed in mL for the change is:
(a) 19.95 (b) 19.9
(c) 9.95 (d) 9.9

23. The formula of a hydrated salt of barium is $BaCl_2 \cdot XH_2O$. If 1.936 g of this compound gives 1.846 g of anhydrous $BaSO_4$ on treatment with H_2SO_4, the value of *X* is :
(a) 7 (b) 5
(c) 3 (d) 2

24. 40% (mass/vol) NaCl has specific gravity 1.12 g/mL. In ppm the concentration of NaCl is:
(a) 5.5×10^5 ppm (b) 3.57×10^6 ppm
(c) 1×10^6 ppm (d) 4×10^5 ppm

25. What mass of NH_3 contains same number of atoms as in 4g-atom of oxygen:
(a) 17 g (b) 68 g
(c) 42 g (d) 34 g

26. The ratio of oxygen atoms in $Ca_3(PO_4)_2$ and H_3PO_3 if each sample of $Ca_3(PO_4)_2$ and H_3PO_4 contains same number of *P* atoms:
(a) $\frac{3}{4}$ (b) $\frac{4}{3}$
(c) $\frac{2}{3}$ (d) $\frac{3}{2}$

27. Select the incorrect statement for exact neutralisation of 1 mole of $Ba(OH)_2$ by:
(a) 1.5 mole of H_3PO_3 (b) 1 mole of H_2SO_4
(c) $\frac{2}{3}$ mole of H_3PO_4 (d) 2 mole of H_3PO_2

28. A gaseous mixture of H_2 and CO_2 contains 44% of CO_2 by mass. The vapour density of mixture is:
(a) 2.72 (b) 1.72
(c) 3.45 (d) 1.36

29. On heating 17.0 g $AgNO_3$, the residue left is :
(a) 1.16 g (b) 10.8 g
(c) 2.32 g (d) 1.08 g

30. How many gram of dibasic acid (molar mass 200) should be present in 100 mL of the aqueous solution to give 0.1 N solution :
(a) 1 g (b) 1.5 g
(c) 0.5 g (d) 20 g

31. Specific volume of a cylindrical virus particle is 6.02×10^{-2} mL / g, having the radius and length 7 Å and 10 Å respectively. What is the molar mass of virus:
(a) 15.4 kg/mol (b) 1.54×10^4 kg /mol
(c) 4.68×10^4 kg /mol (d) 2.08×10^4 kg /mol

32. Percentage of Se (atomic mass = 78.4) in peroxidase anhydrous enzyme is 0.5% by mass. The minimum molar mass of enzyme is :
(a) 1.568×10^3 (b) 1.568×10^4
(c) 25.68 (d) 4.316×10^4

33. 2.5 litre of 1 *M* NaOH solution is mixed with another 3 litre solution of 0.5 *M* NaOH. The molarity of resultent solution is :
(a) 1.0 *M* (b) 0.84 *M*
(c) 0.73 *M* (d) 0.56 *M*

34. What volume of O_2 gas at 0°C and 1 atm is needed to burn completely one litre of propane under same conditions :
(a) 5 litre (b) 10 litre
(c) 7 litre (d) 6 litre

35. How many mole of lead (II) chloride will be formed from a reaction between 6.5 g PbO and 3.2 g HCl.
(a) 0.011 (b) 0.029
(c) 0.044 (d) 0.33

36. The maximum number of molecules is present in :
(a) 15 litre of H_2 gas at STP
(b) 5 litre N_2 gas at STP
(c) 0.5 g of H_2 gas
(d) 5 g of O_2 gas

37. 27g Al will react completely with .... g oxygen:
(a) 8 (b) 16
(c) 24 (d) 32

38. 10 g $CaCO_3$ contains:
(a) 10 mole of $CaCO_3$ (b) 1g-atom of Ca
(c) 6×10^{22} atoms of Ca (d) 0.1 equivalent of Ca

39. Which of the following has highest mass?
(a) 20 g phosphorus
(b) 5 moles of water
(c) 2 equivalent of Na_2CO_3
(d) 12×10^{24} atoms of hydrogen

40. When the same mass of Zn is treated separately with excess of H_2SO_4 and excess of NaOH, the ratio of volumes of H_2 evolved is:
(a) 1 : 1 (b) 1 : 2
(c) 2 : 1 (d) 9 : 4

41. 2.76 g silver carbonate on heating strongly yields a residue weighing:
(a) 2.16 g (b) 2.48 g
(c) 2.32 g (d) 2.64 g

42. A gaseous mixture contains oxygen and nitrogen in the ratio of 1 : 4 by mass. Therefore the ratio of their molecules is:
(a) 1 : 4 (b) 1 : 8
(c) 7 : 32 (d) 3 : 16

43. The largest number of molecules is in:
(a) 36g H_2O (b) 28g CO
(c) 46g C_2H_5OH (d) 54g N_2O_5

44. 0.50 mole of $BaCl_2$ is mixed with 0.20 mole of Na_3PO_4, the maximum number of mole of $Ba_3(PO_4)_2$ that can be formed is:
(a) 0.70 (b) 0.50
(c) 0.20 (d) 0.10

45. A molal solution is one that contains one mole of solute in :
(a) 1000 g of the solvent (b) 1 litre of the solvent
(c) 1 litre of solution (d) 22.4 litres of solution

46. The pair of compounds which can not exist together in solution is:
(a) $NaHCO_3$ and NaOH (b) Na_2CO_3 and $NaHCO_3$
(c) Na_2CO_3 and NaOH (d) $NaHCO_3$ and NaOH

47. In which mode of expression, the concentration of a solution remains independent of temperature?
(a) Molarity (b) Normality
(c) Formality (d) Molality

48. At 1000° C and 1 atm, if the density of the liquid water is $1.0\,g\,cm^{-3}$ and that of water vapour is $0.006\,g\,cm^{-3}$, then the volume occupied by water molecules in 1 litre of steam at this temperature is:
(a) $6\,cm^3$ (b) $60\,cm^3$
(c) $0.6\,cm^3$ (d) $0.06\,cm^3$

49. The difference in the volume of gases obtained after complete decomposition of 100 mL sample of NH_3 and PH_3 each separately. Given that both produce all the product in vapour state:
(a) 25 mL (b) 50 mL
(c) 75 mL (d) 100 mL

50. The molar ratio of Fe^{2+} and Fe^{3+} ions in a mixture of $FeSO_4$ and $Fe_2(SO_4)_3$ if each component of mixture provides equal no. of sulphate ions :
(a) 2 : 3 (b) 3 : 2
(c) 1 : 2 (d) 1 : 4

51. Number of mole of Na^+ ions in 20 litre of 0.4 M Na_3PO_4 is :
(a) 8 (b) 24
(c) 16 (d) 12

52. 28 g KOH is used to completely neutralize CO_2 produced by heating 60 g impure sample $CaCO_3$. The percentage purity of $CaCO_3$ is :
(a) 83.32 (b) 20.83
(c) 41.66 (d) 40.00

53. An aqueous solution of 6.3 g oxalic acid dihydrate is made upto 250 mL. The volume of 0.1 *N* NaOH required to completely to neutralise 10 mL of this solution is : **(IIT 2001)**
(a) 40 mL (b) 20 mL
(c) 10 mL (d) 4 mL

54. How many mole of electron weigh one kilogram ? **(IIT 2002)**
(a) 6.023×10^{23} (b) $\frac{1}{9.108}\times10^{23}$
(c) $\frac{6.023\times10^{54}}{9.108}$ (d) $\frac{1}{9.108\times6.023}\times10^{8}$

55. 0.02 mole of $[Co(NH_3)_5SO_4]Br$ and 0.02 mole of $[Co(NH_3)_5Br]SO_4$ were used to prepare 2 litre solution. One litre of this solution on treatment with excess of $AgNO_3$ gives *Y* and *Z* respectively. Number of mole of *Y* and *Z* obtained are : **(IIT 2003)**
(a) 0.01, 0.02 (b) 0.02, 0.02
(c) 0.01, 0.01 (d) 0.02, 0.01

56. Which has the maximum number of atoms? **(IIT 2003)**
(a) 24 g C (12) (b) 56 g Fe (56)
(c) 27 g Al (27) (d) 108 g Ag (108)

57. Dissolving 120 g of urea (molar mass 60) in 1000 g of water gave a solution of density 1.15 g/mL. The molarity of the solution is : **(IIT 2011)**
(a) 1.78 *M* (b) 2.00 *M*
(c) 2.05 *M* (d) 2.22 *M*

58. A gaseous hydrocarbon gives upon combustion 0.72 g. of water and 3.08 g. of CO_2. The empirical formula of the hydrocarbon is : **[JEE (Main) 2013]**
(a) C_6H_5 (b) C_7H_8
(c) C_2H_4 (d) C_3H_4

59. The molarity of a solution obtained by mixing 750 mL of 0.5(*M*) HCl with 250 mL of 2(*M*) HCl will be : **[JEE (Main) 2013]**
(a) 1.75 *M* (b) 0.975 *M*
(c) 0.875 *M* (d) 1.00 *M*

SOLUTIONS (One Answer Correct)

1. (b) Mole ratio of Zn : Cr : O

$$= \frac{9.81}{65} : \frac{1.8\times10^{23}}{6.023\times10^{23}} : 0.6$$

$$= 0.15 : 0.30 : 0.6$$

$$= 1 : 2 : 4$$

$\therefore$ $ZnCr_2O_4$

2. (d) Meq. of H^+ = Meq. of $H_2SO_4 = 100\times0.001\times2 = 0.2$

$\therefore$ Number of $H^+ = 0.2\times6.023\times10^{23} = 1.2\times10^{23}$

3. (a) No. of atom of A in a g $= \frac{N\times a}{30} = b$

No. of atoms of B in $2a$ g $= \frac{N\times 2a}{90} = \frac{N\times2\times a}{3\times30} = \frac{b\times2}{3}$

4. (c) Volume of nugget = Volume of gold + Volume of quartz

$$\frac{100}{5} = \frac{a}{20} + \frac{100-a}{4} \quad \therefore \quad a = 25\,g$$

5. (c) Eq. of NaOH = Eq. of $H_2SO_4 = 6\times0.5\times2 = 6$

$\therefore$ $\frac{w}{40} = 6$

$$w_{NaOH} = 240\,g$$

Now, 80 g NaOH $\equiv$ 100 g wet NaOH

$$240\,g\ NaOH = \frac{100\times240}{80} = 300\,g$$

6. (c) Meq. of acid = Meq. of KOH

$$\frac{1}{146/n}\times1000 = \frac{0.768}{56}\times1000 \quad \therefore \quad n = 2$$

7. (a) Let a mL of $6N$ and $(100-a)$ mL of $2N$ are mixed

$\therefore$ $a\times6+(100-a)\times2 = 100\times5$

$\therefore$ $a = 75$ mL

$\therefore$ $(100-a) = 25$ mL

8. (c) Let a g NH_3 is dissolved in 105 mL H_2O or 105 g H_2O

$\therefore$ % by mass of NH_3 in solution $= \frac{a}{105+a} = \frac{30}{100}$

$\therefore$ $a = 45$ g

$\therefore$ Mass of solution $= 105+45 = 150$ g

9. (c)

$$AgNO_3 + BaCl_2 \longrightarrow Ba(NO_3)_2 + AgCl\downarrow$$

Meq. added	10×1	90×1	0	0
	10	90	0	0
	0	80	10	10

$\therefore$ $[BaCl_2] = \frac{80}{2\times100} = 0.4\,M$;

$$Ba(NO_3)_2 = \frac{10}{2\times100} = 0.05\,M$$

$$\text{Ionic strength} = \frac{1}{2}\Sigma CZ^2 = \frac{1}{2}[0.4\times2^2+0.4\times2\times1^2+0.05\times2^2+0.05\times2\times1^2]$$

$$= 1.35$$

10. (a) The volume of a liquid increases with temperature and thus same volume masss more in winter.

11. (a) $w_g = 10$ $W_{Solution} = 100\,g$ $\therefore W_{Solvent} = 90$

$\therefore$ % by mass of solute/mass of solvent

$$= \frac{10}{90}\times100 = 11.11\%$$

12. (b) $E_M = 2\times E_O = 2\times8 = 16$,

$E_{MO} = E_M + E_O = 16+8 = 24$

Let w_1 g of metal gives w_2 g oxide

$$\frac{w_1}{16} = \frac{w_2}{24} \quad \therefore \quad \frac{w_2}{w_1} = \frac{24}{16} = 1.5$$

13. (c) 18 mL $H_2O = 18\,g\ H_2O\,(d = 1\,g/mL)$

$\therefore$ Volume of one water molecule

$$= \frac{18}{6.023\times10^{23}} = 3.0\times10^{-23}\ cm^3$$

$\therefore$ $\frac{4}{3}\pi r^3 = 3.0\times10^{-23}$

$\therefore$ $r = 1.925\ Å$

14. (b) $a = \frac{49}{98}$ mole $H_2SO_4 + \frac{3\times10^{23}}{6\times10^{23}}$ mole H_2SO_4 $-\frac{0.02}{2}$ mole H_2SO_4

$\therefore$ $a = 0.5+0.5-0.01$ mole $H_2SO_4 = 0.99$ mol

15. (c) Molar mass of CO = N_2 $\therefore V_{CO} = V_{N_2}$

16. (c) $[OH^-] = 2\,M$

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$$

c	0	0
$c(1-\alpha)$	$c\alpha$	$2c\alpha$

$\because$ $2c\alpha = 2\,M$

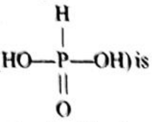
$\therefore$ $c = \frac{2}{2\times\alpha} = \frac{1}{\alpha}$

17. (c) Hardness is mass (in g) of $CaCO_3$ in 10^6 g water $= 10^6$ mL H_2O

$\therefore$ Molarity $= \frac{400\times10^3}{100\times10^6} = 4\times10^{-3}\,M$

18. (b) Volume strength $= 5.6\times$ Normality

19. (d) H_3PO_3



$(HO-\overset{\displaystyle H}{\underset{\displaystyle O}{\overset{|}{\underset{||}{P}}}}-OH)$ is dibasic acid.

20. (b) Let w g solute be dissolved in 60 g water

$\therefore$ Mass of solution $= (w+60)$ g

$$\% \text{ by mass} = 20 = \left[\frac{w}{w+60}\right]\times100$$

$\therefore$ $w = 15$ g

21. (a)

$$H_2 + \frac{1}{2}O_2 \longrightarrow 2H_2O$$

Initial	60	10	0
Find	40	0	–

i.e., Reduction in volume $= 60+10-40 = 30$ mL

22. (a) Let a mL CH_4 be used to form CO and b mL for CO_2

$$2CH_4 + 3O_2 \longrightarrow 2CO + 4H_2O$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

$\therefore$ Volume of O_2 needed $= \frac{3a}{2} + 2b$

Volume of CO formed $= a$

Volume of CO_2 formed $= b$

$\frac{a}{b} = \frac{1}{99}$ (given) ; Also $a + b = 10$

$\therefore a = 0.1$ mL $\therefore b = 9.9$

$\therefore O_2$ needed $= \frac{3 \times 0.1}{2} + 9.9 \times 2 = 19.95$

23. (d) Moles of $BaSO_4 = \frac{1.846}{233}$ (Ba in both)

Moles of $BaCl_2 \cdot XH_2O = \frac{1.936}{(137 + 71 + 18x)}$

$$\therefore \quad \frac{1.936}{137 + 71 + 18x} = \frac{1.846}{233}$$

$$\therefore \quad x = 2$$

24. (a) 100 mL solution $= 100 \times 1.12$ g solution $= 112$ g solution

i.e., 72 gH_2O has 40 gNaCl

$\therefore$ ppm $= \frac{40}{72} \times 10^6 = 5.5 \times 10^5$ ppm

25. (a) No. of atoms in 4g-atom of O $= 4 \times N$

One NH_3 molecule contains 4 atoms

$\therefore 4N$ atom will be present in N molecule of $NH_3 = 17$ g NH_3

26. (b) 1 molecule $Ca_3(PO_4)_2$ has 2 P and 8 O atom

1 molecule H_3PO_3 has 1 P and 3 O atom

If H_3PO_3 sample has 2 P atoms than it should have 6 O atoms

$$\therefore \quad \frac{\text{No. of O in } Ca_3(PO_4)_2}{\text{No. of O in } H_3PO_3} = \frac{8}{6} = \frac{4}{3}$$

27. (a) 1 mole $Ba(OH)_2$ gives 2 mole OH^- and thus requires 2 mole of H^+

1.5 mole $H_3PO_3 = 2 \times 1.5$ mole H^+

$\frac{2}{3}$ mole $H_3PO_4 = 3 \times \frac{2}{3}$ mole H^+

1 mole $H_2SO_4 = 2$ mole H^+

2 mole $H_3PO_2 = 2 \times 1$ mole H^+

28. (b) $$\frac{44}{44} + \frac{56}{2} = \frac{100}{M}$$

$$\therefore \quad M = 3.45$$

$$\therefore \quad \text{V.D.} = 1.72$$

29. (b) $2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$

1 mole (170g) $AgNO_3$ gives 1 mole Ag(108g)

30. (a) $$\text{Meq.} = N \times V$$

$$\frac{w}{200/2} \times 1000 = 0.1 \times 100$$

$$\therefore \quad w = 1.0\text{ g}$$

31. (a) Volume of one virus

$$= \pi r^2 l = \frac{22}{7} \times (7 \times 10^{-8})^2 \times 10 \times 10^{-8}$$

$$= 1.54 \times 10^{-21} \text{ mL}$$

$$\therefore \text{ Molar mass of virus} = \frac{1.54 \times 10^{-21}}{6.02 \times 10^{-2}} \times 6.02 \times 10^{23}$$

$$= 15400 \text{ g/mol} = 15.4 \text{ kg mol}^{-1}$$

32. (a) 0.5 g Se than molar mass $= 100$

78.4 g Se than molar mass $= \frac{100 \times 78.4}{0.5} = 1.568 \times 10^3$

1 molecule of enzyme should contain at least are atom of Se to show minimum molar mass

33. (c) Mole of NaOH in I solution $= 2.5 \times 1 = 2.5$

Mole of NaOH in II solution $= 3 \times 0.5 = 1.5$

Total mole $= 2.5 + 1.5 = 4.0$

$\therefore$ Molarity × total volume = Total mole

$$\therefore \quad M = \frac{4}{5.5} = 0.73 \text{ M}$$

34. (a) $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$

22.4 litre C_3H_8 at NTP requires 5×22.4 litre O_2

35. (b) $PbO + 2HCl \longrightarrow PbCl_2 + H_2O$

Mole at $t = 0$	$\frac{6.5}{224}$	$\frac{3.2}{36.5}$ mole	0	0
	0.029	0.087	0	0
Moleafter reaction	0	0.031	0.029	

36. (a) Mole of H_2 in 15 l $= \frac{15}{22.4} = 0.67$

Mole of N_2 in 5 l $= \frac{5}{22.4} = 0.22$

Mole of H_2 in 0.5 g $= \frac{0.5}{2} = 0.25$

Mole of O_2 in 5 g $= \frac{5}{32} = 0.16$

37. (c) $2Al + \frac{3}{2}O_2 \longrightarrow Al_2O_3$

2 mole of Al reacts with $= \frac{3}{2}$ mole O_2

1 mole of Al reacts with $= \frac{3}{2 \times 2} = \frac{3}{4}$ mole O_2

(27 g) of Al reacts with $= \frac{3}{4} \times 32 = 24$ g O_2

38. (c) 10 g $CaCO_3 = 0.1$ mole $CaCO_3 = 0.1$ mole Ca

$= \frac{0.1}{2}$ eq. Ca $= 6 \times 10^{22}$ atoms Ca $= 0.1$ g -atom Ca

39. (c) $W_P = 20g, W_{H_2O} = 90g, W_{H_2} = 20g$

$W_{Na_2CO_3} = 106g$

40. (a) $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$

41. (a) $\underset{276g}{Ag_2CO_3} \longrightarrow \underset{216g}{2Ag} + CO_2 + \frac{1}{2}O_2$

42. (c) $$\frac{n_{O_2}}{n_{N_2}} = \frac{\frac{w_{O_2}}{32}}{\frac{w_{N_2}}{28}} = \frac{w_{O_2}}{w_{N_2}} \times \frac{28}{32} = \frac{1}{4} \times \frac{28}{32} = \frac{7}{32}$$

43. (a) 36 g $H_2O = 2$ mole H_2O (the largest no. of mole)

44. (d) $3BaCl_2 + 2Na_3PO_4 \longrightarrow Ba_3(PO_4)_2 \downarrow + 6NaCl$

0.50	0.20	0	0
0.20	0.00	0.10	0.60

45. (a) Molality $= \dfrac{\text{Mole of solute}}{\text{mass of solvent in kg}}$

46. (a) $NaHCO_3$ is acid salt and NaOH is base:

$NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$

47. (d) Molality involves only mass which is independent of T.

48. (c) Mass of 1000 mL steam $= 1000 \times 0.0006 = 0.6$g

$\therefore$ Volume of liquid water $= \dfrac{0.6}{1} = 0.6\,\text{cm}^3$

49. (a)

$$\begin{array}{llll} & 2NH_3 & \longrightarrow N_2(g) + & 3H_2(g) \\ \text{V at t} = 0 & 100 & 0 & 0 \\ & 0 & 50 & 150 \end{array}$$

$\therefore\ V_1 = 50 + 150 = 200\,\text{mL}$

$$\begin{array}{llll} & 4PH_3 & \longrightarrow P_4(g) + & 6H_2(g) \\ \text{V at t} = 0 & 100 & 0 & 0 \\ & 0 & 25 & 150 \end{array}$$

$\therefore\ V_2 = 25 + 150 = 175\,\text{mL}$

$\therefore\ \Delta V = 200 - 175 = 25\,\text{mL}$

50. (b) The mixture should contain 3 mole $FeSO_4$ and one mole $Fe_2(SO_4)_3$.

$3FeSO_4 \longrightarrow 3Fe^{2+} + 3SO_4^{2-}$

$Fe_2(SO_4)_3 \longrightarrow 2Fe^{3+} + 3SO_4^{2-}\ \therefore Fe^{2+} : Fe^{3+} :: 3 : 2$

51. (b) Mole of $Na_3PO_4 = 20 \times 0.4 = 8$

1 mole Na_3PO_4 contains 3 mole Na^+ ions

52. (c) Mole of KOH used $= \dfrac{28}{56} = 0.5$

$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$

$\therefore$ Mole of CO_2 required to neutralise KOH $= \dfrac{0.5}{2} = \dfrac{1}{4}$

$CaCO_3 \longrightarrow CaO + CO_2$

$\therefore$ mole of pure $CaCO_3 = \dfrac{1}{4} = 25$ g $CaCO_3$

$\therefore$ % purity $= \dfrac{25}{60} \times 100 = 41.66$

53. (a) Meq. of oxalic acid = Meq. of NaOH

$\dfrac{6.3}{63} \times \dfrac{1000}{250} \times 10 = 0.1 \times V$

$\therefore\ V = 40\,\text{mL}$

54. (d) 9.108×10^{-31} kg = 1 electron

$\therefore\ 1\,\text{kg} = \dfrac{1}{9.108 \times 10^{-31}}$ electron

$= \dfrac{1}{9.108 \times 10^{-31}} \times \dfrac{1}{6.023 \times 10^{23}}$ mole electron

$= \dfrac{10^8}{9.108 \times 6.023}$

55. (c) 0.01 mole of AgBr and 0.01 mole of Ag_2SO_4.

56. (a) 24 g carbon has $\dfrac{24}{12}$ mol

57. (c) Mass of solute = 120 g

Mass of water = 1000 g

Mass of solution = 1120 g

$\therefore$ Volume of solution $\left(\dfrac{m}{d}\right) = \dfrac{1120}{1.15}$ mL

Now Milli mole $= M \times V_{\text{in mL}}$

$\dfrac{120}{60} \times 1000 = \dfrac{M \times 1120}{1.15}$

$\therefore\ M = 2.05$

58. (b) Let the formula of hydrocarbon be C_aH_b

$C_aH_b + O_2 = aCO_2 + \dfrac{b}{2}H_2O$

mole of CO_2 (a) formed $= \dfrac{3.08}{44} = 0.07$

mole of H_2O formed $\left(\dfrac{b}{2}\right) = \dfrac{0.72}{18} = 0.04$

$\therefore\ \dfrac{a}{b/2} = \dfrac{0.07}{0.04}$

or $\dfrac{a}{b} = \dfrac{0.07}{0.08} = \dfrac{7}{8}$

$\therefore$ mole ratio of C and H :: 7 : 8

Thus empirical formula is C_7H_8

59. (c) milli mole of solution I $= 750 \times 0.5 = 375$

milli mole of solution II $= 250 \times 2 = 500$

Total milli mole in mixture $= 375 + 500 = 875$

Total volume = 1000 mL

$\therefore$ Molarity $= \dfrac{875}{1000} = 0.875\,M$

OBJECTIVE PROBLEMS (More Than One Answer Correct).

1. 1 mole of a mixture of CO and CO_2 requires exactly 1 litre solution of 1 *M* NaOH for complete neutralisation. If CO present in mixture is now converted to CO_2 and again the mixture is treated with NaOH, then after this conversion :

(a) mole of CO_2 present initially in mixture = 1

(b) 2 litre NaOH solution of 1 *M* is more required for neutralisation

(c) 2 litre solution of $\frac{1}{2}$ *M* NaOH is required more for neutralisation

(d) 56 g KOH in aqueous solution is required more for neutralisation

2. 2 g of oleum is diluted with water. The solution was then neutralised by 432.5 mL of 0.1 *N* NaOH. Select the correct statements :

(a) % of oleum is 108.11

(b) % of free SO_3 is 26.5 in oleum

(c) Equivalent of H_2SO_4 are 0.03

(d) Equivalent of $SO_3 = 6.625 \times 10^{-3}$

3. Which one is not correct about

$$VO + Fe_2O_3 \longrightarrow FeO + V_2O_5?$$

(a) 2 mole of VO reacts completely with 5 mole of Fe_2O_3

(b) 1 mole of VO reacts completely with 1.5 mole of Fe_2O_3

(c) Eq. mass of $V_2O_5 = M/6$ and of Fe_2O_3 is $M/2$

(d) Eq. mass of VO = $M/3$ and of FeO is $2M/3$

4. 1 mole of H_3PO_3 reacts with NaOH in solution. Select the correct statements:

(a) 1 mole of NaOH will replace *N* H^+ ion from H_3PO_3

(b) 2 mole of NaOH will replace 2 *N* H^+ ions from H_3PO_3

(c) 3 mole of NaOH will replace 3 *N* H^+ ions from H_3PO_3

(d) On complete neutralisation of H_3PO_3, the equivalent mass of $H_3PO_3 = 41$

5. 100 mL of 0.8 *M* NaOH are used to neutralised 100 mL solution obtained by passing 2.70 g SO_2Cl_2 in water. Select the correct statement:

(a) The solution of SO_2Cl_2 has 0.2 *M* H_2SO_4 and 0.4 *M* HCl

(b) The volume ratio of NaOH used for H_2SO_4 and HCl is 1 : 2

(c) The volume ratio of NaOH used for H_2SO_4 and HCl is 1 : 1

(d) Molarity of SO_2Cl_2 solution is 0.1 *M*

6. Which one are correct about the solution that contains 3.42 ppm $Al_2(SO_4)_3$ and 1.42 ppm Na_2SO_4?

(a) $[Al^{3+}] = [Na^+]$

(b) $[SO_4^{2-}] = [Na^+] = [Al^{3+}]$

(c) $[SO_4^{2-}] = [Na^+] + [Al^{3+}]$

(d) $[SO_4^{2-}] = [Na^+]$

7. 1 u is equal to:

(a) 931.48 MeV (b) 1.67×10^{-24} g

(c) $\frac{1}{12}$th mass of C^{12} (d) 1 dalton

8. $\frac{1}{N_A}$ is equal to:

(a) 1.67×10^{-27} kg (b) 1 u

(c) 1 dalton (d) Logschmidt number

9. H_3BO_3 is:

(a) Monobasic acid

(b) Lewis acid

(c) Electron pair acceptor

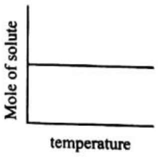
(d) Na_3BO_3 exist as ionic compound

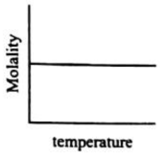
10. Which of the following are primary standard solution?

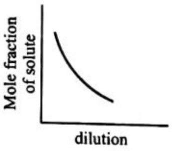
(a) Oxalic acid (b) NaOH

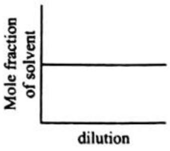
(c) Borax (d) $Na_2CO_3 \cdot 10H_2O$

11. Which of the following graphs correctly represents the variations ?

(a) 

(b) 

(c) 

(d) 

SOLUTIONS (More Than One Answer Correct)

1. (c, d)

$$\underset{a}{\text{CO}} + \underset{b}{\text{CO}_2}$$

$\therefore \quad a + b = 1$

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$

Meq. of CO_2 = Meq. of NaOH $= 1 \times 1000$

$\therefore$ Mole of $CO_2 = \frac{1 \times 1000}{2 \times 1000} = 0.5 \qquad$ (v.f of $CO_2 = 2$)

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2$$

$\therefore$ 0.5 mole CO_2 is formed more.

$\therefore$ NaOH required more = 2 litre of 1/2 M NaOH

$= 56\,g$ KOH = 1 mol KOH

2. (a, b, c)

$$\underset{a}{H_2SO_4} + \underset{b}{SO_3}$$

$\therefore \quad a + b = 2 \qquad$ ...(1)

Also, Meq. of

H_2SO_4 + Meq. of SO_3 = Meq. of NaOH

$$\frac{a}{49} \times 1000 + \frac{b}{40} \times 1000 = 0.1 \times 432.5$$

$\therefore \quad 40a + 49b = 84.77 \qquad$ ...(2)

$\therefore \quad a = 1.47\,g \quad b = 0.53\,g$

$\therefore$ Equivalent of $H_2SO_4 = \frac{1.47}{49} = 0.03$

$\therefore \quad SO_3 + H_2O \longrightarrow H_2SO_4$

Eq. of $SO_3 = \frac{0.53}{40} = 0.01325$

Mass of H_2O to react with SO_3

$= \frac{0.53 \times 18}{80} = 0.11925\,g$

$\because$ 1.47 g H_2SO_4 is associated with 0.53 g H_2O

$\therefore$ 100 g H_2SO_4 is associated with $\frac{0.53 \times 100}{1.47}$ g H_2O

or 8.11 g H_2O

$\therefore$ Solution of oleum is $100 + 8.11 = 108.11\%$

$\therefore$ 108.11% oleum $= 100\,g\ H_2SO_4 + 8.11\,g\ H_2O$

$= 100\,g\ H_2SO_4 + \frac{8.11 \times 80}{18}$

$= 100\,g\ H_2SO_4 + 36\,g\ SO_3$

$= 136\,g$ oleum

136 g oleum has 36 g SO_3

$\therefore$ 2 g oleum has $\frac{36 \times 2}{136} = 0.53\,g\ SO_3$

$\therefore$ % of free $SO_3 = \frac{0.53 \times 100}{2} = 26.5$

3. (b, c, d)

$$2V^{2+} \longrightarrow (V^{5+})_2 + 6e$$

$$2e + (Fe^{3+})_2 \longrightarrow 2Fe^{2+} \times 3$$

$\therefore \quad 2VO + 3Fe_2O_3 \longrightarrow 6FeO + V_2O_5$

$$E = \frac{M}{3} \quad E = \frac{M}{2} \quad E = \frac{M}{3/2} \quad E = \frac{M}{6}$$

4. (a, b, d) H_3PO_3 is dibasic acid.

5. (a, c) $[SO_2Cl_2] = \frac{2.70 \times 1000}{135 \times 100} = 0.2\,M$

$$\begin{array}{llll} SO_2Cl_2 & + \ 2H_2O \longrightarrow & H_2SO_4 & + \ 2HCl \\ 100 \times 0.2 & & & \\ = 20 & & 0 & 0 \\ 0 & & 20 & 40 \end{array}$$

$\therefore \quad M_{H_2SO_4} = \frac{20}{100}; \quad M_{HCl} = \frac{40}{100}$

$\therefore \quad N_{H_2SO_4} = 0.4$ and $N_{HCl} = 0.4$

6. (a, c) 3.42 ppm $Al_2(SO_4)_3 \equiv \frac{96 \times 3 \times 3.42}{342}$ ppm $[SO_4^{2-}]$

$= 2.88$ ppm SO_4^{2-}

$\equiv \frac{27 \times 2 \times 3.42}{342}$ ppm Al^{3+}

$= 0.54$ ppm Al^{3+}

1.42 ppm $Na_2SO_4 \equiv \frac{96 \times 1.42}{142}$ ppm SO_4

$= 0.96$ ppm SO_4^{2-}

$\equiv \frac{46 \times 1.42}{142}$ ppm Na^+

$= 0.46$ ppm Na^+

$$\therefore \quad [Al^{3+}] = \frac{0.54 \times 10^3}{27 \times 10^6} = 2.0 \times 10^{-5}\ M$$

$$[SO_4^{2-}] = \frac{(2.88 + 0.96) \times 10^3}{96 \times 10^6} = 4 \times 10^{-5}\ M$$

$$[Na^+] = \frac{0.46 \times 10^3}{23 \times 10^6} = 2 \times 10^{-5}\ M$$

7. (a,b,c,d) 1u or 1amu = 1dalton. Also amu is replaced by u (now-a-days).

8. (a,b,c) Logschmidt number is referred as the number of molecules of a gas present in 1 mL at STP *i.e.*,

$$\frac{\text{Av. no.}}{22400} = 2.689 \times 10^{19}$$

9. (a,b,c,d) These all are facts.

10. (a,c,d) Standard solution of NaOH can not be prepared by weighing since it reacts with CO_2 on exposure to air.

11. (a,b,c) Mole fraction of solute and solvent change with dilution, however mole of solute remains constant and mole fraction of solute decrease with dilution, mole of solute and molality does not change with temperature.

COMPREHENSION BASED PROBLEMS

Comprehension 1 : Estimation of N in a compound is made by Kjeldahl's method. A sample containing 0.4775 g of $(NH_4)_2C_2O_4$ and inert materials was dissolved in water and made strongly alkaline with KOH, which converted NH_4^+ to NH_3. The liberated ammonia was distilled into exactly 50.0 mL of 0.05035 M H_2SO_4. The excess H_2SO_4 was back titrated with 11.3 mL of 0.1214 M NaOH.

[Molar mass of $(NH_4)_2C_2O_4 = 124.10$ and atomic mass of $N = 14.00$]

[1] Per cent of $(NH_4)_2C_2O_4$:

(a) 10.74 (b) 47.8
(c) 12.74 (d) 42.8

[2] Per cent of N in sample :

(a) 47.8 (b) 40.8
(c) 42.8 (d) 10.74

Comprehension 2 : 50 mL of a solution, containing 1 g each of Na_2CO_3, $NaHCO_3$ and NaOH was titrated with N HCl. What will be the titre readings if :

[1] Only phenolphthalein is used as indicator?

(a) 21.3 mL (b) 55.8 mL
(c) 34.4 mL (d) 68.4 mL

[2] Only methyl orange is used as indicator from the very beginning?

(a) 55.8 mL (b) 21.3 mL
(c) 34.4 mL (d) 68.4 mL

[3] Methyl orange is added after the first end point with phenolphthalein?

(a) 21.3 mL (b) 55.8 mL
(c) 34.4 mL (d) 68.4 mL

Comprehension 3 : HNO_3 used as a reagent has specific gravity of 1.42 g mL^{-1} and contains 70% by strength HNO_3.

[1] Normality of acid is.

(a) 16.78 (b) 15.78
(c) 14.78 (d) 17.78

[2] Volume of acid that contains 63 g pure acid is.

(a) 100 mL (b) 40.24 mL
(c) 63.38 mL (d) 70.68 mL

[3] Volume of water required to make 1N solution from 2 mL conc. HNO_3.

(a) 29.56 mL (b) 30.56 mL
(c) 28.56 mL (d) 31.56 mL

Comprehension 4 : The density of 3M solution of $Na_2S_2O_3$ is 1.25 g mL^{-1}.

[1] The % by mass of $Na_2S_2O_3$ is :

(a) 36.24 (b) 37.92
(c) 40.24 (d) 38.34

[2] Mole fraction of $Na_2S_2O_3$ is :

(a) 0.015 (b) 0.025
(c) 0.065 (d) 0.035

[3] Molalities of Na^+ and $S_2O_3^{2-}$ ions are respectively :

(a) 7.732, 3.866 (b) 3.866, 7.732
(c) 3.732, 7.866 (d) 7.866, 3.732

Comprehension 5 : Oxides of non metals are acidic although N_2O, NO, CO and H_2O are neutral. On the other hand oxides of metals are either amphoteric or basic. However in higher oxidation state same metals forms acidic oxides.

[1] Which is used for absorbing CO :

(a) Amm. $AgNO_3$ (b) Amm. Cu_2Cl_2
(c) Turpentine oil (d) Pyrogallol

[2] SO_2 can be absorbed in :

(a) Lime water (b) Baryta water
(c) KOH (d) All of these

[3] Acetylene can be absorbed in :

(a) Amm. $AgNO_3$ (b) H_2SO_4
(c) NaOH (d) Na_2CO_3

SOLUTIONS

Comprehension 1

[1] (b) Meq. of $(NH_4)_2C_2O_4$ = Meq. of NH_3

= Meq. of H_2SO_4 used

$$\frac{w}{124.10/2} \times 1000 = \text{Meq. of } NH_3 = 3.663$$

[Meq. of H_2SO_4 used

$= (0.05035 \times 2 \times 50 - 11.3 \times 0.1214) = 3.663$]

$\therefore\ w_{(NH_4)_2C_2O_4} = 0.2273$ g

$\therefore$ Percentage of $(NH_4)_2C_2O_4 = \frac{0.2273}{0.4775} \times 100 = \mathbf{47.8\%}$

[2] (d) Meq. of N = Meq. of NH_3

or $\frac{w}{14} \times 1000 = 3.663$

or $w_{N_2} = 0.0513$ g

$\therefore$ Percentage of N $= \frac{0.0513}{0.4775} \times 100 = \mathbf{10.74\%}$

Comprehension 2

[1] (c) The end point using phenolphthalein as indicator uses complete NaOH and half Meq. of Na_2CO_3.

$\therefore$ Meq. of NaOH + $\frac{1}{2}$ Meq. of Na_2CO_3

= Meq. of HCl

$$\frac{1}{40} \times 1000 + \left[\frac{1}{2} \times \frac{1}{53} \times 1000\right] = 1 \times V_1$$

$$V_1 = \mathbf{34.4\ mL}$$

[2] (a) The end point using methyl orange from the beginning uses all the equivalents of bases taken.

$\therefore$ Meq. of NaOH + Meq. of Na_2CO_3 +

Meq. of $NaHCO_3$ = Meq. of HCl

$$\frac{1}{40} \times 1000 + \frac{1}{53} \times 1000 + \frac{1}{84} \times 1000 = 1 \times V_2$$

$\therefore$ $V_2 = \mathbf{55.8\ mL}$

[3] (a) The end point using methyl orange when I end point using phenolphthalein has already been detected, consumes half Meq. of Na_2CO_3 and complete $NaHCO_3$.

$\frac{1}{2}$ Meq. of Na_2CO_3 + Meq. of $NaHCO_3$ = Meq. of HCl

$$\frac{1}{2} \times \frac{1}{53} \times 1000 + \frac{1}{84} \times 1000 = 1 \times V_3$$

$\therefore$ $V_3 = \mathbf{21.3\ mL}$

Comprehension 3

[1] (b) Strength of HNO_3 = 70%

Volume of solution = 100 mL

and Volume of HNO_3 = 70 mL

$\therefore$ Mass of HNO_3 in solution $= 70 \times 1.42$ g

$\therefore$ Eq. of HNO_3 in solution $= \frac{70 \times 1.42}{63}$

$$\therefore\quad N_{HNO_3} = \frac{70 \times 1.42}{63 \times 100/1000} \quad \left(\because N = \frac{\text{Eq.}}{V \text{ in litre}}\right)$$

$= \mathbf{15.78}$

[2] (c) $\because$ 70×1.42 g of pure acid is present in 100 mL

$\therefore$ 63 g of pure acid present in $= \frac{100 \times 63}{70 \times 1.42} = \mathbf{63.38\ mL}$

[3] (a) Meq. of conc. HNO_3 = Meq. of dil. HNO_3

($\because$ Meq. does not change on dilution)

$\therefore\quad 2 \times 15.78 = V \times 1$

$\therefore\quad V = 31.56$ mL

$\therefore$ Volume of water added $= 31.56 - 2 = \mathbf{29.56\ mL}$

Comprehension 4

Molarity of $Na_2S_2O_3$ is 3 *M*.

$\therefore$ Mole of $Na_2S_2O_3 = 3$

$\therefore$ Mass of $Na_2S_2O_3 = 3 \times 158 = 474$ g

and V of solution = 1 litre = 1000 mL

$\therefore$ Mass of solution $= 1000 \times 1.25 = 1250$ g

$\therefore$ Mass of water $= 1250 - 474 = 776$ g

[1] (b) % by mass of $Na_2S_2O_3 = \frac{\text{mass of } Na_2S_2O_3}{\text{mass of solution}} \times 100$

$= \frac{474}{1250} \times 100 = \mathbf{37.92}$

[2] (c) Mole fraction of $Na_2S_2O_3$

$$= \frac{\text{Mole of } Na_2S_2O_3}{\text{Mole of } Na_2S_2O_3 + \text{Mole of } H_2O}$$

$$= \frac{3}{3 + 776/18} = \mathbf{0.065}$$

[3] (a) Molality of $Na^+ = \frac{\text{Mole of } Na^+}{\text{Mass of water in g}} \times 1000$

$= \frac{6 \times 1000}{776} = \mathbf{7.732}$

Molality of $S_2O_3^{2-} = \frac{3 \times 1000}{776} = \mathbf{3.866}$

Comprehension 5

[1] (b) It is a fact.

[2] (d) SO_2 is acidic oxide and reacts with bases.

[3] (a) $CH \equiv CH + AgNO_3 \longrightarrow AgC \equiv CAg$

STATEMENT EXPLANATION PROBLEMS

Read the following statements (**S**) and explanations (**E**). Choose the correct answers from the codes (a), (b), (c) and (d) :

(a) **S** is correct but **E** is wrong
(b) **S** is wrong but **E** is correct
(c) Both **S** and **E** are correct and **E** is correct explanation of **S**
(d) Both **S** and **E** are correct but **E** is not correct explanation of **S**

1. S : Equivalent mass of H_3BO_3 and Na_3BO_3 are $M / 3$.
E : Equivalent mass of H_3BO_3 is M/1 and Na_3BO_3 is M/3.

2. S : 1 equivalent of H_2SO_4 contains 1 equivalent of H, S and O each.
E : A species contains same number of equivalents of its components.

3. S : Equivalent mass of ozone in the change $O_3 \longrightarrow O_2$ is 8.
E : 1 mole of O_3 on decomposition gives 3 /2 mole of O_2.

4. S : CO and C_2H_2 both can be absorbed in ammoniacal CuCl.
E : CH_4 is absorbed on animal charcoal.

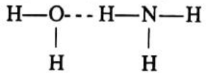
5. S : Acidimetry and alkalimetry are the terms used in volumetric analysis.
E : The reactant left after the chemical reaction is called limiting reagent.

6. S : $NaNO_3$ has no definite mclecule.
E : Its formula mass is 85.

7. S : 31.26 mL of 0.165 M solution of $Ba(OH)_2$ is exactly neutralised by 25 mL of citric acid $C_6H_8O_7$ of molarity 0.138.
E : The acid is tribasic in nature.

8. S : 1 equivalent of $K_2Cr_2O_7$ has 1 equivalent of K, Cr and O each.
E : Equivalent and milliequivalent reacts in equal number to give same equivalent of product.

9. S : The H-bonding of NH_3 and H_2O is represented as:



$$\begin{array}{c}H—\underset{\displaystyle H}{\underset{|}{O}}\text{- - -}H—\underset{\displaystyle H}{\underset{|}{N}}—H\end{array}$$

E : H_2O is more acidic than NH_3 and thus, H_2O is a proton donor.

10. S : H_3BO_3 is monobasic Lewis acid but salt Na_3BO_3 exist.
E : H_3BO_3 reacts with NaOH to give Na_3BO_3.

11. S : Av. No. was proposed 6.019×10^{23} on O–16 scale and 6.02×10^{23} on C–12 scale.
E : The numerical value of Avogadro's number depends upon the atomic mass scale.

12. S : Atomicity of phosphorus is four.
E : Atomicity is the number of atoms present in 1 molecule.

13. S : Density = specific gravity × 0.99823 at 20°C.
E : Density = specific gravity at 4°C.

14. S : Density is expressed as g mL^{-1} whereas specific gravity is dimension less.
E : Specific gravity is ratio of the masses of solution and solvent.

15. S : In the titration of Na_2CO_3 with HCl using methyl orange indicator, the volume of acid required is twice that of the acid required using phenolphthalien as indicator.
E : Two moles of HCl are required for the complete neutralisation of one mole of Na_2CO_3.

16. S : Sulphate is estimated as $BaSO_4$ and not as $MgSO_4$.
E : Ionic radius of Mg^{2+} is smaller than Ba^{2+}.

17. S : Atomic masses of most of the elements are fractional.
E : Atomic mass $= \frac{\Sigma MX}{100}$; where M is mass of isotope and X is its % abundance.

18. S : Analytical molarity of 1 M HCl is zero.
E : Equilibrium molarity of 1 M HCl is zero.

19. S : Equivalence point is a theoretical value.
E : End point is an experimental value.

20. S : Actual yield in case of most of the reaction is lesser than theoretical yield.
E : The reactants are either not 100% pure or some side reactions follows.

ANSWERS (Statement Explanation Problems)

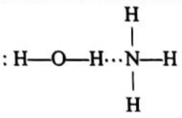
1. (b) H_3BO_3 is monobasic acid; Na_2CO_3 is a salt having total charge on cation or anion = 3
2. (c) Equivalent reacts in equal number.
3. (d) $2O_3 \longrightarrow 3O_2$,

   i.e., 2 mole $O_3 \equiv 3$ mole $O_2 = 3 \times 4$ eq. O_2

   $$\therefore \quad E_{O_3} = \frac{M}{6} = \frac{48}{6} = 8$$
4. (d) Both are facts.
5. (a) The reactant used is called limiting reagent.
6. (d) $NaNO_3$ has solid lattice.
7. (c) Meq. of $Ba(OH)_2$ = Meq. of acid

   $$31.26 \times 0.165 \times 2 = 25 \times M \times n = 25 \times 0.138 \times n$$

   $$\therefore \quad n = 3$$
8. (c) Explanation is correct reason for statement.
9. (b) H—bonding is as :



$$H—O—H \cdots \underset{\displaystyle H}{\overset{\displaystyle H}{N}}—H$$

10. (a) $B(OH)_3 + NaOH \longrightarrow Na[B(OH)_4]$
11. (c) Explanation is correct reason for statement.
12. (c) — do —
13. (d) Both are facts.
14. (c) Statement is correct reason for statement.
15. (d) $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$,

    phenolphthalein is used for

    $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl + CO_2$
16. (d) $BaSO_4$ is insoluble.
17. (c) Explanation is correct reason for statement.
18. (b)

    $$\begin{array}{lccc} & HCl \longrightarrow & H^+ \; + & Cl^- \\ & 1 & 0 & 0 \\ \text{After dissociation} & 0 & 1 & 1 \end{array}$$
19. (d) These are facts.
20. (c) Explanation is correct reason for statement.

MATCHING TYPE PROBLEMS

Type I : Only One Match Possible

1. Match the given concentrations with their property.

Concentration	**Property**
A. Molality	a. Ionic solute
B. Ionic strength	b. Very low concentration
C. ppb	c. $\frac{1}{2}\Sigma CZ^2$
D. Formality	d. Independent of temperature

2.

List-A **Gases**	**List-B** **Adsorbents**
A. Cl_2	a. $FeSO_4$ solution
B. O_3	b. Alkaline pyragallol
C. NO	c. Turpentine oil
D. CO	d. $NaOH_{aq.}$ or $KOH_{aq.}$
E. O_2	e. Amm. $CuCl_2$

Type II : More Than One Match Are Possible

3. Experimental determination of molar mass of compounds may be made by the following methods. Match them properly. More than one match are possible :

A. Gases	a. Victor Meyer's method
B. Volatile liquids	b. Hofmann's method
C. Non volatile solids	c. Duma's method
D. Solids of low m. mass	d. Ebullioscopy or cryoscopy
E. Solids of high m. mass such as polymers	e. Osmotic pressure
	f. Raoult's law

4.

List A	**List B**
A. 1.8 mL H_2O_l ($d = 1\,g/mL$)	a. $\frac{1}{10}N_A$ molecules of H_2O
B. 1.8 mL H_2O_v at STP	b. 2.24 litre at STP H_2O_v
C. 8.03×10^{-5} mole $H_2O(v)$	c. 1.8 g of H_2O_v
	d. 1.446×10^{-3} g H_2O
	e. 4.84×10^{19} molecules of H_2O

5.

List-A **Concentrations expressed in**	**List-B** **Factors influencing**
A. Molarity	a. Temperature
B. Molality	b. Dilution
C. Mole fraction of solute	c. Addition of solute
D. Strength of solution	

6.

List-A **Adsorbent**	**List-B** **Gases**
A. Lime water	a. SO_2
B. Conc. H_2SO_4	b. H_2S
C. Heated Mg	c. H_2O_v
	d. NH_3
	e. O_2
	f. N

ANSWERS

1. A–d; B–c; C–b; D–a.
2. A–d; B–c; C–a; D–e; E–b.
3. A–a, b, c; B–a, b, c, f; C–d, e, f; D–d, f; E–e.
4. A–a, b, c; B–d, e; C–d, e.
5. A–a, b, c; B–b, c; C–b, c; D–a, b, c.
6. A–a, b; B–c, d; C–e, f.

3

Atomic Structure

Fundamental particles of atom

(1) Atom consists of two parts

(a) *Nucleus:* Contains neutrons and protons.

(b) *Extra nuclear part:* Contains electrons.

(2) The characteristics of fundamental particles are given below :

Particle	Symbol	Mass in amu	Mass in kg	Charge in esu	Charge in coulomb
Electron	$_{-1}e^0$	0.000548	9.1091×10^{-31}	-4.803×10^{-10}	-1.602×10^{-19}
Proton	$_{+1}p^1$	1.00757	1.6725×10^{-27}	$+4.803 \times 10^{-10}$	$+1.602 \times 10^{-19}$
Neutron	$_0n^1$	1.00893	1.6748×10^{-27}	0	0

Note : 1. The radius of electron is 4.28×10^{-14} cm

2. The radius of proton is 1.53×10^{-13}cm

Atomic number (Z):

$\because$ Z = No. of protons in the nucleus of an atom

= No. of electrons in the extra nuclear part of neutral atom.

Mass number (A): It is equal to sum of numbers of protons and no. of neutrons in an atom or the number of nucleons.

$$A = p + n \qquad ...(1)$$

Size of the nucleus: (1) The size of the various nuclei (r) can be calculated from

$$\text{radius } (r) = (1.3 \times 10^{-13}) A^{1/3} \qquad ...(2)$$

where A is the mass no. and r is the radius of nucleus in cm.

(2) If nucleus is assumed to be spherical, the density of nucleus (d) may be expressed as

$$d = \frac{\text{Mass of nucleus}}{\text{Volume of nucleus}} = \frac{\text{Mass no.}}{\text{Avogadro's no.}} \times \frac{1}{4/3\pi r^3} ...(3)$$

(3) The dimensions of nucleus are of the order of 10^{-6} nm.

(4) The dimensions of atom are of the order of 10^{-1} nm.

(5) The density of nucleus $= 1.68 \times 10^{14}$ g cm^{-3}

Theory of relativity and velocity of particle: According to the theory of relativity, the mass (m_1) of a particle (electron) at high speed is given by

$$m_1 = \frac{m}{\sqrt{\left[1 - \left(\frac{u}{c}\right)^2\right]}} \qquad ...(4)$$

where m is the mass in the rest; u is velocity and c is velocity of light

If $\quad u = c, \quad$ then $\quad m_1 = \infty$

Planck's quantum theory: Radiant energy is emitted or absorbed only in discrete units or packets of energy called photon (quantum). The energy 'E' associated with a quantum is given by $E = h\nu$ where h is Planck's constant and ν is frequency of radiations.

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu} \qquad \left(\because \frac{1}{\lambda} = \bar{\nu}\right) \quad ...(5)$$

$$h = 6.625 \times 10^{-34} \text{ J-sec} = 6.625 \times 10^{-27} \text{ erg - sec}$$

c is velocity of light $= 3.0 \times 10^8$ m sec^{-1}

$= 3.0 \times 10^{10}$ cm sec^{-1}

ν is frequency of light in sec^{-1}, $\bar{\nu}$ is wave no. in m^{-1} or cm^{-1}.

It is thus clear that energy of photon decreases with increase in λ.

Note : Energy 'E' associated with a photon can also be written as

$$E = \frac{12375}{\lambda} \text{eV}$$

where E is energy in eV and λ is wavelength of light in Å.

Bohr's model for H or H like atoms, *i.e.*, one electron systems

(1) The electrons are in continuous motions round the nucleus in closed orbits of definite energy level known as shells. Shells are named as *K*, *L*, *M*, *N*... or numbered as 1, 2, 3, 4, ... from the nucleus. As the distance of shell increases from the nucleus, energy level of shell increases.

(2) As long as an electron occupy a definite energy level, it does not radiate out energy. The emission or absorption of energy occurs only when electron jumps from one level to other

$$\Delta E = E_{n_2} - E_{n_1} = hv \qquad \text{...(6)}$$

If $n_2 > n_1$ emission spectra

If $n_2 < n_1$ absorption spectra

(3) The angular momentum of electron in closed shell is always quantized, *i.e.*, integer multiple of $h/(2\pi)$.

$$\text{Angular momentum} = n \cdot \frac{h}{2\pi} \quad \text{or} \quad mur = n \cdot \frac{h}{2\pi} \qquad \text{...(7)}$$

Some important results of Bohr's model

For H atom or H like atoms, *i.e.*, He^+, Li^{2+}...

Radius: $r_n = n^2 \times r_1$ and $r_n = \dfrac{n^2h^2}{4\pi^2me^2Z}$ ...(8)

where Z is at. no., e is charge on electron, m is mass of electron and n is no. of shell.

and for H atom $\quad r_1 = 0.529$ Å ...(9)

Energy: $\quad E_T = \text{PE} + \text{KE}$

where E_T is total energy of an electron in a shell.

$$\text{PE is potential energy} = -\frac{Ze^2}{r_n}$$

$$\text{KE is kinetic energy} = \frac{1}{2}\frac{Ze^2}{r_n}$$

$$\therefore \quad E_T = -\frac{Ze^2}{r_n} + \frac{1}{2}\frac{Ze^2}{r_n} = -\frac{Ze^2}{2r_n} \qquad \text{...(10)}$$

$$\therefore \quad E_T = \frac{1}{2}\text{PE} \qquad \text{...(11)}$$

$$\text{KE} = -\frac{\text{PE}}{2} \qquad \text{...(12)}$$

Also, by Eqs. (8) and (10), we get

$$E_T = -\frac{2\pi^2me^4Z^2}{n^2h^2} \qquad \text{...(13)}$$

$$\text{for H atom, } E_T = -\frac{21.72 \times 10^{-12}}{n^2}\text{ erg}$$

$$= -\frac{21.72 \times 10^{-19}}{n^2}\text{ joule} = -\frac{13.6}{n^2}\text{ eV}$$

These equations also reveal that

$$E_n \propto -\frac{1}{n^2} \quad \text{and} \quad E_n = \frac{E_1}{n^2} \qquad \text{...(14)}$$

where E_n and E_1 are energy levels in *n*th shell and 1st shell.

$$\text{Also} \quad r_{\text{H like atom}} = \frac{r_{\text{for H}}}{Z} \qquad \text{...(15)}$$

$$\text{and} \quad E_{n\ \text{H like atom}} = E_{n\ \text{for H}} \times Z^2 \qquad \text{...(16)}$$

Velocity of electron in an orbit :

For H like atom: $u_n = \dfrac{2\pi Ze^2}{nh}$ ...(17)

For H atom: $u_n = \dfrac{2\pi e^2}{nh}$ ...(18)

$$\therefore \quad u_n = \frac{u_1}{n} \qquad \text{...(19)}$$

where u_1 is velocity of electron in 1st orbit.

Time required (T) to complete one revolution by an electron round the nucleus in an orbit :

$$T = \frac{2\pi r_n}{u_n} \qquad \text{... (20)}$$

Number of revolution per sec. made by an electron round the nucleus in an orbit :

$$\text{number of revolution} = \frac{u_n}{2\pi r_n} \qquad \text{... (21)}$$

Note: (1) The use of above formulae from Eqs. (8) to (21) is permitted only in CGS units. If MKS units are used: the factor $\dfrac{1}{4\pi\varepsilon_0}$ should be used accordingly.

In CGS $\quad \dfrac{1}{4\pi\varepsilon_0} = 1$

In MKS $\quad \dfrac{1}{4\pi\varepsilon_0} = 9 \times 10^9\ \text{Nm}^2\text{C}^{-2}$

(2) If +13.6 eV energy is given to H atom, the electron in H atom will be knocked out giving rise to the formation of H^+. That is why ionisation potential of H = 13.6 eV, *i.e.*, the energy level of 1st shell with a negative sign.

Frequency (ν), wavelength (λ) and wave number ($\bar{\nu}$) during electronic transition :

$$\Delta E = E_{n_2} - E_{n_1} = \frac{hc}{\lambda} = h\nu = hc\bar{\nu}$$

$$\text{or} \quad h\nu = \frac{hc}{\lambda} = \frac{2\pi^2me^4Z^2}{h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\text{or} \quad \frac{1}{\lambda} = \bar{\nu} = \frac{2\pi^2mZ^2e^4}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\bar{\nu} = \frac{1}{\lambda} = Z^2R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \qquad \text{...(22)}$$

where λ is the wavelength of radiations during electronic transition from n_2 to n_1. R_H is Rydberg constant and is equal to 109678 cm^{-1}.

(1) When $n_1 = 1$ $\quad n_2 = 2, 3, 4$ ...Lyman series in UV region

(2) When $n_1 = 2$ $n_2 = 3, 4, 5$ ...Balmer series in visible region

(3) When $n_1 = 3$ $n_2 = 4, 5, 6$ ...Paschen series in IR region

(4) When $n_1 = 4$ $n_2 = 5, 6, 7$ ...Brackett series in IR region

(5) When $n_1 = 5$ $n_2 = 6, 7, 8$ ...Pfund series in IR region

To derive no. of subshell in a shell

A result of Sommerfeld model suggests that

$$\frac{n}{k} = \frac{\text{length of major axis}}{\text{length of minor axis}} \qquad \text{...(23)}$$

e.g., if principal quantum no. $n = 4$

The values of k can be 1, 2, 3, 4 only, since k is an integer

$\therefore$ 4th shell have 4 subshells.

Total spin and magnetic moment: The total spin (s) of an atom is given by $s = \frac{1}{2} \times n$, where n is number of unpaired electrons.

The spin magnetic moment (μ) of electron (excluding orbital magnetic moment) in Bohr Magneton (B.M.) is given by:

$$\mu_{\text{effective}} = \sqrt{4s(s+1)} \qquad \text{...(24)}$$

If $\quad s = \frac{1}{2} \times n$

$$\therefore \quad \mu_{\text{effective}} = \sqrt{n(n+2)}\ \text{B.M.} \qquad \text{...(25)}$$

To derive the possible no. of λ in line spectrum when an electron de-excites from one level to other.

If an electron jumps from n_2 into n_1 orbit then $\Delta n = (n_2 - n_1)$ and possible number of λ given out during the jump $= \Sigma \Delta n$ ...(26)

Say an electron is in 4th shell in H atom. It is to be de-excited to ground state level, *i.e.*, 1st shell.

The possible no. of λ given out $= \Sigma \Delta n = \Sigma(4-1)$

$= \Sigma 3 = 1 + 2 + 3 = 6$

Particle and wave nature of electron, *i.e.*, dual nature.

de Broglie proposed a relationship in between λ of a moving particle with its velocity on the basis of quantum theory.

$$\lambda = \frac{h}{mu} = \frac{h}{P} = \frac{h}{\sqrt{2m(\text{KE})}} \quad (\because \text{KE} = \frac{1}{2}mu^2) \qquad \text{...(27)}$$

where m is mass of moving particle

u is its velocity

P is momentum of particle equal to mu or $\sqrt{2m(\text{KE})}$

h is Planck's constant.

The circumference of the nth orbit (if closed) is equal to integer multiple of wavelength.

Thus, $\quad 2\pi r_n = n\lambda$

Also, Frequency (ν) of matter wave

$$= \frac{u}{\lambda} = \frac{u}{h/mu} = \frac{mu^2}{h} = \frac{2\text{KE}}{h} \qquad \text{...(28)}$$

Heisenberg's uncertainty principle:

According to this principle, it is impossible to determine momentum and position of a subatomic particle precisely and simultaneously.

$$\Delta p \cdot \Delta x \geq \frac{h}{4\pi} \qquad \text{...(29)}$$

$$m \cdot \Delta u\, \Delta x \geq \frac{h}{4\pi}$$

$$\Delta u \cdot \Delta x \geq \frac{h}{4\pi m} \qquad \text{...(30)}$$

where Δp is uncertainty in momentum, Δx is uncertainty in position and Δu is uncertainty in velocity.

The four quantum numbers: The four quantum numbers are results of Schrodinger wave equation.

(1) Principal quantum no.

(a) Denoted by 'n'

(b) The values of 'n' are from 1 to n

$n=1$	K shell
$n=2$	L shell
$n=3$	M shell
$n=4$	N shell

(c) 'n' signify for the size and energy level of major energy shell.

(2) Azimuthal or angular quantum no.

(a) Denoted by 'l'

(b) The values of 'l' are from 0 to $(n-1)$

$l=0$	s subshell
$l=1$	p subshell
$l=2$	d subshell
$l=3$	f subshell

(c) 'l' signify for shape and energy level of subshells.

(3) Magnetic quantum no.

(a) Denoted by 'm'

(b) The values of 'm' are from $\pm l$ to $\mp l$

$$\begin{array}{lllllll} \text{Let} & l=1 & m=-1 & 0 & & +1 & \\ & & p_x \text{ or } p_y & p_z & & p_y \text{ or } p_x & \\ \text{Let} & l=2 & m=-2 & -1 & 0 & +1 & +2 \\ & & d_{xy} \text{ or} & d_{xz} \text{ or} & d_{z^2} & d_{yz} \text{ or} & d_{x^2-y^2} \\ & & d_{x^2-y^2} & d_{yz} & & d_{xz} \text{ or} & d_{xy} \end{array}$$

(c) 'm' signify for the possible no. of orientations of subshells.

(4) Spin quantum no.

(a) Denoted by 's'

(b) The values of 's' are $+\frac{1}{2}$ and $-\frac{1}{2}$

(c) '*s*' signify for the direction of spin of electron in a sub-subshell or orbital.

Angular momentum

Angular momentum of an electron in an orbit $= n\dfrac{h}{2\pi}$ ...(31)

Angular momentum of an electron in an orbital

$$= \frac{h}{2\pi} \times \sqrt{[(l+1)l]} \qquad ...(32)$$

Pauli exclusion principle

(1) It is impossible for two electrons of an atom to have all their four quantum no. same.

(2) *e.g.,* $\boxed{\uparrow\downarrow}$ is correct for $1s^2$

$\boxed{\uparrow\uparrow}$ is wrong for $1s^2$

(3) Following results have been obtained by Pauli exclusion principle.

(a) Maximum no. of electrons in a shell can be $2n^2$.

(b) Maximum no. of electrons in a subshell can be 2, 6, 10, 14, in *s, p, d, f* respectively.

(c) Maximum no. of electrons in a sub-subshell is 2 only.

Note: Electronic transition between subshells is possible only when $\Delta l = \pm 1$.

Aufbau principles

The electronic configuration is written on the basis of following rules.

(1) The electrons in a poly electronic atom are filled one by one in order of increasing energy level.

e.g., ${}_1$H: $1s^2$ is correct

$2s^2$ is wrong

because energy level of $1s < 2s$.

(2) Hund's rules:

(a) In filling a group of orbitals of equal energy (or subshells) it is preferred to assign electrons to empty orbitals rather than pair them in a particular subshell, because the former arrangement leads to lower energy level.

(b) Same spin of unpaired electrons in sub-subshell also gives rise to lower energy level.

e.g., ${}_7$H: $1s^2, 2s^2 2p^3$

For $2p^3$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ is correct

$\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{}$ is wrong (statement *a*)

$\boxed{\uparrow}\boxed{\downarrow}\boxed{\uparrow}$ is wrong (statement *b*)

(3) (*n* + *l*) rule:

(a) The subshell with lower values of $(n + l)$ possesses lower energy level and should be filled first.

e.g., ${}_{19}$K: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1$ is wrong

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1$ is correct

$n + l$ of $4s = 4 + 0 = 4$

$n + l$ of $3d = 3 + 2 = 5$

Thus, $4s$ should be filled first.

(b) If $(n + l)$ is same for two subshells, the one with lower values of *n* possess lower energy and should be filled first.

e.g., ${}_{21}$Sc: $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 4p^1$ is wrong

$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1, 4s^2$ is correct

$n + l$ of $4p = 4 + 1 = 5$

$n + l$ of $3d = 3 + 2 = 5$

Thus, $3d$ should be filled first. $\because$ n of $3d < n$ of $4s$

(4) A subshell having nearly completely filled or nearly half filled configuration tends to acquire exactly completely filled or exactly half filled nature in order to attain stability, *i.e.,* lower energy level.

e.g., ${}_{24}$Cr: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^4, 4s^2$ is wrong

$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$ is correct

${}_{29}$Cu: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^9, 4s^2$ is wrong

$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$ is correct

${}_{46}$Pd: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^8$, $5s^2$ is wrong

$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}$ is correct

Photo Electric Effect

When a photon strikes the metallic surface, it gives up its energy to the electron. Part of this energy (say *W*) is used by the electrons to escape from the metal, the remaining imparts the kinetic energy $\left(\frac{1}{2}mu^2\right)$ to the photoelectrons. If the incident radiation has frequency *ν*, then its photons have energy *hν*, it follows from the conservation of energy principle that

$$h\nu = W + \left(\frac{1}{2}\right)mu^2 \qquad ...(33)$$

or

$$\left(\frac{1}{2}\right)mu^2 = h\nu - W \qquad ...(34)$$

The equation shows that if KE is plotted against frequency of incident radiations, a straight line is obtained with a slope equal to Planck's constant. The equation expresses the fact that if a photon strikes a metal then it can release an electron from the metal provided the photon energy (*i.e.,* *hν*) is greater than the binding energy or work function (*W*) of the electron in the metal. Further the released electron will escape out with kinetic energy equal to ($h\nu - W$).

Instead of irradiating a metal, one can irradiate atoms with photons of known frequency, the above equation may be written as: $h\nu = \text{IE} + \text{KE}$.

This suggests that the photon energy is partly used to knock out an electron from the atom (*i.e.*, IE) and the remainder shows up as the kinetic energy of the released photoelectron.

The potential applied on the surface to reduce the velocity of photo-electron to zero is known as stopping potential V_0, thus, kinetic energy $= eV_0$

Thus, $h\nu = W + (\text{Stopping potential} \times \text{charge})$

$$h\nu = W + eV_0 \qquad ...(35)$$

where e is electronic charge and V_0 is stopping potential.

Number of Nodes

Total number of nodes in a shell $= (n - 1)$ ...(36)

Angular nodes $= l$ ...(37)

Spherical nodes $= n - l - 1$ ...(38)

Wave function of H atom in ground state:

$$\text{Wave function, } \psi_{1s} = \left[\frac{1}{\sqrt{\pi a_0^3}}\right] e^{-r/a_0} \qquad ...(39)$$

• NUMERICAL PROBLEMS •

1. The mass-charge ratio for A^+ ion is 1.97×10^{-7} kg C^{-1}. Calculate the mass of A atom.

2. Calculate the force of attraction between an electron and a body having two proton charge when they are 0.529×10^{-8} cm apart. Charge on one electron and one proton is -1.6×10^{-19} C and $+1.6 \times 10^{-19}$ C.

3. Two carbon discs of 1.0 g each are 1.0 cm apart have equal and opposite charges. If forces of attraction between them is 1.00×10^{-5} N, calculate the ratio of excess electrons to total atoms on the negatively charged disc. (Permitivity constant is 9.0×10^9 N m^2C^{-2})

4. α-particles of 6 MeV energy is scattered back from a silver foil. Calculate the maximum volume in which the entire positive charge of the atom is supposed to be concentrated. (Z for silver = 47)
$K = 9.0 \times 10^9$ Nm^2C^{-2}.

5. What is the relationship between eV and the wavelength in metre of the energetically equivalent photon?

6. What is the mass of one photon?

7. Write down the numerical value of h and its unit.

8. Calculate the energy per quantum associated with light of wavelengths,
(a) 5890 Å (b) 250×10^{-9} m
(c) 4.0×10^{-8} cm (d) 600 nm
Also calculate the energy per mol of photon in case (d).

9. AIR service on Vividh Bharati is transmitted on 219 m band. What is its transmission frequency in Hertz?

10. A certain laser transition emits 6.37×10^{15} quanta per second per square metre. Calculate the power out put in joule per square metre per second. Given $\lambda = 632.8$ nm.

11. The dissociation energy of H_2 is 430.53 k J mol^{-1}. If H_2 is exposed to radiation energy of wavelength 253.7 nm, what % of radiant energy will be converted into kinetic energy?

12. Iodine molecule dissociates into atoms after absorbing light of 4500 Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms. (Bond energy of $I_2 = 240$ k J mol^{-1}) **(IIT 1995)**

13. A bulb emits light of λ 4500 Å. The bulb is rated as 150 watt and 8% of the energy is emitted as light. How many photons are emitted by the bulb per second? **(IIT 1995)**

14. Calculate the number of photons emitted in 10 hour by a 60W sodium lamp. ($\lambda_{photon} = 5893$ Å)

15. Calculate the energy required to excite one litre of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H—H bond is 436 k J mol^{-1}. **(IIT 2000)**
Also calculate the minimum frequency of photon to break this bond.

16. Suppose 10^{-17} J of light energy is needed by the interior of the human eye to see an object. How many photons of green light ($\lambda = 550$ nm) are needed to generate this minimum amount of energy?

17. O_2 undergoes photochemical dissociation into one normal oxygen atom and one oxygen atom, 1.967 eV more energetic than normal. The dissociation of O_2 into two normal atoms of oxygen requires 498 k J mol^{-1}. What is the maximum wavelength effective for photochemical dissociation of O_2?

18. A certain dye absorbs light of $\lambda = 4530$ Å and then fluorescence light of 5080 Å. Assuming that under given conditions 47% of the absorbed energy is re-emitted out as fluorescence, calculate the ratio of quanta emitted out to the no. of quanta absorbed.

19. A photon of 300 nm is absorbed by a gas and then re-emits two photons. One re-emitted photon has wavelength 496 nm. Calculate energy of other photon re-emitted out.

20. Certain sun glasses having small crystals of AgCl incorporated in the lenses, on exposure to light of appropriate wavelength turns to gray colour to reduce the glare following the reaction:

$$AgCl \xrightarrow{h\nu} \underset{(Gray)}{Ag} + Cl$$

If the heat of reaction for the decomposition of AgCl is 248 k J mol^{-1}, what maximum wavelength is needed to induce the desired process?

21. Atomic radius is of the order of 10^{-8} cm and nuclear radius is of the order of 10^{-13} cm. Calculate what fraction of atom is occupied by nucleus?

22. Prove that $u_n = \sqrt{\left(\frac{Ze^2}{mr_n}\right)}$ where u is velocity of electron in a one electron atom of at. no. Z at a distance r_n from the nucleus, m and e are mass and charge of electron.

23. Calculate the velocity of an electron placed in III orbit of H atom. Also calculate the no. of revolution/sec round the nucleus.

24. Find out the energy of H atom in first excitation state. The value of permitivity factor $4\pi\varepsilon_0 = 1.11264 \times 10^{-10}$ C^2 $N^{-1}m^{-2}$.

25. Consider the hydrogen atom to be a proton embedded in a cavity of radius a_0 (Bohr's radius), whose charge is neutralized by the addition of an electron to the cavity in vacuum, infinitely slowly.

(a) Estimate the average of total energy of an electron in its ground state in a hydrogen atom as the work done in the above neutralization process. Also, if the magnitude of the average kinetic energy is half the magnitude of the average potential energy, find the average potential energy. **(IIT 1996)**

(b) Also derive the wavelength of the electron when it is a_0 from the proton. How does this compare with the wavelength of an electron in the ground state Bohr's orbit?

26. What is the principal quantum no. of H atom orbital if the electron energy is $-3.4\,\text{eV}$? Also report the angular momentum of electron.

27. The velocity of electron in a certain Bohr's orbit of H atom bears the ratio $1:275$ to the velocity of light :

(a) What is the quantum number (n) of orbit?

(b) Calculate the wave number of radiations emitted when electron jumps from $(n+1)$ state to ground state.

28. The ionisation energy of H atom is 13.6 eV. What will be ionisation energy of He^+ and Li^{2+} ions?

29. The ionisation energy of He^+ is 19.6×10^{-18} J atom^{-1}. Calculate the energy of first stationary state of Li^{2+}.

30. Electromagnetic radiations of wavelength 242 nm is just sufficient to ionise sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1}.

(Roorkee 1992)

31. Calculate the shortest and longest wavelength in H spectrum of Lyman series. $R_H = 109678\,\text{cm}^{-1}$.

32. Convert the value of Rydberg constant ($R_H = 109678\,\text{cm}^{-1}$) into Rydberg an unit of energy (*i.e.*, 1 Rydberg (1 Rh) $=2.18\times10^{-18}$ J).

33. How many spectral lines are emitted by atomic hydrogen excited to the *nth* energy level?

34. Calculate the Rydberg constant R if He^+ ions are known to have the wavelength difference between the first (of the longest wavelength) lines of Balmer and Lyman series equal to 133.7 nm.

35. The λ of H_α line of Balmer series is 6500 Å. What is the λ of H_β line of Balmer series?

36. Calculate the longest wavelength which can remove the electron from I Bohr's orbit. Given $E_1 = 13.6\,\text{eV}$.

37. Calculate the frequency of the spectral line emitted when the electron in $n=3$ in H atom de-excites to ground state. $R_H = 109737\,\text{cm}^{-1}$.

38. Calculate the wavelength of radiations emitted producing *a* line in Lyman series, when an electron falls from fourth stationary state in hydrogen atom. ($R_H = 1.1\times10^7\,\text{m}^{-1}$) **(Roorkee 1995)**

39. The ionisation energy of a H like Bohr's atom in 4 Rydberg.

(a) Calculate the wavelength radiated when electron jumps from the first excited state to ground state.

(b) What is the radius of I orbit of this atom?
Given $1R_h = 2.18\times10^{-18}$ J.

40. The IP_1 of H is 13.6 eV. It is exposed to electromagnetic waves of 1028 Å and gives out induced radiations. Find the wavelength of these induced radiations.

41. Calculate λ of the radiations when the electron jumps from III to II orbit for H atom. The electronic energy in II and III Bohr's orbit of H atom are -5.42×10^{-12} and -2.41×10^{-12} erg respectively.

42. The energy E for an electron in H atom is $-\frac{21.7\times10^{-12}}{n^2}$ erg. Calculate the energy required to remove electron completely from $n=2$ orbit. Also calculate the longest wavelength of light that can be used to cause this transition.

43. Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral lines of lowest energy in the visible region of its atomic spectra.
$R_H = 1.1\times10^7\,\text{m}^{-1}$, $c = 3\times10^8$ m sec^{-1} and $h = 6.62\times10^{-34}$ J sec. **(Roorkee 1993)**

44. Energy required for excitation of electron in 1 mole H atom from ground state to 2nd excited state is 2.67 times lesser than dissociation energy per mole of $H_2(g)$. Calculate the amount of energy needed to excite each H atom of $H_2(g)$ confined in 1.0 litre at 27°C and 1 bar pressure. $R = 0.083$ bar litre K^{-1} mol^{-1}; $R_H = 1.1\times10^7\,\text{m}^{-1}$.

45. 1.8 g hydrogen atoms are excited to radiations. The study of spectra indicates that 27% of the atoms are in IIIrd energy level and 15% of atoms in IInd energy level and the rest in ground state. IP of H is 13.6 eV. Calculate

(a) no. of atoms present in III and II energy levels.

(b) total energy evolved when all the atoms return to ground state.

46. For He^+ and Li^{2+}, the energies are related to the quantum no. n, through an expression: $E_n = -\frac{Z^2B}{n^2}$; where Z is the atomic no. of species and $B = 2.179\times10^{-18}$ J.

(a) What is the energy of lowest level of a He^+ ion?

(b) What is the energy of III level of Li^{2+} ion?

47. What hydrogen like ion has the wavelength difference between the first lines of Balmer and Lyman series equal to 593 nm? $R_H = 109678\,\text{cm}^{-1}$.

48. Wavelength of high energy transition of H atom is 91.2 nm. Calculate the corresponding wavelength of He^+ ion. **(IIT 2003)**

49. Calculate the ratio of wavelengths of m^{th} line of Lyman series and Balmer series of H-atom.

50. To what series does the spectral lines of atomic hydrogen belong if its wave number is equal to the difference between the wave numbers of the following two lines of the Balmer series: 486.1 and 410.2 nm? What is the wavelength of that line?

51. A series of lines in the spectrum of atomic H lies at wavelengths 656.46, 486.27, 434.17, 410.29 nm. What is the wavelength of next line in this series?

52. A hydrogen-like atom (atomic number Z) is in a higher excited state of quantum number n. This excited atom can make a transition to the first excited state by successively emitting two photons of energies 10.20 eV and 17.00 eV respectively. Alternatively, the atom from the same excited state can make a transition to the second excited state by successively emitting two photons of energy 4.25 eV and 5.95 eV respectively. Determine the values of n and Z.

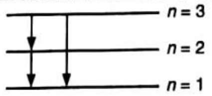
53. Estimate the difference in energy between 1st and 2nd Bohr's orbit for a H atom. At what minimum at. no., a transition from $n = 2$ to $n = 1$ energy level would result in the emission of X-rays with $\lambda = 3.0 \times 10^{-8}$ m? Which hydrogen atom like species does this atomic no. corresponds to? **(IIT 1993)**

54. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum? **(IIT 1993)**

55. Calculate the wavelength emitted during the transition of electron in between two levels of Li^{2+} ion whose sum is 4 and difference is 2.

56. Consider the following two electronic transition possibilities in a hydrogen atom as pictured given:

(1) The electron drops from third Bohr's orbit to second Bohr's orbit followed with the next transition from second to first Bohr's orbit.



(2) The electron drops from third Bohr's orbit to first Bohr's orbit directly.

Show that :

(a) The sum of the energies for the transitions $n = 3$ to $n = 2$ and $n = 2$ to $n = 1$ is equal to the energy of transition for $n = 3$ to $n = 1$.

(b) Are wavelengths and frequencies of the emitted spectrum are also additive in the same way as their energies are?

57. The angular momentum of an electron in a Bohr's orbit of H atom is 4.2178×10^{-34} kg - m^2 / sec. Calculate the spectral line emitted when electron falls from this level to next lower level.

58. Find the quantum no. 'n' corresponding to the excited state of He^+ ion if on transition to the ground state that ion emits two photons in succession with wavelengths 108.5 and 30.4 nm.

59. A single electron atom has nuclear charge $+Ze$ where Z is atomic number and e is electronic charge. It requires 42.7 eV to excite the electron from the second Bohr's orbit to third Bohr's orbit. Find :

(a) the atomic number of element.

(b) the energy required for transition of electron from third to fourth orbit.

(c) the wavelength required to remove electron from first Bohr's orbit to infinity.

(d) the kinetic energy of electron in first Bohr's orbit.

60. Calculate the angular frequency of an electron occupying the second Bohr's orbit of He^+ ion.

61. Two hydrogen atoms collide head on and end up with zero kinetic energy. Each atom then emits a photon of wavelength 121.6 nm. Which transition leads to this wavelength? How fast were the hydrogen atoms travelling before collision?
($R_H = 1.097 \times 10^7 m^{-1}$ and $m_H = 1.67 \times 10^{-27}$ kg.)

62. Calculate the wavelength of a 100 g rubber ball moving with a velocity 100 m sec^{-1}. Is the wavelength of ball short enough to be observed? **(IIT 2004)**

63. Calculate momentum of radiations of wavelength 0.33 nm.

64. How much will the kinetic energy and total energy of an electron in H atoms change if the atom emits a photon of wavelength 4860 Å?

65. Find out the number of waves made by a Bohr's electron in one complete revolution in its 3rd orbit. **(IIT 1994)**

66. Find out the following :

(a) The velocity of electron in first Bohr's orbit of H-atom ($r = a_0$).

(b) de Broglie wave length of the electron in first Bohr's orbit of H-atom.

(c) The orbital angular momentum of 2p-orbitals in terms of $\frac{h}{2\pi}$ units. **(IIT 2005)**

67. Calculate the wavelength of moving electron having 4.55×10^{-25} joule of kinetic energy.

68. Calculate the momentum of electron moving with 1/3rd velocity of light.

69. With what velocity must an electron travel so that its momentum is equal to that of a photon of wavelength of $\lambda = 5200$ Å?

70. Calculate u_{rms} for an electron at 27°C. Given $m_e = 9.108 \times 10^{-28}$ g.

71. Calculate the wavelength of helium atom whose speed is equal to its rms speed at 27°C.

72. An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 Å? **(IIT May 1997)**

73. The vapours of Hg absorb some electrons accelerated by a potential difference of 4.5 volt as a result of which light is emitted. If the full energy of single incident electron is supposed to be converted into light emitted by single Hg atom, find the wave number $(1/\lambda)$ of the light.

74. Calculate the accelerating potential that must be imparted to a proton beam to give it an effective wavelength of 0.005 nm.

75. An electron moves in an electric field with a kinetic energy of 2.5 eV. What is the associated de Broglie wavelength?

76. Show that de Broglie wavelength of electron accelerated through V volt is nearly given by:

$$\underset{(\text{in Å})}{\lambda} = \left[\frac{150}{V}\right]^{1/2}$$

77. A dust particle having mass equal to 10^{-11} g, diameter of 10^{-4} cm and velocity 10^{-4} cm sec^{-1}. The error in measurement of velocity is 0.1%. Calculate uncertainty in its position. Comment on the result.

78. Calculate the uncertainty in velocity of an electron if the uncertainty in its position is of the order of 1 Å.

79. Calculate the uncertainty in velocity of a cricket ball (mass = 0.15 kg) if its uncertainty in position is of the order of 1 Å.

80. What is the maximum precision with which the momentum of an electron can be known if the uncertainty in the position of electron is ±0.001 Å? Will there be any problem in describing the momentum if it has a value of $\frac{h}{2\pi a_0}$, where a_0 is Bohr's radius of first orbit, *i.e.*, 0.529 Å?

81. The position of a proton is measured with an accuracy of $\pm 1.0 \times 10^{-11}$ m. Find the uncertainty in the position of proton 1 second later. Assume u_{proton} = velocity of light.

82. An electron has a total energy of 2 MeV. Calculate the effective mass of the electron in kg and its speed. Assume rest mass of electron 0.511 MeV.

83. On the basis of Heisenberg's uncertainty principle, show that the electron cannot exist within the nucleus.

84. Energy required to stop the ejection of electrons from Cu plate is 0.24 eV. Calculate the work function when radiations of $\lambda = 253.7$ nm strike the plate.

85. A stationary He^+ ion emitted a photon corresponding to the first line (H_α) of the Lyman series. That photon liberated a photo electron from a stationary H atom in ground state. What is the velocity of photo electron? $R_H = 109678\ \text{cm}^{-1}$.

86. The photo electric emission requires a threshold frequency ν_0. For a certain metal $\lambda_1 = 2200$ Å and $\lambda_2 = 1900$ Å produce electrons with a maximum kinetic energy KE_1 and KE_2. If $KE_2 = 2KE_1$, calculate ν_0 and corresponding λ_0.

87. The minimum energy required to overcome the attractive forces between electron and the surface of Ag metal is 7.52×10^{-19} J. What will be the maximum kinetic energy of electron ejected out from Ag which is being exposed to U.V. light of $\lambda = 360$ Å?

88. The binding energy of electrons in a metal is 250 kJ mol^{-1}. What is the threshold frequency of metal?

89. Wavelength of the K_α characteristic X-ray of iron and potassium are 1.931×10^{-8} and 3.737×10^{-8} cm respectively. What is the atomic number and name of the element for which characteristic K_α wavelength is 2.289×10^{-8} cm?

90. What is the significance of $\psi_{4,2,0}$?

91. Suggest the angular and spherical nodes in
(a) $4p$ (b) $3p$ (c) $3s$.

92. The wave function (ψ) of $2s$-orbital is given by:

$$\psi_{2s} = \frac{1}{2\sqrt{32\pi}} \cdot \left[\frac{1}{a_0}\right]^{3/2} \left[2 - \frac{r}{a_0}\right] e^{-r/2a_0}$$

At $r = r_0$, radial node is formed. Calculate r_0 in terms of a_0. **(IIT 2004)**

93. Nitrogen atom has at. no. 7 and oxygen has at. no. 8. Calculate total no. of electrons in nitrate ion.

94. A neutral atom of an element has $2K$, $8L$, $9M$ and $2N$ electrons. Find out the following :
(a) Atomic no.
(b) Total no. of s electrons
(c) Total no. of p electrons
(d) Total no. of d electrons
(e) Valency of element
(f) No. of unpaired electrons.

95. Oxygen consists of isotopes of O^{16}, O^{17} and O^{18} and carbon consists of isotopes of C^{12} and C^{13}. How many types of CO_2 molecules can be formed? Also report their molar masses.

96. The atomic masses of two isotopes of O are 15.9936 and 17.0036. Calculate in each atom :
(a) No. of neutrons (b) No. of protons
(c) No. of electrons (d) Mass no.

97. Write down electronic configuration of the following and report no. of unpaired electron in each.
(a) Mn^{+4} (b) Cr^{+2} (c) Fe^{+3} (d) Ni^{+2} (e) Cl^-
(f) Zn^{+2} (g) Fe^{+2} (h) Na (i) Mg (j) Cr^{+3}

98. Predict total spin for each configuration.

(a) $1s^2$ (b) $1s^2, 2s^2 2p^6$ (c) $1s^2, 2s^2 2p^5$

(d) $1s^2, 2s^2 2p^3$ (e) $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^2$.

99. A compound of vanadium has a magnetic moment of 1.73 BM. Work out the electronic configuration of the vanadium ion in the compound. **(IIT July 1997)**

100. Point out the angular momentum of an electron in

(a) $4s$ orbital (b) $3p$ orbital (c) $4th$ orbit

101. Given below are the sets of quantum numbers for given orbitals. Name these orbitals.

(a) $n=2$	(b) $n=4$	(c) $n=3$	(d) $n=4$	(e) $n=3$
$l=1$	$l=2$	$l=1$	$l=0$	$l=2$
$m=-1$	$m=0$	$m=\pm1$	$m=0$	$m=\pm2$

102. What values are assigned to quantum number n, l, m for

(a) $2s$ (b) $2p_z$ (c) $4d_{x^2-y^2}$ (d) $4d_{z^2}$?

103. Arrange the electrons represented by the following sets of quantum number in decreasing order of energy.

(1) $n=4$ $l=0$ $m_e=0$ $m_s=+\frac{1}{2}$

(1) $n=3$ $l=1$ $m_e=1$ $m_s=-\frac{1}{2}$

(1) $n=3$ $l=2$ $m_e=0$ $m_s=+\frac{1}{2}$

(1) $n=3$ $l=0$ $m_e=0$ $m_s=-\frac{1}{2}$

104. Write down the quantum numbers of all the electrons present in outermost orbit of Argon.

105. An oxide of nitrogen has vapour density 46. Find the total number of electrons in its 92 g.

106. Calculate the total number of electrons in

(a) 1.6 g CH_4

(b) one molecule of CO_2

(c) N_2 molecule.

107. ${}_4Be^7$ captures a K electron into its nucleus. What is the mass number and at. no. of the nucleide formed?

108. Write electronic configuration of ${}_{12}Mg$, ${}_{17}Cl$, ${}_{23}V$ and find out their period and groups in periodic table.

SOLUTIONS (Numerical Problems)

1. Given, $\frac{m}{e} = 1.97 \times 10^{-7}$ (since $e = 1.602 \times 10^{-19}$ C)

$\therefore$ $m = 1.97 \times 10^{-7} \times 1.602 \times 10^{-19}$ kg

$\mathbf{m = 3.16 \times 10^{-26}}$ **kg**

2. Force of attraction, $F = K \times \frac{q_1 q_2}{d^2}$

where $K = 9.0 \times 10^9$ Nm^{2}C^{-2};

$d = 0.529 \times 10^{-8}$ cm $= 0.529 \times 10^{-10}$ m

$$\therefore \quad F = \frac{9.0 \times 10^9 \times (-1.6 \times 10^{-19}) \times 2 \times 1.6 \times 10^{-19}}{(0.529 \times 10^{-10})^2}$$

$= \mathbf{1.65 \times 10^{-7}}$ **Newton**

3. $\because$ $F = K\frac{q_1 q_2}{r^2}$

Also, $q_1 = q_2 = q$

$K = 9.0 \times 10^9$ Nm^{2}C^{-2} and $r = 1 \times 10^{-2}$ m

$$\therefore \quad 1.0 \times 10^{-5} = \frac{9.0 \times 10^9 \times q^2}{(1 \times 10^{-2})^2}$$

$q = 3.3 \times 10^{-10}$ C on each disc

Charge on one electron $= 1.602 \times 10^{-19}$ C

$\therefore$ Number of electrons on disc

$$= \frac{3.3 \times 10^{-10}}{1.602 \times 10^{-19}} = 2.08 \times 10^9$$

$\therefore$ Number of atoms in 1 g carbon

$$= \frac{6.02 \times 10^{23}}{12} = 5.0 \times 10^{22}$$

$$\therefore \text{Ratio of electrons to atoms} = \frac{2.08 \times 10^9}{5.0 \times 10^{22}}$$

$= \mathbf{4.17 \times 10^{-14}}$ **electron /atom**

4. $E = \frac{1}{4\pi\varepsilon_0} \frac{(Ze)(2e)}{r} = K \cdot \frac{(Ze)(2e)}{r}$

$$r = \frac{9 \times 10^9 \times 47 \times 2 \times (1.6 \times 10^{-19})^2}{6 \times 10^6 \times 1.6 \times 10^{-19}} = 2.25 \times 10^{-14} \text{ m}$$

$\therefore$ Maximum volume $= \frac{4}{3}\pi r^3 = \mathbf{48 \times 10^{-42}}$ $\mathbf{m^3}$

5. $$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{\lambda_{\text{(in m)}}}$$

Let $E_{\text{photon}} = 1 \text{eV} = 1.602 \times 10^{-19}$ J

$$\therefore \quad \lambda = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{1.602 \times 10^{-19}} = \mathbf{12.40 \times 10^{-7}} \textbf{ m}$$

6. Photons are supposed to be massless bundles of energy. However, mass can be calculated by $\lambda = h / mu$

7. $\mathbf{h = 6.625 \times 10^{-27}}$ **erg sec** $= \mathbf{6.625 \times 10^{-34}}$ **joule sec**

The unit of h = **Joule sec or erg sec.** $\left(\begin{array}{l} \because h\nu = E \\ \therefore h = \frac{E}{\nu} = \frac{\text{erg}}{\text{sec}^{-1}} \end{array} \right)$

8. $E = \frac{hc}{\lambda} = h\nu$

where E is energy associated per photon of wavelength λ.

(a) $\therefore$ $E = \frac{6.625 \times 10^{-27} \times 3.0 \times 10^{10}}{5890 \times 10^{-8}} = \mathbf{3.37 \times 10^{-12}}$ **erg**

(b) $E = \frac{6.625 \times 10^{-27} \times 3.0 \times 10^{10}}{250 \times 10^{-7}} = \mathbf{7.95 \times 10^{-12}}$ **erg**

(c) $E = \frac{6.625 \times 10^{-27} \times 3.0 \times 10^{10}}{4 \times 10^{-8}} = \mathbf{4.97 \times 10^{-9}}$ **erg**

(d) $E = \frac{6.625 \times 10^{-27} \times 3.0 \times 10^{10}}{600 \times 10^{-7}} = \mathbf{3.3 \times 10^{-12}}$ **erg**

E/mol photon $= NE = 6.023 \times 10^{23} \times 3.3 \times 10^{-12}$ erg

$= \mathbf{19.88 \times 10^{11}}$ **erg**

9. Given, $\lambda = 219$ m

Thus, $\nu = \frac{c}{\lambda}$ or $\nu = \frac{3.0 \times 10^8}{219} = \mathbf{1.37 \times 10^6}$ **Hz**

10. Energy falling per square metre per second

= No. of quanta falling per square metre per second

$\times$ Energy of one quantum

$$= 6.37 \times 10^{15} \times \frac{hc}{\lambda} = 6.37 \times 10^{15} \times \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{632.8 \times 10^{-9}}$$

$= \mathbf{2 \times 10^{-3}}$ $\mathbf{Jm^{-2}\ sec^{-1}}$

11. Energy required to break H—H bond

$$= \frac{430.53 \times 10^3}{6.023 \times 10^{23}} \text{ J/ molecule} = 7.15 \times 10^{-19} \text{ J}$$

Energy of photon used for this purpose $= \frac{hc}{\lambda}$

$$= \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{253.7 \times 10^{-9}} = 7.83 \times 10^{-19} \text{ J}$$

$\therefore$ Energy left after dissociation of bond

$= (7.83 - 7.15) \times 10^{-19}$

or Energy converted into KE $= 0.68 \times 10^{-19}$ J

$\therefore$ % of energy used in kinetic energy

$$= \frac{0.68 \times 10^{-19}}{7.83 \times 10^{-19}} \times 100 = \mathbf{8.68\%}$$

12. Energy given to I$_2$ molecule

$$= \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3.0 \times 10^8}{4500 \times 10^{-10}} = 4.417 \times 10^{-19} \text{ J}$$

Also, energy used for breaking up of I$_2$ molecule

$$= \frac{240 \times 10^3}{6.023 \times 10^{23}} = 3.984 \times 10^{-19} \text{ J}$$

$\therefore$ Energy used in imparting kinetic energy to two I atoms

$= [4.417 - 3.984] \times 10^{-19}$ J

$\therefore$ KE/iodine atom $= [(4.417 - 3.984)/2] \times 10^{-19}$

$= \mathbf{0.216 \times 10^{-19}}$ **J**

13. Energy of one photon $= \frac{hc}{\lambda}$

$$= \frac{6.625\times10^{-34}\times3.0\times10^{8}}{4500\times10^{-10}}\text{ J} = 4.42\times10^{-19}\text{ J}$$

Energy emitted by bulb $= 150\times\frac{8}{100}$ J/sec (watt = J/s)

$$\therefore \quad n\times4.42\times10^{-19} = 150\times\frac{8}{100}$$

(where n is no. of photons)

$$\therefore \quad \mathbf{n = 27.2\times10^{18}}$$

14. The energy of the photon

$$= \frac{hc}{\lambda} = \frac{6.625\times10^{-34}\times3.0\times10^{8}}{5893\times10^{-10}}\text{ joule}$$

$$= 3.37\times10^{-19}\text{ J}$$

Now, total energy emitted by Na lamp

$$= \text{watt}\times\text{time} = 60\times1 = 60\text{ joule per second}$$

$$\because \quad 3.37\times10^{-19}\text{ J energy} = 1\text{ photon}$$

$$\therefore \quad 60\text{ J energy} = \frac{60}{3.37\times10^{-19}}\text{ photon}$$

i.e., no. of photons emitted out in one second.

No. of photons emitted out in 10 hour

$$= 10\times3600\frac{60}{3.37\times10^{-19}} = \mathbf{6.40\times10^{24}}$$

15. Mole of H_2 present in one litre

$$= \frac{PV}{RT} = \frac{1\times1}{0.0821\times298} = 0.0409$$

Thus, energy needed to break H—H bonds in 0.0409 mole of H_2

$$= 0.0409\times436 = 17.83\text{ kJ}$$

Also energy needed to excite one H atom from 1st to 2nd energy level

$$= 13.6\left(1-\frac{1}{4}\right) = 10.2\text{ eV} = 10.2\times1.6\times10^{-19}\text{ J}$$

$\therefore$ Energy needed to excite $0.0409\times2\times6.02\times10^{23}$ atoms of H

$$= 10.2\times1.6\times10^{-19}\times0.0409\times2\times6.02\times10^{23}\text{ J}$$

$$= 80.36\text{ kJ}$$

Thus, total energy needed $= 17.83+80.36 = \mathbf{98.19\ kJ}$

Energy required to break (H—H) bond $= \frac{436\times10^{3}}{6.023\times10^{23}}$ joule

$$\because \quad E = h\nu$$

$$\therefore \quad \frac{436\times10^{3}}{6.023\times10^{23}} = 6.625\times10^{-34}\ \nu$$

$$\therefore \quad \nu = \mathbf{10.93\times10^{14}\ sec^{-1}\ or\ Hz}$$

16. The energy required to see object $= 10^{-17}$ joule

Energy of photon of $\lambda(550\times10^{-9}\text{ m}) = \frac{hc}{\lambda}$

$$= \frac{6.625\times10^{-34}\times3.0\times10^{8}}{550\times10^{-9}} = 3.61\times10^{-19}\text{ joule}$$

$$\because \quad 3.61\times10^{-19}\text{ J} = 1\text{ photon}$$

$$\therefore \quad 10^{-17}\text{ J} = \frac{10^{-17}}{3.61\times10^{-19}} = 27.7\text{ photon}$$

$\therefore$ No. of photons for generating minimum amount of energy = **28** (an integer value)

Note : The integer value should be reported in all such cases where minimum no. of photon is asked because fraction of a photon is never absorbed. Further more the number reported should be higher one and never lower one because lower integer will not provide minimum value.

17.

$$O_2 \xrightarrow{h\nu} O_{\text{Normal}} + O_{\text{Excited}}$$

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

Energy required for simple dissociation of O_2 into two normal atoms

$$= 498\times10^{3}\text{ J mol}^{-1} = \frac{498\times10^{3}}{6.023\times10^{23}}\text{ J molecule}^{-1}$$

If one atom in excited state has more energy, *i.e.*, 1.967 eV

$$= 1.967\times1.602\times10^{-19}\text{ J}$$

The energy required for photochemical dissocaition of O_2

$$= \frac{498\times10^{3}}{6.023\times10^{23}} + 1.967\times1.602\times10^{-19}$$

$$= 82.68\times10^{-20} + 31.51\times10^{-20}$$

$$= 114.19\times10^{-20}\text{ joule}$$

$$\because \quad E = \frac{hc}{\lambda}$$

$$114.19\times10^{-20} = \frac{6.625\times10^{-34}\times3.0\times10^{8}}{\lambda}$$

$$\lambda = 1740.52\times10^{-10}\text{ m} = \mathbf{1740.52\ \text{Å}}$$

18. E of light absorbed in one photon $= \frac{hc}{\lambda_{\text{absorbed}}}$

Let n_1 photons are absorbed, therefore,

$$\text{Total energy absorbed} = \frac{n_1 hc}{\lambda_{\text{absorbed}}}$$

Now, E of light re-emitted out in one photon $= \frac{hc}{\lambda_{\text{emitted}}}$

Let n_2 photons are re-emitted then,

Total energy re-emitted out $= n_2\times\frac{hc}{\lambda_{\text{emitted}}}$

As given $\quad E_{\text{absorbed}}\times\frac{47}{100} = E_{\text{re-emitted out}}$

$$\frac{hc}{\lambda_{\text{absorbed}}}\times n_1\times\frac{47}{100} = n_2\times\frac{hc}{\lambda_{\text{emitted}}}$$

$$\therefore \quad \frac{n_2}{n_1} = \frac{47}{100}\times\frac{\lambda_{\text{emitted}}}{\lambda_{\text{absorbed}}} = \frac{47}{100}\times\frac{5080}{4530}$$

$$\therefore \quad \frac{n_2}{n_1} = \mathbf{0.527}$$

19. $E_{\text{photon absorbed}} = \frac{6.625\times10^{-34}\times3.0\times10^{8}}{300\times10^{-9}} = 6.625\times10^{-19}\text{ J}$

$$E_{\text{photon re-emitted out}} = \frac{6.625\times10^{-34}\times3.0\times10^{8}}{496\times10^{-9}} = 4.0\times10^{-19}\text{ J}$$

$$\therefore \quad E_{\text{absorbed}} = E_{\text{I photon}} + E_{\text{II photon re-emitted out}}$$

$$\therefore \quad E_{\text{II photon}} = 6.625\times10^{-19} - 4.0\times10^{-19}$$

$$= \mathbf{2.625\times10^{-19}\ joule}$$

20. Energy needed to change $= 248 \times 10^3 \text{ J/mol}$

If photon is used for this purpose, then according to Einstein law one molecule absorbs one photon. Therefore,

$$\therefore \quad N_A \cdot \frac{hc}{\lambda} = 248 \times 10^3$$

$$\lambda = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8 \times 6.023 \times 10^{23}}{248 \times 10^3}$$

$$= \mathbf{4.83 \times 10^{-7} \text{ m}}$$

21. Volume of nucleus $= \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(10^{-13})^3 \text{ cm}^3$

Volume of atom $= \frac{4}{3}\pi(10^{-8})^3 \text{ cm}^3$

$$\therefore \quad \frac{V_{\text{Nucleus}}}{V_{\text{Atom}}} = \frac{10^{-39}}{10^{-24}} = 10^{-15}$$

$$\therefore \quad V_{\text{Nucleus}} = \mathbf{10^{-15}} \times V_{\textbf{Atom}}$$

22. Kinetic energy of electron $= \frac{1}{2}mu^2$

Also, from Bohr's concept KE $= \frac{1}{2}\frac{Ze^2}{r_n}$

$$\frac{1}{2}mu^2 = \frac{1}{2}\frac{Ze^2}{r_n}$$

$$u = \sqrt{\left(\frac{Ze^2}{mr_n}\right)}$$

23. For CGS system $u_n = \sqrt{\left(\frac{Ze^2}{mr_n}\right)}$

For electron $\because \; e = 4.803 \times 10^{-10}$ esu

$m = 9.108 \times 10^{-28}$ g

Radius of III orbit $= r_1 \times n^2 = \mathbf{0.529 \times 10^{-8} \times 9 \text{ cm}}$

$$\therefore \quad u_n = \sqrt{\left(\frac{1 \times (4.803 \times 10^{-10})^2}{9.108 \times 10^{-28} \times 0.529 \times 10^{-8} \times 9}\right)}$$

$$u_n = \mathbf{7.29 \times 10^7 \text{ cm sec}^{-1}}$$

Now, circumference of III orbit

$$= 2 \times \pi \times 0.529 \times 10^{-8} \times 9 = 29.93 \times 10^{-8} \text{ cm}$$

$\therefore$ No. of revolutions/sec

$$= \frac{u_n}{2\pi r} = \frac{7.29 \times 10^7}{29.93 \times 10^{-8}} = \mathbf{2.44 \times 10^{14}}$$

24. In MKS system, $E_n = -\frac{2\pi^2 Z^2 me^4}{(4\pi\varepsilon_0)^2 n^2 h^2} \qquad \because \; n = 2$

$$= -\frac{2 \times (3.14)^2 \times (1)^2 \times 9.108 \times 10^{-31} \times (1.602 \times 10^{-19})^4}{(1.11264 \times 10^{-10})^2 \times (2)^2 \times (6.625 \times 10^{-34})^2}$$

$= \mathbf{5.443 \times 10^{-19} \text{ joule}}$

25. (a) Work obtained in the neutralization process is given by

$$W = -\int_{\infty}^{a_0} F \cdot da = -\int_{\infty}^{a_0} \frac{1}{4\pi\varepsilon_0} \frac{(-)e^2}{a_0^2} \cdot da_0$$

$$W = -\frac{e^2}{4\pi\varepsilon_0 \cdot a_0}$$

This work is to be called as potential energy. However in doing so, one should note that this energy is simply lost during the process of attraction in between proton and electron. As reported in the problem at this condition, the electron simply possesses potential energy. Thus,

$$\text{TE} = \text{PE} + \text{KE} = \text{PE} = -\frac{e^2}{4\pi\varepsilon_0 a_0} \qquad \text{...(1)}$$

Now in order, the electron to be captured by the proton to form a ground state hydrogen atom, it should also attain kinetic energy $\frac{e^2}{8\pi\varepsilon_0 a_0}$ (as it is half of the potential energy given in question). Thus, the total energy of the electron if it attains the ground state in H atom,

$$\text{TE} = \text{PE} + \text{KE} = -\frac{e^2}{4\pi\varepsilon_0 a_0} + \frac{e^2}{8\pi\varepsilon_0 a_0} = -\frac{e^2}{8\pi\varepsilon_0 a_0}$$

(b) The wavelength of electron when it is simply at a distance a_0 from the proton can be given as:

$$\lambda = \frac{h}{mu} = \frac{h}{p}$$

Also, $\quad \text{KE} = \frac{1}{2}mu^2 = \frac{p^2}{2m} \qquad (\because p = mu)$

Thus, $\quad \lambda = \frac{h}{\sqrt{2m(\text{KE})}}$

Since, KE $= 0$ at this situation, thus $\lambda = \infty$

Also when electron is at a distance a_0 in Bohr's orbit of H atom

$$\lambda = \frac{h}{\sqrt{2m(\text{KE})}} = \frac{h}{\sqrt{\frac{2me^2}{2a_0 \cdot 4\pi\varepsilon_0}}}$$

$$\lambda = \frac{h}{\sqrt{\frac{e^2 m}{4\pi\varepsilon_0 a_0}}}$$

26. E_1 for H $= -13.6$eV

Now, $\quad E_n = \frac{E_1}{n^2}$

$$\therefore \quad -3.4 = \frac{-13.6}{n^2} \quad \therefore \quad n = 2$$

Now, Angular momentum$(mur) = n \cdot \frac{h}{2\pi} = \frac{2 \times 6.626 \times 10^{-34}}{2 \times 3.14}$

$$= \mathbf{2.1 \times 10^{-34} \text{ J-sec}^{-1}}$$

27. Velocity of electron $= \frac{1}{275} \times$ velocity of light

$$= \frac{1}{275} \times 3 \times 10^{10} = 1.09 \times 10^8 \text{ cm sec}^{-1}$$

Since, $\quad u_n = \frac{2\pi e^2}{nh}$

$$\therefore \quad 1.09 \times 10^8 = \frac{2 \times 3.14 \times (4.803 \times 10^{-10})^2}{6.625 \times 10^{-27} \times n}$$

$\therefore \quad n = 20.06 \times 10^{-1} = \mathbf{2}$ **(an integer value)**

Also when electron jumps from $(n+1)$, *i.e.*, 3 to ground state

$$\bar{\nu} = \frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{3^2}\right] = 109678\left[\frac{1}{1} - \frac{1}{9}\right]$$

$$= \mathbf{9.75 \times 10^4\ cm^{-1}}$$

28. E_1 for $He^+ = E_1$ for $H \times Z^2 = 13.6 \times 4 = \mathbf{54.4\ eV}$

E_1 for $Li^{2+} = E_1$ for $H \times Z^2 = 13.6 \times 9 = \mathbf{122.4\ eV}$

29. E_1 for $Li^{2+} = E_1$ for $H \times 9$

E_1 for $He^+ = E_1$ for $H \times 4$

$\therefore$ E_1 for $Li^{2+} = E_1$ for $He^+ \times \frac{9}{4} = 19.6 \times 10^{-18} \times \frac{9}{4}$

$$= \mathbf{44.1 \times 10^{-18}\ J\ atom^{-1}}$$

30. Energy associated with a photon of 242 nm

$$= \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{242 \times 10^{-9}} = 8.21 \times 10^{-19} \text{ joule}$$

$\because$ 1 atom of Na for ionisation requires $= 8.21 \times 10^{-19}$ J

$\therefore$ 6.023×10^{23} atoms of Na for ionisation requires

$$= 8.21 \times 10^{-19} \times 6.023 \times 10^{23} = 49.45 \times 10^4 \text{ J}$$

$$= \mathbf{494.5\ kJ\ mol^{-1}}$$

31. For Lyman series $n_1 = 1$

For shortest λ of Lyman series; energy difference in two levels showing transition should be maximum, *i.e.*, $n_2 = \infty$

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

$\frac{1}{\lambda} = 109678$

$\therefore$ $\lambda = 911.7 \times 10^{-8}$ cm $= \mathbf{911.7\ Å}$

For longest λ of Lyman series; energy difference in two levels showing transition should be minimum, *i.e.*, $n_2 = 2$

$\therefore$ $\frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = 109678 \times \frac{3}{4}$

$\therefore$ $\lambda = 1215.67 \times 10^{-8}$ cm $= \mathbf{1215.67\ Å}$

32. Rydberg constant $= 109678\ cm^{-1}$

$$E = h\nu = \frac{h.c}{\lambda} = hc\bar{\nu}$$

$\therefore$ $\bar{\nu}$ in cm^{-1} $\therefore$ $\bar{\nu} = 109678\ cm^{-1}$

$\therefore$ $E = 6.626 \times 10^{-34} \times 3.0 \times 10^{10} \times 109678$ J/atom

$E = 2.18 \times 10^{-18}$ J/atom $= \mathbf{1\ Rh}$

Also, $\mathbf{E = N \times Rh\ J / mole}$

33. Spectral lines emitted when electron jumps from n to 1 is $\Sigma(n-1)$ or $\Sigma\Delta n$

$\because$ $\Sigma n = n\frac{(n+1)}{2}$

$\therefore$ If $n = n - 1$

Then $\Sigma(n-1) = (n-1)\frac{(n-1+1)}{2} = \mathbf{\frac{1}{2}n(n-1)}$

34. $\frac{1}{\lambda_1} = Z^2R_H\left[\frac{1}{2^2} - \frac{1}{3^2}\right]$; $\therefore$ $\lambda_1 = \frac{36}{5R_HZ^2}$

$\frac{1}{\lambda_2} = Z^2R_H\left[\frac{1}{1^2} - \frac{1}{2^2}\right]$; $\therefore$ $\lambda_2 = \frac{4}{3R_HZ^2}$

$\lambda_1 - \lambda_2 = 133.7 \times 10^{-9}$ and $Z = 2$

$\therefore$ $R_H = \mathbf{1.095 \times 10^5\ cm^{-1}}$

35. For H_α line of Balmer series $n_1 = 2, n_2 = 3$

For H_β line of Balmer series $n_1 = 2, n_2 = 4$

$\therefore$ $\frac{1}{\lambda_{H_\alpha}} = R_H\left[\frac{1}{2^2} - \frac{1}{3^2}\right]$ ...(1)

and $\frac{1}{\lambda_{H_\beta}} = R_H\left[\frac{1}{2^2} - \frac{1}{4^2}\right]$ ...(2)

By Eqs. (1) and (2) $\frac{\lambda_\beta}{\lambda_\alpha} = \frac{\frac{1}{4} - \frac{1}{9}}{\frac{1}{4} - \frac{1}{16}}$

$\therefore$ $\lambda_\beta = \lambda_\alpha \times \left[\frac{80}{108}\right] = 6500 \times \frac{80}{108} = \mathbf{4814.8\ Å}$

36. The photon capable of removing electron from I Bohr's orbit must possess energy

$$= 13.6\text{eV} = 13.6 \times 1.602 \times 10^{-19} \text{ J} = 21.787 \times 10^{-19} \text{ J}$$

$\because$ $E = \frac{hc}{\lambda}$

$$21.787 \times 10^{-19} = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{\lambda}$$

$\therefore$ $\lambda = 912.24 \times 10^{-10}$ m $= \mathbf{912.24\ Å}$

This is longest λ because a photon having λ higher than this will possess energy lesser then required, as $E \propto \frac{1}{\lambda}$.

37. $\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$\therefore$ $\frac{c}{\lambda} = \nu = R_H \cdot c\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$$= 109737 \times 3.0 \times 10^{10}\left[\frac{1}{1^2} - \frac{1}{3^2}\right]$$

$$= \mathbf{2.92 \times 10^{15}\ sec^{-1}}$$

38. $\because$ $\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

Given $R_H = 1.1 \times 10^7$; for Lyman series $n_1 = 1$ and $n_2 = 4$ (given)

$\therefore$ $\frac{1}{\lambda} = 1.1 \times 10^7\left[\frac{1}{1^2} - \frac{1}{4^2}\right]$

$\therefore$ $\lambda = \mathbf{0.9696 \times 10^{-7}\ metre}$

39. Energy of I orbit of H like atom

$$= 4R_h = 4 \times 2.18 \times 10^{-18} \text{ joule}$$

E_1 for $H = -2.18 \times 10^{-18}$ J

$\because \quad E_{\text{H like atom}} = E_{1\,\text{H}} \times Z^2$

$-4 \times 2.18 \times 10^{-18} = -2.18 \times 10^{-18} \times Z^2$

$\therefore \quad Z = 2$

i.e., Atomic no. of H like atom is 2 or it is He^+.

(a) For de-excitation of '*e*' in He^+ from $n_2 = 2$ to $n_1 = 1$

$$E_2 - E_1 = \frac{hc}{\lambda}$$

Now $\quad E_1 = -4R_h$

$\therefore \quad E_2 = -\frac{4R_h}{4} = -R_h \quad \left(\because E_2 = \frac{E_1}{n^2}\right)$

$\therefore \quad E_2 - E_1 = 3R_h = 3 \times 218 \times 10^{-18}$ J

$\therefore \quad E_2 - E_1 = \frac{hc}{\lambda}$

$\therefore \quad \lambda = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{3 \times 2.18 \times 10^{-18}} = 303.89 \times 10^{-10}$ m

$= \mathbf{303.89}$ **Å**

(b) Radius (r_1) of H like atom $= \frac{r_H}{Z} = \frac{0.529 \times 10^{-8}}{2}$

$= \mathbf{2.645 \times 10^{-9}}$ **cm**

40. E_1 of H atom $= -13.6$eV

Energy given to H atom $= \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{1028 \times 10^{-10}}$

$= 1.933 \times 10^{-18}$ J $= 12.07$eV

$\therefore$ Energy of H atom after excitation

$= -13.6 + 12.07 = -1.53$eV

$\therefore \quad E_n = \frac{E_1}{n^2} \quad \therefore \quad n^2 = \frac{-13.6}{-1.53} \approx 9 \quad \therefore \quad n = 3$

Thus, electron in H atom is excited to 3rd shell

$\therefore$ I induced $\lambda_1 = \frac{hc}{(E_3 - E_1)}$

$\because \quad E_1 = -13.6$eV; $E_3 = -1.53$eV

$\therefore \quad \lambda_1 = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{(-1.53 + 13.6) \times 1.602 \times 10^{-19}} = 1028 \times 10^{-10}$ m

$\therefore \quad \lambda = \mathbf{1028}$ **Å**

$\therefore$ II induced $\lambda_2 = \frac{hc}{(E_2 - E_1)}$

$\because \quad E_1 = -13.6$eV; $E_2 = -\frac{13.6}{4}$eV

$\therefore \quad \lambda_2 = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{\left(-\frac{13.6}{4} + 13.6\right) \times 1.602 \times 10^{-19}}$

$= 1216 \times 10^{-10}$ m $= \mathbf{1216}$ **Å**

$\therefore$ III induced $\lambda_3 = \frac{hc}{(E_3 - E_2)}$

$\because \quad E_1 = -13.6$eV; $E_2 = -\frac{13.6}{4}$eV; $E_3 = -\frac{13.6}{9}$eV

$\therefore \quad \lambda_3 = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{\left(-\frac{13.6}{9} + \frac{13.6}{4}\right) \times 1.602 \times 10^{-19}}$

$= 6568 \times 10^{-10}$ m $= \mathbf{6568}$ **Å**

41. E_3 for H $= -2.41 \times 10^{-12}$ erg

E_2 for H $= -5.42 \times 10^{-12}$ erg

$\therefore$ For a jump from III to II shell

$$\Delta E = E_3 - E_2 = \frac{hc}{\lambda}$$

$\therefore \quad \lambda = \frac{hc}{E_3 - E_2}$

$= \frac{6.625 \times 10^{-27} \times 3.0 \times 10^{10}}{-2.41 \times 10^{-12} + 5.42 \times 10^{-12}}$

$= 6602.9 \times 10^{-8}$ cm $= \mathbf{6603}$ **Å**

42. $E_n = -\frac{21.7 \times 10^{-12}}{n^2}$ erg

$\therefore \quad E_2 = -\frac{21.7 \times 10^{-12}}{4} = -5.425 \times 10^{-12}$ erg

$\therefore$ For removal of electron $E_2 = \frac{hc}{\lambda}$; E_2 should be given to remove electron, *i.e.*, +ve.

$\therefore \quad \lambda = \frac{6.625 \times 10^{-27} \times 3.0 \times 10^{10}}{5.425 \times 10^{-12}}$

$= 3663.6 \times 10^{-8}$ cm $= \mathbf{3663.6}$ **Å**

So, the longest wavelength is **3663.6 Å.**

43. For visible line spectrum, *i.e.*, Balmer series $n_1 = 2$. Also for minimum energy transition $n_2 = 3$.

$\because \quad \frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$\therefore \quad \frac{1}{\lambda} = R_H\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = 1.1 \times 10^7\left[\frac{1}{4} - \frac{1}{9}\right]$

$= 1.1 \times 10^7 \times \frac{5}{36}$

$\therefore \quad \lambda = 6.55 \times 10^{-7}$ metre

Now $\quad E = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3.0 \times 10^8}{6.55 \times 10^{-7}}$

$= 3.03 \times 10^{-19}$ joule

if *N* electrons show this transition in 1 g-atom of H then

Energy released $= E \times N = 3.03 \times 10^{-19} \times 6.023 \times 10^{23}$

$= 18.25 \times 10^4$ J

$= \mathbf{182.5}$ **kJ**

44. Total mole of $H_2 = \frac{1 \times 1}{300 \times 0.083} = 0.040$

$\therefore$ Total mole of H atoms $= 0.040 \times 2 = 0.08$

Energy needed to excite 1 mole H atom from $n = 1$ to $n = 3$ is:

$$E = \frac{h \cdot c}{\lambda} = hc \cdot R_H\left[\frac{1}{1^2} - \frac{1}{3^2}\right] \times N_A$$

$E = 6.625 \times 10^{-34} \times 3.0 \times 10^8 \times 1.1 \times 10^7 \times \frac{8}{9} \times 6.023 \times 10^{23}$

$= 11.71 \times 10^5$ J/mol

Energy required for dissociation of 1 mole H_2 molecules to H atoms

$= 11.71 \times 10^5 \times 2.67 = 31.25 \times 10^5$ J/mol

$\therefore$ Total energy needed

$$= \underset{\text{for 0.08 mole H atom}}{\text{Excitation energy}} + \underset{\text{for 0.04 mole } H_2}{\text{Dissociation energy}}$$

$$= 11.71 \times 10^5 \times 0.08 + 31.25 \times 10^5 \times 0.04$$

$$= 9.37 \times 10^4 + 12.5 \times 10^4$$

$$= \mathbf{21.87 \times 10^4 \text{ J}}$$

45. 1 g H contains $= N$ atoms

$\therefore$ 1.8 g contains $= N \times 1.8$ atoms

$$= 6.023 \times 10^{23} \times 1.8 = 10.84 \times 10^{23} \text{ atoms}$$

(a) $\therefore$ No. of atoms in III shell $= \dfrac{10.84 \times 10^{23} \times 27}{100}$

$$= \mathbf{292.68 \times 10^{21} \text{ atoms}}$$

$\therefore$ No. of atoms in II shell $= \dfrac{10.84 \times 10^{23} \times 15}{100}$

$$= \mathbf{162.6 \times 10^{21} \text{ atoms}}$$

and No. of atoms in I shell $= \dfrac{10.84 \times 10^{23} \times 58}{100}$

$$= \mathbf{628.72 \times 10^{21} \text{ atoms}}$$

(b) When all the atoms return to I shell, then

$$E' = (E_3 - E_1) \times 292.68 \times 10^{21}$$

$$= \left(-\frac{13.6}{9} + 13.6\right) \times 1.602 \times 10^{-19} \times 292.68 \times 10^{21}$$

$$= 5.668 \times 10^5 \text{ joule}$$

$$E'' = (E_2 - E_1) \times 162.6 \times 10^{21}$$

$$= \left(-\frac{13.6}{4} + 13.6\right) \times 1.602 \times 10^{-19} \times 162.6 \times 10^{21}$$

$$= 2.657 \times 10^5 \text{ joule}$$

$\therefore \quad E = E' + E'' = 5.668 \times 10^5 + 2.657 \times 10^5$ joule

$$= \mathbf{832.50 \text{ kJ}}$$

46. (a) E_1 for He $= -\dfrac{2^2 \times 2.179 \times 10^{-18}}{1^2} = \mathbf{-8.716 \times 10^{-18} \text{ J}}$

(b) E_3 for $Li^{2+} = -\dfrac{3^2 \times 2.179 \times 10^{-18}}{3^2} = \mathbf{-2.179 \times 10^{-18} \text{ J}}$

47. We have $\dfrac{1}{\lambda} = R_H Z^2 \left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$

For I line of Balmer series:

$$\frac{1}{\lambda_B} = R_H \cdot Z^2 \left[\frac{1}{2^2} - \frac{1}{3^2}\right] = \frac{5}{36} \times R_H \times Z^2$$

or $\quad \lambda_B = \dfrac{36}{5 \cdot R_H \cdot Z^2}$ ...(1)

For I line of Lyman series:

$$\frac{1}{\lambda_L} = R_H \cdot Z^2 \left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \frac{3}{4} \times R_H \times Z^2$$

or $\quad \lambda_L = \dfrac{4}{3R_H \cdot Z^2}$ ...(2)

Given, $\lambda_B - \lambda_L = 59.3 \times 10^{-7}$ cm

or $\quad \dfrac{36}{5R_H \cdot Z^2} - \dfrac{4}{3R_H \cdot Z^2} = 59.3 \times 10^{-7}$

$$\frac{1}{R_H \cdot Z^2}[7.2 - 1.333] = 59.3 \times 10^{-7}$$

or $\quad Z^2 = \dfrac{5.867}{R_H \times 59.3 \times 10^{-7}} = \dfrac{5.867}{109678 \times 19.3 \times 10^{-7}}$

$\therefore \quad \mathbf{Z = 3}$

$\therefore$ H like atom is $\mathbf{Li^{2+}}$.

48. For H atom : $\quad \dfrac{1}{\lambda_H} = R_H \left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$ ...(1)

For He$^+$ ion : $\quad \dfrac{1}{\lambda_{He^+}} = R_H \cdot Z^2 \left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$ ...(2)

By Eqs. (1) and (2), $\quad \dfrac{\lambda_{He^+}}{\lambda_H} = \dfrac{1}{Z^2}$

or $\quad \lambda_{He^+} = \lambda_H \times \dfrac{1}{Z^2} = 91.2 \times \dfrac{1}{2^2} = \mathbf{22.8 \text{ nm}}$

49. m^{th} line of Lyman series $n_1 = 1, n_2 = (m+1)$

$\therefore \quad \dfrac{1}{\lambda_L} = R_H \left[\dfrac{1}{1^2} - \dfrac{1}{(m+1)^2}\right]$ ...(1)

Similarly m^{th} line of Balmer series, $n_1 = 2, n_2 = m+2$

$\therefore \quad \dfrac{1}{\lambda_B} = R_H \left[\dfrac{1}{2^2} - \dfrac{1}{(m+2)^2}\right]$ ...(2)

$\therefore \quad \dfrac{\lambda_B}{\lambda_L} = \dfrac{[(m+1)^2 - 1][4 \times (m+2)^2]}{(m+1)^2[(m+2)^2 - 4]}$

50. Given, $\lambda_1 = 486.1 \times 10^{-9}$, $\text{m} = 486.1 \times 10^{-7}$ cm

$\lambda_2 = 410.2 \times 10^{-9}$, $\text{m} = 410.2 \times 10^{-7}$ cm

$$\bar{\nu} = \bar{\nu}_2 - \bar{\nu}_1 = \frac{1}{\lambda_2} - \frac{1}{\lambda_1} = R_H \left[\frac{1}{2^2} - \frac{1}{n_2^2}\right] - R_H \left[\frac{1}{2^2} - \frac{1}{n_1^2}\right]$$

$\bar{\nu} = R_H \left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$ ...(1)

For I case of Balmer series:

$$\frac{1}{\lambda_1} = R_H \left[\frac{1}{2^2} - \frac{1}{n_1^2}\right] = 109678 \left[\frac{1}{2^2} - \frac{1}{n_1^2}\right]$$

or $\quad \dfrac{1}{486.1 \times 10^{-7}} = 109678 \left[\dfrac{1}{2^2} - \dfrac{1}{n_1^2}\right]$

$\therefore \quad n_1 = 4$

For II case of Balmer series:

$$\frac{1}{\lambda_2} = \frac{1}{410.2 \times 10^{-7}} = 109678 \left[\frac{1}{2^2} - \frac{1}{n_2^2}\right]$$

$\therefore \quad n_2 = 6$

Thus, given transition occurs from **6th level to 4th level.**

Also by Eq. (1) $\quad \bar{\nu} = \dfrac{1}{\lambda} = 109678 \left[\dfrac{1}{4^2} - \dfrac{1}{6^2}\right]$

$\therefore \quad \mathbf{\lambda = 2.63 \times 10^{-4} \text{ cm}}$

51. The given series lies in the visible region and thus appears to be Balmer series.

Therefore, $n_1 = 2$ and $n_2 = ?$ for next line

Furthermore if $\lambda = 410.29\times10^{-7}$ cm and $n_1 = 2$ then n_2 may be calculated by

$$\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{410.29\times10^{-7}} = 109678\left[\frac{1}{2^2} - \frac{1}{n_2^2}\right]$$

$\therefore$ $\mathbf{n_2 = 6}$

Thus, next line will be obtained during the jump of electron from 7th to 2nd shell, *i.e.*,

$$\frac{1}{\lambda} = R_H\left[\frac{1}{2^2} - \frac{1}{7^2}\right] = 109678\left[\frac{1}{4} - \frac{1}{49}\right]$$

$\therefore$ $\lambda = 397.2\times10^{-7}$ cm

$\mathbf{\lambda = 397.2}$ **nm**

52. Total energy liberated during transition of electron from nth shell to first excited state (*i.e.*, 2nd shell)

$= 10.20 + 17.0 = 27.20\text{eV} = 27.20\times1.602\times10^{-12}$ erg

$$\because \quad \frac{hc}{\lambda} = R_H\times Z^2 hc\left[\frac{1}{2^2} - \frac{1}{n^2}\right]$$

$$\therefore \quad 27.20\times1.602\times10^{-12} = R_H\times Z^2\times h\times c\left[\frac{1}{2^2} - \frac{1}{n^2}\right] \quad ...(1)$$

Similarly, total energy liberated during transition of electron from nth shell to second excited *i.e.*, 3rd shell)

$= 4.25 + 5.95 = 10.20\text{eV} = 10.20\times1602\times10^{-12}$ erg

$$\therefore \quad 10.20\times1.602\times10^{-12} = R_H\times Z^2\times h\times c\left[\frac{1}{3^2} - \frac{1}{n^2}\right] \quad ...(2)$$

Dividing Eq. (1) by Eq. (2), $\mathbf{n = 6}$

On substituting the value of n in Eqs. (1) or (2),

$$\mathbf{Z = 3}$$

53. E_1 for H $= -13.6$eV

E_2 for H $= -\frac{13.6}{2^2} = -\frac{13.6}{4} = -3.4$ eV

$\therefore$ $E_2 - E_1 = -3.4 - (-13.6) = +10.2$eV

$\therefore$ Difference in two levels $=$ **10.2 eV**

Also for transition of H like atom

$\lambda = 3.0\times10^{-8}$ m

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

$[\because R_H = 109677\text{cm}^{-1} = 109677\times10^2\ \text{m}^{-1}]$

$$\therefore \quad \frac{1}{3\times10^{-8}} = 109677\times10^2\times Z^2\left[\frac{3}{4}\right]$$

$\therefore$ $Z^2 = 4$ $\therefore$ $\mathbf{Z = 2}$

54. For He$^+$, $\quad \frac{1}{\lambda} = R_H\cdot Z^2\left[\frac{1}{2^2} - \frac{1}{4^2}\right]$

For H, $\quad \frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

Since λ is same

$$\therefore \quad Z^2\left[\frac{1}{2^2} - \frac{1}{4^2}\right] = \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$\because$ $Z = 2$

$$\therefore \quad \left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$\therefore$ $\mathbf{n_1 = 1}$ and $\mathbf{n_2 = 2}$

55. Let the transition occurs in between the levels n_1 and n_2. Thus, if $n_2 > n_1$, then given

$n_1 + n_2 = 4$

$n_2 - n_1 = 2$

$\therefore$ $n_1 = 1$ and $n_2 = 3$

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

$= 109678\times3^2\times\left[\frac{8}{9}\right]$ $\quad$ ($\because$ $Z = 3$ for Li)

$\therefore$ $\mathbf{\lambda = 1.14\times10^{-6}}$ **cm**

56. (a) $\quad \Delta E = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

For 3 to 2 $\quad \Delta E_{3\to2} = R_H\left[\frac{1}{2^2} - \frac{1}{3^2}\right]$ ...(1)

For 2 to 1 $\quad \Delta E_{2\to1} = R_H\left[\frac{1}{1^2} - \frac{1}{2^2}\right]$ ...(2)

For 3 to 1 $\quad \Delta E_{3\to1} = R_H\left[\frac{1}{1^2} - \frac{1}{3^2}\right]$ ...(3)

It is evident from Eqs. (1), (2) and (3), that

$$\Delta E_{3\to1} = \Delta E_{3\to2} + \Delta E_{2\to1}$$

(b) Also $E = h\nu$; thus, frequencies are also additive.

but $E = \frac{hc}{\lambda}$ and thus, wavelengths are not additive.

57. Given, $\quad mur = \frac{nh}{2\pi}$

$\therefore$ $\frac{nh}{2\pi} = 4.2178\times10^{-34}$

or $\quad n = \frac{4.2178\times10^{-34}\times2\times3.14}{6.625\times10^{-34}} = 4$

Thus, $\quad \frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

The transition spectral line for 4th to 3rd shell is

$$\frac{1}{\lambda} = 109678\left[\frac{1}{3^2} - \frac{1}{4^2}\right]$$

$\therefore$ $\mathbf{\lambda = 1.8\times10^{-4}}$ **cm**

58. Given, $\lambda_2 = 30.4 \times 10^{-7}$ cm

$\lambda_1 = 108.5 \times 10^{-7}$ cm

Let excited state of He^+ be n_2. It comes from n_2 to n_1 and then n_1 to 1 to emit two successive photon

$$\frac{1}{\lambda_2} = R_H . Z^2 \left[\frac{1}{1^2} - \frac{1}{n_1^2}\right]$$

$$\frac{1}{30.4 \times 10^{-7}} = 109678 \times 4 \left[\frac{1}{1^2} - \frac{1}{n_1^2}\right]$$

$\therefore \quad n_1 = 2$

Now for $\lambda_1 : n_1 = 2$ and $n_2 : ?$

$$\frac{1}{\lambda_1} = R_H \, Z^2 \left[\frac{1}{2^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{108.5 \times 10^{-7}} = 109678 \times 4 \left[\frac{1}{2^2} - \frac{1}{n_2^2}\right]$$

$\therefore \quad n_2 = 5$

Thus, excited state for He is **5th orbit.**

59. (a) $\because \quad 1\,\text{eV} = 1.602 \times 10^{-12}$ erg

Also, $\Delta E = \frac{hc}{\lambda} = E_3 - E_2 = R_H \cdot c \cdot h \cdot Z^2 \left[\frac{1}{2^2} - \frac{1}{3^2}\right]$

$$42.7 \times 1.602 \times 10^{-12} = 109678 Z^2 \left[\frac{1}{2^2} - \frac{1}{3^2}\right] \times 3 \times 10^{10} \times 6.626 \times 10^{-27}$$

$\therefore \quad Z^2 = 22.6 \quad \therefore \; Z \approx 5$

(b) $\Delta E = E_4 - E_3 = R_H \cdot c \cdot h \cdot Z^2 \left[\frac{1}{3^2} - \frac{1}{4^2}\right]$

$$= 109678 \times 3 \times 10^{10} \times 6.626 \times 10^{-27} \times 5^2 \times \frac{7}{16 \times 9}$$

$= \mathbf{26.5 \times 10^{-12}}$ **erg**

(c) $\frac{1}{\lambda} = R_H \cdot Z^2 \left[\frac{1}{1^2} - \frac{1}{\infty^2}\right]$

$\frac{1}{\lambda} = 109678 \times 25$

$\therefore \quad \lambda = 3.65 \times 10^{-7}$ cm

(d) $KE = \frac{1}{2}mu^2 = \frac{1}{2}m\left(\frac{2\pi Ze^2}{nh}\right)^2 = \frac{2\pi^2 Z^2 e^4 m}{n^2 h^2}$

$$= \frac{2 \times (3.14)^2 \times 5^2 \times (4.803 \times 10^{-10})^4 \times 9.108 \times 10^{-28}}{1^2 \times (6.625 \times 10^{-27})^2}$$

$= \mathbf{5.45 \times 10^{-10}}$ **erg**

60. Velocity of electron in He^+ ion in an orbit $(u) = \frac{2\pi Ze^2}{nh}$

Radius of He^+ ion in an orbit $(r_n) = \frac{n^2h^2}{4\pi^2 me^2 Z}$

$\therefore$ Angular frequency or angular velocity ω

$$= \frac{u}{r_n} = \frac{2\pi Ze^2 \times 4\pi^2 me^2 Z}{nh \times n^2 h^2} = \frac{8\pi^3 Z^2 me^4}{n^3 h^3}$$

$\because \quad n = 2, \quad m = 9.108 \times 10^{-28}$ g, $\quad Z = 2, h = 6.625 \times 10^{-27}$

$$\therefore w = \frac{8 \times (22/7)^3 \times (2)^2 \times 9.108 \times 10^{-28} \times (4.803 \times 10^{-10})^4}{(2)^3 \times (6.625 \times 10^{-27})^3}$$

$= \mathbf{2.067 \times 10^{16}}$ $\mathbf{sec^{-1}}$

61. Wavelength emitted in U.V. region and thus $n_1 = 1$; For H atom

$$\therefore \quad \frac{1}{\lambda} = R_H \left[\frac{1}{1^2} - \frac{1}{n^2}\right]$$

$$\frac{1}{121.6 \times 10^{-9}} = 1.097 \times 10^7 \left[\frac{1}{1^2} - \frac{1}{n^2}\right]$$

$\therefore \quad n = 2$

Also the energy released is due to collision and all the kinetic energy is released in form of photon. Thus,

$$\frac{1}{2}mu^2 = \frac{hc}{\lambda}$$

or $\quad \frac{1}{2} \times 1.67 \times 10^{-27} \times u^2 = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{121.6 \times 10^{-9}}$

$\therefore \quad u = \mathbf{4.43 \times 10^4}$ $\mathbf{m\,sec^{-1}}$

62. According to de Broglie equation $\lambda = \frac{h}{mu}$

$\because \quad m = 100\,\text{g} = 100 \times 10^{-3}$ kg, $u = 100\,\text{m}\,\text{sec}^{-1}$

$$\therefore \quad \lambda = \frac{6.625 \times 10^{-34}}{100 \times 100 \times 10^{-3}} = 6.625 \times 10^{-35} \text{ m}$$

63. We have $\quad \lambda = \frac{h}{mu}$

$\therefore \quad mu = \frac{h}{\lambda}$

i.e., Momentum $= \frac{6.625 \times 10^{-34}}{0.33 \times 10^{-9}} = \mathbf{2.01 \times 10^{-24}}$ $\mathbf{kg\,m\,sec^{-1}}$

64. Energy emitted out in form of photon

$$= \frac{hc}{\lambda} = \frac{6.625 \times 10^{-27} \times 3 \times 10^{10}}{4860 \times 10^{-8}}$$

$= 4.089 \times 10^{-12}$ erg $= 4.089 \times 10^{-19}$ J $= 2.553$ eV

The total energy loss of electron for atom $=$ **2.553 eV**

Also we have total energy $= -$ Kinetic energy (from Bohr's equation).

$\therefore$ Kinetic energy of electron in atom changes by (increases)

$=$ **2.553 eV**

65. r_n for H $= r_1 \times n^2$

r_3 for H $= 0.529 \times 9 \times 10^{-8}$ cm $\quad (\because r_1 = 0.529$ Å$)$

Also, $\quad u_n = \frac{u_1}{n}$

$\therefore \quad u_3 = \frac{2.19 \times 10^8}{3}$ cm sec^{-1}

$(\because u_1 = 2.19 \times 10^8$ cm sec$^{-1})$

$\therefore$ No. of waves in one round

$$= \frac{2\pi r_3}{\lambda} = \frac{2\pi r_3}{h/mu_3} = \frac{2\pi r_3 \times u_3 \times m}{h}$$

$$= \frac{2 \times 22 \times 0.529 \times 9 \times 10^{-8} \times 2.19 \times 10^8 \times 9.108 \times 10^{-28}}{7 \times 3 \times 6.62 \times 10^{-27}} = 3$$

66. (a) $\because \quad mur = \frac{n \cdot h}{2\pi}$

$\therefore \quad u = \frac{n \cdot h}{2\pi mr}$

$$= \frac{1 \times 6.626 \times 10^{-27}}{2 \times 3.14 \times 9.108 \times 10^{-28} \times 0.529 \times 10^{-8}}$$

$$= 2.19 \times 10^{8} \text{ cm/sec}$$

(b) $\lambda = \frac{h}{mu}$

$$= \frac{6.626 \times 10^{-27}}{9.108 \times 10^{-28} \times 2.19 \times 10^{8}} = 3.32 \times 10^{-8} \text{ cm}$$

$$= 3.32 \text{ Å}$$

(c) Orbital angular momentum of $2p$-orbital

$$= \frac{h}{2\pi}\sqrt{l(l+1)}$$

$$= \frac{h}{2\pi}\sqrt{1(1+1)} \quad (\because l = 1)$$

$$= \frac{h}{2\pi} \times \sqrt{2} = \sqrt{2} \times \bar{h} \left(\bar{h} = \frac{h}{2\pi}\right)$$

67. Kinetic energy $= \frac{1}{2}mu^2 = 4.55 \times 10^{-25}$ J

$\therefore \quad u^2 = \frac{4.55 \times 10^{-25} \times 2}{9.108 \times 10^{-31}}$

$\therefore \quad u = 10^{3} \text{ m sec}^{-1}$

Now, $\quad \lambda = \frac{h}{mu} = \frac{6.625 \times 10^{-34}}{9.108 \times 10^{-31} \times 10^{3}}$

$$= \mathbf{7.27 \times 10^{-7}} \textbf{ metre}$$

68. Momentum of electron $= m' \cdot u$

where m' is mass of electron in motion $= \frac{m}{\sqrt{1-\left(\frac{u}{c}\right)^2}}$

Also, $\quad u = c/3$

$\therefore \quad \text{Momentum} = \frac{9.108 \times 10^{-28}}{\sqrt{1-\left(\frac{c}{3 \times c}\right)}} \times \frac{3 \times 10^{10}}{3}$

$$= \frac{9.108 \times 10^{-28} \times 3 \times 10^{10}}{0.94 \times 3}$$

$$= \mathbf{9.69 \times 10^{-18}} \textbf{ g cm sec}^{\mathbf{-1}}$$

69. $\because \quad \lambda = \frac{h}{mu}$

$\therefore$ Momentum, $mu = \frac{h}{\lambda} = \frac{6.625 \times 10^{-34}}{5200 \times 10^{-10}} \text{ kg m sec}^{-1}$ ...(1)

Also momentum of electron $= mu = 9.108 \times 10^{-31} \times u$ ...(2)

Since, both are same, therefore, by Eqs. (1) and (2)

$$9.108 \times 10^{-31} \times u = \frac{6.625 \times 10^{-34}}{5200 \times 10^{-10}}$$

$\therefore \quad u = \mathbf{1400} \textbf{ m sec}^{\mathbf{-1}}$

70. $u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 300}{9.108 \times 10^{-31} \times 6.023 \times 10^{23}}}$

$$= \mathbf{11.68 \times 10^{4}} \textbf{ m/sec}$$

71. u_{rms} of He $= \sqrt{\frac{3RT}{m}} = \sqrt{\frac{3 \times 8.314 \times 100}{4 \times 10^{-3}}} = \mathbf{1367.7} \textbf{ ms}^{\mathbf{-1}}$

Now, $\quad \lambda = \frac{h}{mu} = \frac{6.625 \times 10^{-34}}{\frac{4 \times 10^{-3} \times 1367.7}{6.023 \times 10^{23}}} = \mathbf{7.29 \times 10^{-11}} \textbf{ m}$

72. For an electron, $\quad \frac{1}{2}mu^2 = e.V$

and $\quad \lambda = \frac{h}{mu}$

Thus, $\quad \frac{1}{2}m\frac{h^2}{m^2\lambda^2} = e.V$

or $V = \frac{1}{2}\frac{h^2}{m\lambda^2 \cdot e}$

$$= \frac{1 \times (6.62 \times 10^{-34})^2}{2 \times 9.108 \times 10^{-31} \times (1.54 \times 10^{-10})^2 \times 1.602 \times 10^{-19}}$$

$$= \mathbf{63.3} \textbf{ volt}$$

73. Energy of an accelerated electron

$$= Q.V = 1.602 \times 10^{-19} \times 4.5 = 7.209 \times 10^{-19} \text{ J}$$

This energy is completely converted into light.

i.e., $\quad \frac{hc}{\lambda} = 7.209 \times 10^{-19}$

$$\frac{6.625 \times 10^{-34} \times 3.0 \times 10^{8}}{\lambda} = 7.209 \times 10^{-19}$$

$\therefore \quad \frac{1}{\lambda} = \text{wave no.} = \mathbf{3.63 \times 10^{6}} \textbf{ metre}^{\mathbf{-1}}$

74. For proton,

$u = \frac{h}{m\lambda}; \quad \because$ mass of proton $= 1.67 \times 10^{-27}$ kg

$$u = \frac{6.625 \times 10^{-34}}{1.67 \times 10^{-27} \times 0.005 \times 10^{-9}} = 7.94 \times 10^{4} \text{ metre sec}^{-1}$$

Now accelerating potential is V, then velocity (u) acquired by the charge particle having charge Q and mass m.

$\because \quad Q.V = \frac{1}{2}mu^2$

$$u = \sqrt{\left(\frac{2QV}{m}\right)} = \sqrt{\left(\frac{2 \times 1.602 \times 10^{-19} \times V}{1.67 \times 10^{-27}}\right)}$$

or $\quad 7.94 \times 10^{4} = \sqrt{\left(\frac{2 \times 1.602 \times 10^{-19} \times V}{1.67 \times 10^{-27}}\right)}$

$\therefore \quad V = \mathbf{32.85} \textbf{ volt}$

75. $\quad \text{KE} = \frac{1}{2}mu^2 = \frac{1}{2}m\left[\frac{h}{m\lambda}\right]^2$

$$\text{KE} = \frac{1}{2}\frac{h^2}{m\lambda^2}$$

$\therefore \quad \lambda^2 = \frac{h^2}{2m\text{KE}}$

$\therefore \quad \lambda = \sqrt{\frac{h^2}{2m\text{KE}}} = \frac{6.626 \times 10^{-27}}{\sqrt{2 \times 9.108 \times 10^{-28} \times 2.5 \times 1.602 \times 10^{-12}}}$

$$= \mathbf{7.7 \times 10^{-8}} \textbf{ cm}$$

76. $$\lambda = \frac{h}{mu} = \frac{h}{\sqrt{2eVm}} \qquad (\because \text{eV} = 1/2\,mu^2)$$

$$= \frac{6.626\times10^{-34}}{\sqrt{2\times1.6\times10^{-19}\times V\times9.1\times10^{-31}}}$$

$$= \frac{6.626\times10^{-34}}{5.396\times10^{-25}\,[V]^{1/2}} = \frac{1.227\times10^{-9}}{[V]^{1/2}}\ \text{metre}$$

$$= \frac{12.27\times10^{-10}}{[V]^{1/2}}\ \text{metre} = \frac{12.27}{[\text{V}]^{1/2}}\ \text{Å}$$

$$= \left[\frac{\mathbf{150}}{\mathbf{V}}\right]^{1/2}\ \textbf{Å}$$

77. $$\Delta u = \frac{0.1\times10^{-4}}{100} = 1\times10^{-7}\ \text{cm sec}^{-1}$$

$\because$ $$\Delta u\cdot\Delta x = \frac{h}{4\pi m}$$

$\therefore$ $$\Delta x = \frac{6.625\times10^{-27}}{4\times3.14\times10^{-11}\times1\times10^{-7}} = 5.27\times10^{-10}\ \text{cm}$$

The uncertainty in position as compared to particle size

$$= \frac{\Delta x}{\text{diameter}} = \frac{5.27\times10^{-10}}{10^{-4}} = \mathbf{5.27\times10^{-6}\ cm}$$

The factor being small and almost being negligible for microscopic particles.

78. According to Heisenberg's uncertainty principle

$$\Delta u\cdot\Delta x \approx \frac{h}{4\pi m}$$

$$\Delta u \approx \frac{h}{4\pi m\cdot\Delta x}$$

$$= \frac{6.625\times10^{-34}}{4\times\frac{22}{7}\times9.108\times10^{-31}\times10^{-10}}$$

$$= \mathbf{5.8\times10^{5}\ m\ sec^{-1}}$$

79. $$\Delta u\cdot\Delta x \approx \frac{h}{4\pi m}$$

$$\Delta u = \frac{h}{4\pi m\cdot\Delta x} = \frac{6.625\times10^{-34}}{4\times\frac{22}{7}\times0.15\times10^{-10}}$$

$$= \mathbf{3.51\times10^{-24}\ m\ sec^{-1}}$$

80. $$\Delta x\cdot\Delta p = \frac{h}{4\pi}$$

$\because$ $$\Delta x = 0.001\ \text{Å} = 10^{-13}\ \text{m}$$

$\therefore$ $$\Delta p = \frac{6.625\times10^{-34}}{2\times3.14\times10^{-13}} = \mathbf{5.27\times10^{-22}\ Ns}$$

Now if the given momentum $= \dfrac{h}{2\pi a_0}$

$$= \frac{6.625\times10^{-34}}{2\times3.14\times0.529\times10^{-10}}$$

$$= \mathbf{2\times10^{-24}\ Ns}$$

The uncertainty in momentum seems to be about $\left(\dfrac{5.27\times10^{-22}}{2\times10^{-24}}\right)$ or 263.5 times as large as the momentum itself is. Because of this reason, the concept of Bohr's orbit has been replaced by probabilities of locating electron cloud.

81. $$\Delta x_0\cdot\Delta u = \frac{h}{4\pi m}$$

$\therefore$ $$\Delta u = \frac{h}{4\pi m\cdot\Delta x_0}$$

or $\Delta u = \dfrac{\Delta x}{t}$ *i.e.*, the distance travelled by proton in time t.

$\therefore$ $$\Delta x = \frac{t\cdot h}{4\pi m\cdot\Delta x_0}$$

$$= \frac{6.626\times10^{-34}\times1}{4\times3.14\times1.672\times10^{-27}\times1.0\times10^{-11}}$$

$$= \mathbf{3.15\times10^{3}\ m}$$

82. Mass of electron in motion $= \dfrac{2}{931}$ amu

$$= \frac{2}{931}\times1.66\times10^{-27}\ \text{kg}$$

$(\because 1\,\text{amu} = 931\,\text{MeV})$

$$= \mathbf{35.6\times10^{-31}\ kg}$$

Also, $$m_e = \frac{m_e^0}{\sqrt{1-\left[\frac{u}{c}\right]^2}}$$

or $$35.6\times10^{-31} = \frac{\frac{0.511}{931}\times1.66\times10^{-27}}{\sqrt{1-\left[\frac{u}{3\times10^{10}}\right]^2}}$$

$\therefore$ $$u = \mathbf{2.9\times10^{10}\ cm\ sec^{-1}}$$

83. Radius of the nucleus is of the order of 10^{-13} cm and thus uncertainty in position of electron, *i.e.*, (Δx), if it is within the nucleus will be 10^{-13} cm.

Now, $$\Delta x\cdot\Delta u \geq \frac{h}{4\pi m}$$

$\therefore$ $$\Delta u = \frac{6.626\times10^{-27}}{4\times3.14\times9.108\times10^{-28}\times10^{-13}}$$

$$= \mathbf{5.79\times10^{12}\ cm/sec}$$

i.e., order of velocity of electron will be 100 times greater than the velocity of light which is impossible. Thus, possibility of electron to exist within the nucleus is zero.

84. Energy of photon = work function $+1/2\,mu^2$

Energy of photon = work function $+ eV_0$ ...(1)

where e is electronic charge and V_0 is stopping potential and eV_0 is equal to energy required to stop the ejection of electron.

$\because$ $$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{6.625\times10^{-34}\times3.0\times10^{8}}{253.7\times10^{-9}}$$

$$= 7.834\times10^{-19}\ \text{J}$$

$$= \frac{7.834\times10^{-19}}{1.602\times10^{-19}}\ \text{eV} = 4.89\,\text{eV}$$

$\therefore$ By Eq. (1) 4.89 = work function + 0.24

Work function = **4.65 V**

85. Energy of photon liberated from He^+ during emission of H_α line of Lyman series $= hc \cdot R_H Z^2 \left[\frac{1}{1^2} - \frac{1}{2^2}\right]$

$$= 6.625 \times 10^{-27} \times 3 \times 10^{10} \times 109678 \times 2^2 \left[\frac{3}{4}\right]$$

$$= 6.54 \times 10^{-11} \text{ erg}$$

This energy is used in liberating electron from H atom from ground state, therefore,

$$6.54 \times 10^{-11} = E_1 \text{ of H} + \frac{1}{2} mu^2$$

$$= 13.6 \times 1.602 \times 10^{-12} + \frac{1}{2} mu^2$$

$$\frac{1}{2} mu^2 = 6.54 \times 10^{-11} - 2.179 \times 10^{-11}$$

$$= 4.361 \times 10^{-11} \text{ erg}$$

$$u^2 = \frac{4.361 \times 10^{-11} \times 2}{9.108 \times 10^{-28}}$$

$\therefore$ $$\mathbf{u = 3.09 \times 10^8 \text{ cm sec}^{-1}}$$

86. Energy of photon

= Kinetic energy of photo electron + Threshold frequency

$\therefore \quad h\nu_1 = KE_1 + h\nu_0 \quad$ ...(1)

and $\quad h\nu_2 = KE_2 + h\nu_0 \quad$ ...(2)

Multiplying Eq. (1) by 2 and subtracting Eq. (2) from it

$$2h\nu_1 - h\nu_2 = h\nu_0 \qquad (\because 2KE_1 = KE_2)$$

or $$(2\nu_1 - \nu_2) = \nu_0$$

$\therefore$ $$\nu_0 = \left[\frac{2c}{\lambda_1} - \frac{c}{\lambda_2}\right] = \frac{3 \times 10^8}{10^{-10}}\left[\frac{2}{2200} - \frac{1}{1900}\right]$$

$$(1 \text{ Å} = 10^{-10} \text{ m})$$

$$\nu_0 = \mathbf{1.1483 \times 10^{15} \text{ sec}^{-1}}$$

Also, $$\lambda_0 = \frac{c}{\nu_0} = \frac{3 \times 10^8}{1.1483 \times 10^{15}} = 2.6126 \times 10^{-7} \text{ m}$$

$$= \mathbf{2612.6 \text{ Å}}$$

87. Energy absorbed $= \frac{hc}{\lambda}$

$$= \frac{6.625 \times 10^{-27} \times 3.0 \times 10^{10}}{360 \times 10^{-8}} = 5.52 \times 10^{-11} \text{ erg}$$

$$= 5.52 \times 10^{-18} \text{ joule}$$

Now this energy is used in overcoming forces of attraction between surface of metal and imparting velocity to electron, therefore,

$E_{\text{absorbed}} = E$ used in attractive forces + Kinetic energy of electron

$\therefore$ Kinetic energy $= 5.52 \times 10^{-18} - 7.52 \times 10^{-19}$ joule

$$= \mathbf{47.68 \times 10^{-19} \text{ joule}}$$

88. Binding energy of electron $= 250 \text{ kJ mol}^{-1}$

$\therefore$ Binding energy of one electron $= \frac{250 \times 10^3}{6.023 \times 10^{23}}$ J

$$= 4.15 \times 10^{-19} \text{ J}$$

Also, Binding energy $= h\nu_0$

Where ν_0 is threshold frequency.

$\therefore$ $$4.15 \times 10^{-19} = 6.625 \times 10^{-34} \times \nu_0$$

$\therefore$ $$\nu_0 = \mathbf{6 \times 10^{14} \text{ sec}^{-1}}$$

89. The frequency of emitted X-rays is given by

$$\sqrt{\nu} = a(Z - b)$$

(according to Mosley's law, where a and b are characteristic constants)

or $$\sqrt{\frac{c}{\lambda}} = a(Z - b) \qquad \text{(where } c \text{ is velocity of light)}$$

Thus, for $_{26}Fe$ ($\because Z = 26$) $\therefore \sqrt{\frac{c}{\lambda_1}} = a(26 - b)$ ...(1)

For $_{19}K$ ($\because Z = 19$) $\therefore \sqrt{\frac{c}{\lambda_2}} = a(19 - b)$ ...(2)

By Eqs. (1) and (2) $$\sqrt{\frac{\lambda_2}{\lambda_1}} = \frac{26 - b}{19 - b}$$

$$\lambda_1 = 1.931 \times 10^{-8} \text{ cm}, \ \lambda_2 = 3.737 \times 10^{-8} \text{ cm}$$

$$\sqrt{\frac{3.737 \times 10^{-8}}{1.931 \times 10^{-8}}} = \frac{26 - b}{19 - b}$$

$$1.39 = \frac{26 - b}{19 - b}$$

or $26.41 - 1.39b = 26 - b$ or $b = 1.05$ ...(3)

By Eqs. (1) and (3)

$$\sqrt{\frac{3.0 \times 10^{10}}{1.931 \times 10^{-8}}} = a(26 - 1.05)$$

$\therefore$ $$a = 5 \times 10^7$$

Now, if $\lambda = 2.289 \times 10^{-8}$ cm, then

$$\sqrt{\frac{3.0 \times 10^{10}}{2.289 \times 10^{-8}}} = 5 \times 10^7 (Z - 1.05)$$

$\therefore$ $$\mathbf{Z = 24} \qquad (\because Z \text{ is integer})$$

Therefore, atomic no. of element is **24** and so it is **chromium.**

90. ψ value represents an orbital. The given value is for $4d_{z^2}$ ($n = 4, l = 2, m = 0$).

91. Angular nodes $= l$, spherical node $= n - l - 1$

(a) 1, 2 (b) 1, 1 (c) 0, 2

92. $$\psi_{2s} = \frac{1}{2\sqrt{32\pi}} \cdot \left[\frac{1}{a_0}\right]^{3/2} \cdot \left[2 - \frac{r}{a_0}\right] \cdot e^{-r/2a_0}$$

For radial node at $r = r_0$, $\psi_{2s}^2 = 0$. This is possible only when

$$\left[2 - \frac{r_0}{a_0}\right] = 0 \text{ or } 2 = \frac{r_0}{a_0} \text{ or } r_0 = \mathbf{2a_0}$$

93. Formula of nitrate ion $= NO_3^-$

$\therefore$ No. of electron in NO_3 = Electrons in N + 3 × Electrons in O + 1 (due to negative charge)

$$= 7 + 3 \times 8 + 1 = \mathbf{32}$$

94. Electronic configuration of neutral atom:

$$\frac{1s^2}{K}, \frac{2s^2 2p^6}{L}, \frac{3s^2 3p^6 3d^1}{M}, \frac{4s^2}{N}$$

(a) At. no. = Total no. of electron in neutral atom = **21**

(b) Total no. of s electrons $= \mathbf{8}$

(c) Total no. of p electrons $= \mathbf{12}$

(d) Total no. of d electrons $= \mathbf{1}$

(e) Valency of element **+2** and **+3** (due to no. of electrons in outer shell and penultimate d sub-shell)

(f) No. of unpaired 'e' $= \mathbf{1}$ (of $3d$)

95. Total no. of molecules of $CO_2 = 12$

(1) $C^{12}O^{16}O^{16}$	Molar mass $= \mathbf{44\ g\ mol^{-1}}$
(2) $C^{12}O^{17}O^{17}$	Molar mass $= \mathbf{46\ g\ mol^{-1}}$
(3) $C^{12}O^{18}O^{18}$	Molar mass $= \mathbf{48\ g\ mol^{-1}}$
(4) $C^{12}O^{16}O^{17}$	Molar mass $= \mathbf{45\ g\ mol^{-1}}$
(5) $C^{12}O^{16}O^{18}$	Molar mass $= \mathbf{46\ g\ mol^{-1}}$
(6) $C^{12}O^{17}O^{18}$	Molar mass $= \mathbf{47\ g\ mol^{-1}}$

Similarly six molecules with C^{13} isotope.

96.

	I isotope of O	II isotope of O
Atomic masses are	15.9936	17.0036
∴ Mass no. are	**16**	**17** (Integer values)
∴ No. of neutrons	$= 16 - 8 = \mathbf{8}$	$= 17 - 8 = \mathbf{9}$
and No. of electrons	$= \mathbf{8}$	$= \mathbf{8}$

∵ Mass No. − At. No. = No. of neutrons

97.

	Electronic configuration	No. of unpaired (e)
(a)	$_{25}Mn^{+4}$: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^3$	3
(b)	$_{24}Cr^{+2}$: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^4$	4
(c)	$_{26}Fe^{+3}$: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5$	5
(d)	$_{28}Ni^{+2}$: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^8$	2
(e)	$_{17}Cl^-$: $1s^2, 2s^2 2p^6, 3s^2 3p^6$	0
(f)	$_{30}Zn^{+2}$: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}$	0
(g)	$_{26}Fe^{+2}$: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6$	4
(h)	$_{11}Na$: $1s^2, 2s^2 2p^6, 3s^1$	1
(i)	$_{12}Mg$: $1s^2, 2s^2 2p^6, 3s^2$	0
(j)	$_{24}Cr^{+3}$: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^3$	3

Note : In case of writing electronic configuration of cation, first write configuration of neutral atom and then take out desired electrons from outermost shell, *e.g.*,

$_{25}Mn$: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^2$

$_{25}Mn^+$: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$

98. Count unpaired electrons in each.

$$\text{Total spin} = \text{No. of unpaired electron} \times \left(\pm\frac{1}{2}\right)$$

∴ (a) **Total spin in** $1s^2 = \mathbf{0} \times \left(\pm\frac{1}{2}\right) = \mathbf{0}$

(b) **Total spin in** $1s^2, 2s^2 2p^6 = \mathbf{0} \times \left(\pm\frac{1}{2}\right) = \mathbf{0}$

(c) **Total spin in** $1s^2, 2s^2 2p^5 = \mathbf{1} \times \left(\pm\frac{1}{2}\right) = \pm\frac{1}{2}$

(d) **Total spin in** $1s^2, 2s^2 2p^3 = \mathbf{3} \times \left(\pm\frac{1}{2}\right) = \pm\frac{3}{2}$

(e) **Total spin in** $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^2$

$$= \mathbf{5} \times \left(\pm\frac{1}{2}\right) = \pm\frac{5}{2}$$

99. No. of unpaired electrons are given by

Magnetic moment $= \sqrt{[n(n+2)]}$

where n is no. of unpaired electrons

or $1.73 = \sqrt{[n(n+2)]}$ or $1.73 \times 1.73 = n^2 + 2n$ $\therefore n = 1$

Now vanadium atom must have one unpaired electron and thus its configuration is

$$_{23}V^{4+} : 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1$$

100. Angular momentum in an orbital $= \frac{h}{2\pi}\sqrt{[(l+1)\times l]}$

(a) $l = 0$ for $4s$ orbital

∴ Angular momentum = 0

(b) $l = 1$ for $3p$ orbital

∴ Angular momentum $= \frac{h}{\sqrt{2}\pi}$

(c) Angular momentum in an orbit $= \frac{nh}{2\pi}$

$n = 4$ for 4th orbit

∴ Angular momentum $= \frac{2h}{\pi}$

101. (a) $\because n = 2$ and $l = 1$ $\quad \therefore 2p$

Also $m = -1$ $\quad \therefore \mathbf{2p_x}$ **or** $\mathbf{2p_y}$

(b) $\mathbf{4d_{z^2}}$

(c) $\mathbf{3p_x}$ **or** $\mathbf{3p_y}$

(d) **4s**

(e) $\mathbf{3d_{x^2-y^2}}$ **or** $\mathbf{3d_{xy}}$

102.

(a)	$\mathbf{2s}$	: $\mathbf{n = 2}$	$\mathbf{l = 0}$	$\mathbf{m = 0}$
(b)	$\mathbf{2p_z}$	: $\mathbf{n = 2}$	$\mathbf{l = 1}$	$\mathbf{m = 0}$
(c)	$\mathbf{4d_{x^2-y^2}}$	: $\mathbf{n = 4}$	$\mathbf{l = 2}$	$\mathbf{m = -2}$ **or +2**
(d)	$\mathbf{4d_{z^2}}$	: $\mathbf{n = 4}$	$\mathbf{l = 2}$	$\mathbf{m = 0}$

103. Find $(n+l)$ for each set

(1) Lower is the value of $(n+l)$, lower is energy level.

(2) If $(n+l)$ are same then orbital with lower values of n possess lower energy.

∵ Decreasing order of energy $\mathbf{3 > 1 > 2 > 4}$.

104. $_{18}Ar : 1s^2, 2s^2 2p^6, 3s^2 3p^6$

Quantum numbers for $3p^6$ electrons

$n = 3$	$l = 1$	$m = -1$ or $+1$	$s = +\frac{1}{2}$ or $-\frac{1}{2}$
$n = 3$	$l = 1$	$m = 0$	$s = +\frac{1}{2}$ or $-\frac{1}{2}$
$n = 3$	$l = 1$	$m = +1$ or -1	$s = +\frac{1}{2}$ or $-\frac{1}{2}$
$n = 3$	$l = 1$	$m = -1$ or $+1$	$s = -\frac{1}{2}$ or $+\frac{1}{2}$
$n = 3$	$l = 1$	$m = 0$	$s = -\frac{1}{2}$ or $+\frac{1}{2}$
$n = 3$	$l = 1$	$m = +1$ or -1	$s = -\frac{1}{2}$ or $+\frac{1}{2}$

105. Let oxide of nitrogen be N_2O_a

$$\text{Molar mass of } N_2O_a = 46 \times 2 = 92\,\text{g mol}^{-1}$$

$\therefore$ $2 \times 14 + 16(a) = 92$

$\therefore$ $a = 4$

$\therefore$ Oxide is N_2O_4

$92\text{ g } N_2O_4 = 1\text{ mole of } N_2O_4 = N \text{ molecules of } N_2O_4$

$\because$ 1 molecule of N_2O_4 has 46 electrons

$\therefore$ N molecules of N_2O_4 have $46 \times N$ electrons

where N is Avogadro's number.

106. (a) 16 g CH_4 has N molecules

1.6 g CH_4 has $\frac{N}{10}$ molecules

Now 1 molecule of CH_4 has $(6+4)e = 10e$

$\therefore$ $N/10$ molecules of CH_4 have $= N$ **electrons**

(b) No. of electrons in 1 molecule of $CO_2 = 6 + 16 = \mathbf{22}$

(c) No. of electrons in 1 molecule of $N_2 = 7 + 7 = \mathbf{14}$

107. $${}_4\text{Be}^7 + {}_{-1}e^0 \longrightarrow {}_3\text{Li}^7$$

$\therefore$ At. No. = **3;** Mass No. = **7**

108.

${}_{12}\text{Mg}$: $1s^2, 2s^2 2p^6, 3s^2$

${}_{17}\text{Cl}$: $1s^2, 2s^2 2p^6, 3s^2 3p^5$

${}_{23}\text{V}$: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^3, 4s^2$

To locate periods: The no. of outermost shell suggest the period of element. Therefore, **Mg** in **III** period, **Cl** in **III** period, **V** in **IV** period.

To locate groups: First locate block and then group as given below:

(a) *s*-Block: (1) The configuration ns^1 or ns^2 followed with $(n-1)s^2 p^6$ represents *s*-block.

(2) In *s*-block ns^1 represents for I gp.

ns^2 represents for II gp.

Therefore, **Mg is *s*-block element of II group.**

(b) *p*-Block: (1) The configuration $ns^2 np^{1 \text{ to } 6}$ represent *p*-block.

(2) In *p*-block no. of $(ns + np)$ electrons represent group.

$ns^2 np^1 = \text{III gp.}$ $ns^2\ np^4 = \text{VI gp.}$

$ns^2 np^2 = \text{IV gp.}$ $ns^2\ np^5 = \text{VII gp.}$

$ns^3 np^3 = \text{V gp.}$ $ns^2\ np^6 = \text{zero gp.}$

Therefore, **Cl is *p*-block element of VII group.**

(c) *d*-Block: (1) The configuration ns^1 or ns^2 followed with $(n-1)s^2\ p^6\ d^{1-10}$ represents *d*-block.

(2) In *d*-block = [No. of '*e*' in outer shell penultimate + No. of '*e*' in penultimate shell] $-8 = \Delta =$ group number

$\Delta = 3$	III group
$\Delta = 4$	IV group
$\Delta = 5$	V group
$\Delta = 6$	VI group
$\Delta = 7$	VII group
$\Delta = 8$ $\Delta = 9$ $\Delta = 10$	VIII group
$\Delta = 11$	I group
$\Delta = 12$	II group

$\therefore$ **${}_{23}$V is *d*-block element of V group.**

• SINGLE INTEGER ANSWER PROBLEMS •

1. The ratio of speeds of electron in I orbit of H-atom to IV orbit of He^+-ion is.....
2. The transition of electron occurs in H-atom from 6th to 3rd orbit. The no. of spectral lines given are .....
3. The no. of waves made by an electron during its revolution in 5th orbit is.....
4. Energy of an electron in an orbit of H-atom is $-\frac{R_H}{4}$. The no. of degenerate orbitals in this orbit are .....
5. The number of revolutions/sec made by an electron in II orbit is 8 times of the number of revolution/sec made by electron in nth orbit. The value of n is .....
6. A transition of electron from an higher orbit to 2nd orbit produces 10 spectral lines. The higher orbit no. is .....
7. A transition for H atom from II to I orbit has same wavelength as from nth orbit to 2nd orbit for He^+ ion. The value of 'n' is .....
8. Suppose 3.1×10^{-18} J energy is needed by the interior of the human eye to see an object. How many photon of light of $\lambda = 400$ nm will be needed to see the object? $(h = 6.6 \times 10^{-34}$ Js)
9. Humphry series is obtained when electron in H-atom jumps from a higher orbit to n orbit. The value of n is .....
10. The total values of m for each orbital in M shell are .....
11. No. of elliptical orbitals in 5th shell are .....
12. No. of nodal planes in $3d$ orbitals are .....
13. The magnetic moment of $_{41}Nb$ is found to be 5.916. Total no. of unpaired electron are .....
14. An absorption of 12.088 eV energy by an electron in ground state of H-atom brings in the excitation of electron to which orbit?
15. Total no. of degenerate orbital in $\psi_{4,2,0}$ orbital of H-atom.
16. The ratio of the time required for an electron taking one round of 2nd orbit of H-atom and He^+ ion respectively.
17. Total number of nodes in 3rd shell is ......
18. Number of unpaired electrons in V^{3+} ion is ......
19. Total spin of electrons in Cr atom is ......
20. Number of lobes in d_{z^2} orbital is ......
21. Possible number of molecules of H_2O using ^1_1H and all isotopes of oxygen.
22. If radius of I orbit of H-atom is 0.5×10^{-8} cm, the de Broglie wavelength of electron in I orbit is $a\,\pi$ Å. The closest value of a is.....
23. The energy required to stop the ejection of electrons from a metal plate in photoelectric effect is 0.89 eV. The radiations of 253.7 nm strike the metal plate to show ejection of electrons. The work function of metal in eV is.....
24. The wavelength ratio of two radiations is 1 : 5. The ratio of their energy is.....
25. The ratio of velocity of electrons in 1st orbit and 3rd orbit is.....
26. The wavelength of certain line in Balmer series is observed to be 4341Å. To what value of n_2 does this corresponds ?
27. Number of unpaired electrons in $_{28}Ni^{2+}$ ion is.....
28. An oil drop has 1.1214×10^{-18} coulomb charge. Number of electrons associated with this oil drop is .....
29. Number of orbitals not having spherical shape in 3rd shell is .....
30. n_2 values for II line of Humphry series corresponds to.....
31. Total spin of electrons in Mn^{3+} ion is $\pm a$. The value of a is.....
32. The lowest value of n which allows g-orbitals to exist is.....
33. Values of magnetic quantum numbers in an outer shell of an element are nine. What is the outermost shell of element ?
34. Which energy level in He^+ has same energy level as the 4th energy level of H ?
35. N and Ne both have same number of electrons having their spin in one direction. The maximum number of electrons having same spin orientation is.....
36. The magnetic moment of Mn^{a+} is 4.90 B.M. The value of a is.....
37. How many elements possess same number of s-electrons as p-electrons?
38. 10^{-18} J of energy is needed to carry out the reaction. How many photons of light of 450 nm are needed to generate this energy.
39. Cr^{n+} has magnetic moment equal to 5.916 BM. The value of n is ......
40. $E_n = -\frac{Z^2 B}{n^2}$ where Z is the atomic number of species and $B = 2.179 \times 10^{-18}$ J. If energy level of Li^{2+} ion in a particular shell is -2.179×10^{-18} J, the principal quantum number of shell is ......
41. The value of angular quantum number from which electron drops to emit I line of Lyman series.
42. The velocity of electron in a certain Bohr's orbit of H atom bears the ratio 1 : 275 to the velocity of light. The number of waves made by electron during one complete revolution round this orbit is ......

43. The binding energy of electrons in a metal is 2.5×10^{a} kJ mol^{-1} and threshold frequency of metal is $6 \times 10^{14} sec^{-1}$. The value of a is ......

44. Total number of molecules of CO_2 formed by using C–12 isotope and O-16, O-17 and O-18 isotopes are ......

45. Angular momentum in an orbit is $3\hbar$. The value of n is ......

46. Number of lobes present in d_{z^2} orbital is ......

47. The quantum number 6 corresponding to the excited state of He^{+} ion if on deexcitation to the ground state that ion emits photons in succession with two wavelengths only. The quantum number of the shell in which the electron comes first before occupying ground state is ......

48. How many orbitals of He^{+} ion possess same energy level in 2^{nd} shell?

49. The ratio of e/m for H^{+} and He^{2+} is ......

50. H atom is in an excited state. It is subjected to radiation to excite further in next excited state. If photon of energy 1.89 eV is required to do show, the finally excited state of H atom is in ...... orbit.

51. The total values of magnetic quantum number of an electron when the value of $n = 2$ is ......

52. How many sets of four quantum numbers are possible for electrons present in He^{2-} ......

53. Number of electrons in the nucleus of an element of atomic number 14 is ......

54. If two electrons in an atom round the nucleus one each in circular orbit of R and $4R$. The time taken for one complete revolution in $4R$ shell is ...... times of R shell.

55. The maximum number of electrons that can have principal quantum no., $n = 3$ and spin quantum no. $m_s = -\frac{1}{2}$ is .... **(IIT 2011)**

56. The work function (ϕ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metal is : **(IIT 2011)**

Metal	Li	Na	K	Mg	Cu	Ag	Fe	Pt	W
ϕ (ev)	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6.3	4.75

57. The atomic masses of He and Ne are 4 and 20 a.m.u., respectively. The value of the de Broglie wavelength of He gas at –73°C is "M" times that of the de Broglie wavelength of Ne at 727°C. M is : **[JEE (Advanced) I 2013]**

ANSWERS

1. Two **2.** Six **3.** Five **4.** Four **5.** Four **6.** Six **7.** Four **8.** Seven **9.** Six **10.** Nine **11.** Four **12.** Two
13. Five **14.** Three **15.** Five **16.** Four **17.** Two **18.** Two **19.** Three **20.** Two **21.** Three **22.** One **23.** Four **24.** Five
25. Three **26.** Five **27.** Two **28.** Seven **29.** Eight **30.** Eight **31.** Two **32.** Five **33.** Three **34.** Eight **35.** Five **36.** Three
37. Two **38.** Three **39.** One **40.** Three **41.** One **42.** Two **43.** Two **44.** Six **45.** Three **46.** Two **47.** Two **48.** Four
49. Two **50.** Three **51.** Four **52.** Four **53.** Zero **54.** Eight **55.** Nine **56.** Four **57.** Five

OBJECTIVE PROBLEMS (One Answer Correct)

1. A Bohr orbit of H-atom having energy $=-\frac{Rh}{9}$ has degenerate levels :
(a) 2 (b) 4
(c) 5 (d) 9

2. If speed of an electron of mass 'm' in an orbit represents its wavelength, then its wavelength is given by :
(a) $\sqrt{\frac{m}{h}}$ (b) $\sqrt{\frac{h}{p}}$
(c) $\sqrt{\frac{h}{m}}$ (d) $\sqrt{\frac{h}{2k\varepsilon}}$

3. Out of which λ values are definitely observed during emission or absorption spectrum of H-atom?
(a) Lyman (b) Balmer
(c) Paschen (d) All of these

4. The wavelength of m^{th} line Balmer series for an orbital is 4103 Å. The value of m represents:
(a) 2 (b) 4
(c) 6 (d) 8

5. Spin angular momentum of electron is given by :
(a) $\frac{\sqrt{3}}{4}\frac{h}{\pi}$ (b) $\sqrt{\frac{3}{4}}\cdot\frac{h}{\pi}$
(c) $\sqrt{\frac{3h}{4\pi}}$ (d) $\sqrt{\frac{4h}{3\pi}}$

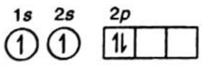
6. Which of the following does not contain same number of electrons in its outer shell as Pd has in its outer shell?
(a) Ag^+ (b) Cd^{2+}
(c) Cu^{2+} (d) Cu^+

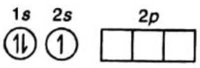
7. Which of the following transitions are allowed in the normal electronic spectrum of H-atom?
(a) $4p$ to $3p$ (b) $4d$ to $3s$
(c) $4p$ to $3d$ (d) $3s$ to $2s$

8. The wavelength of an electron accelerated by a potential difference of 500 V is:
(a) 5.5×10^{-11} m (b) 3.89×10^{-11} m
(c) 5.5×10^{-10} m (d) 3.89×10^{-10} m

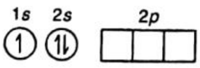
9. Completely filled or half filled set of d-orbitals is assumed to be spherically symmetrical. Which of the following has spherical symmetry?
(a) Pd^{2+} (b) O^{2-}
(c) Cr (d) Ni

10. In absence of Pauli principle, the configuration of $_3Li$ would have been:

(a) 

(b) 

(c) 

(d) 

11. A $3p$-orbital has:
(a) two spherical nodes
(b) two non-spherical nodes
(c) one spherical and one non-spherical node
(d) one spherical and two non-spherical node

12. Which has maximum number of unpaired electron?
(a) Mg^{2+} (b) Ti^{3+}
(c) V^{3+} (d) Fe^{2+}

13. For a d-electron, the orbital angular momentum is:
(a) $\sqrt{6}\,\hbar$ (b) $\sqrt{2}\,\hbar$
(c) $\hbar$ (d) $2\,\hbar$

14. The first use of quantum theory to explain the structure of atom was by:
(a) Heisenberg (b) Bohr
(c) Planck (d) Einstein

15. The energy of an electron in the first orbit of H-atom is 13.6 eV. The possible value of excited state for electron in Bohr orbit of H-atom is :
(a) −3.4 eV (b) −4.2 eV
(c) −6.8 eV (d) +6.8 eV

16. The electrons, identified by quantum number n and l, (i) $n=4, l=1$; (ii) $n=4, l=0$; (iii) $n=3, l=2$; (iv) $n=3, l=1$ can be placed into order of increasing energy, from the lowest to highest, as:
(a) (iv) < (ii) < (iii) < (i) (b) (ii) < (iv) < (i) < (iii)
(c) (i) < (iii) < (ii) < (iv) (d) (iii) < (i) < (iv) < (ii)

17. Select the correct statement:
(a) The electron density in the XY plane of $3d_{X^2Y^2}$ orbital is zero.
(b) The energy of $3d$-orbitals is less than $4s$-orbital.
(c) The $3d$-orbitals are far away from nucleus than $4s$-orbital.
(d) Wave function of atomic orbital represents an orbital.

18. Select the correct statement:
(a) Electromagnetic waves with minimum wavelength is radiowave
(b) X-rays are deflected in electric and magnetic field
(c) $E=h\nu$ represents dual nature of electron
(d) No. of nodal planes in $3p$ sub-shell is one

19. The radius of first Bohr's orbit in H-atoms is r_1. The corresponding wavelength of an electron in 2nd orbit is:
(a) $6\pi r_1$ (b) $4\pi r_1$
(c) $2\pi r_1$ (d) $3\pi r_1$

20. The ratio of angular momentum of electron in two successive orbit is a ($a>1$) and their difference is b. Then a/b is equal to :
(a) $\frac{n}{n+1}$ (b) $\frac{n+1}{n}$
(c) $\frac{n+1}{n}\cdot\frac{h}{2\pi}$ (d) $\frac{n+1}{n}\cdot\frac{2\pi}{h}$

21. The de Broglie wavelength of a particle of mass m and temperature T K is given by :

(a) $\frac{h}{\sqrt{2mkT}}$ (b) $\frac{h}{\sqrt{3mkT}}$

(c) $\frac{h}{\sqrt{4mkT}}$ (d) $\frac{h}{\sqrt{mkT}}$

22. A proton (p) a deutron (D) and an α-particle (α) possess same kinetic energy. The order of de Broglie wavelengths is :

(a) $\lambda_p > \lambda_\alpha > \lambda_D$ (b) $\lambda_D > \lambda_\alpha > \lambda_p$

(c) $\lambda_p > \lambda_D > \lambda_\alpha$ (d) $\lambda_\alpha > \lambda_D > \lambda_p$

23. Number of waves in a Bohr orbit of H-atom is 3. Its potential energy would be ....

(a) – 3.4 eV (b) – 3.02 eV

(c) –1.51 eV (d) – 13.6 eV

24. If a_0 be the radius of first Bohr orbit of H-atom, the de Broglie wavelength of an electron moving in the III Bohr orbit is :

(a) $6\pi a_0$ (b) $2\pi a_0$

(c) $4\pi a_0$ (d) πa_0

25. An electron during its transition shows a decrease in its kinetic energy by 1/4 value. The potential energy change during this transition will be :

(a) $\frac{1}{2}$KE (b) $\frac{3}{4}$KE

(c) $\frac{3}{5}$KE (d) $\frac{3}{8}$KE

26. The momentum of a photon is p, the energy associated with photon is given by :

(a) $\frac{p}{E}$ (b) $\frac{E}{p}$

(c) $p \cdot E$ (d) $\sqrt{\frac{E}{p}}$

27. The ratio of momentum of a proton and an α-particle which are accelerated from rest by a potential difference of 200 V. m_p and m_α are masses of proton and α-particles :

(a) $\sqrt{\frac{2m_p}{m_\alpha}}$ (b) $\sqrt{\frac{m_p}{2m_\alpha}}$

(c) $\frac{m_p}{2m_\alpha}$ (d) $\frac{2m_\alpha}{m_p}$

28. A source of light having wavelength λ ejects photo electron with maximum kinetic energy 1 eV. On irradiating same metal with wavlength $\lambda/3$, the ejected photoelectron possess kinetic energy of 4eV. The work function of metal is :

(a) 2 eV (b) 1 eV

(c) 3 eV (d) 0.5 eV

29. Nodal plane of $3p_y$ orbital lies along the plane :

(a) xy (b) yz

(c) zx (d) either of these

30. The frequency of revolution of electron II excited state He^+ and I excited state of H-atom :

(a) $\frac{27}{32}$ (b) $\frac{32}{27}$

(c) $\frac{1}{8}$ (d) $\frac{4}{1}$

31. When photon of energy 4.25 eV strikes the surface, the ejected electron has maximum kinetic energy T_A expressed in eV and de Broglie wavelength λ_A. The maximum kinetic energy of photoelectrons lilberated by another metal B by photons of 4.70 eV is T_B ($T_B = T_A - 1.5$eV). If de Broglie wavelength of the electron is λ_B ($\lambda_B = 2\lambda_A$), then which is not correct?

(a) work function of A is 2.25 eV

(b) $T_B = 0.5$ eV

(c) work function of B is 1.20 eV

(d) $T_A = 2.0$ eV

32. The photoelectric work function for a metal surface is 4.125 eV. The cut of wavelength for this surface is :

(a) 3011 Å (b) 2062.5 Å

(c) 4125 Å (d) 6000 Å

33. A black body has maximum wavelength λ_m at 2000 K. Its corresponding wavelength at 3000 K will be :

(a) $\frac{3\lambda}{2}$ (b) $\frac{2\lambda}{3}$

(c) $\frac{16\lambda}{81}$ (d) $\frac{81\lambda}{16}$

34. If particles are moving with same velocity, then which has maximum de-Broglie wavelength?

(a) Proton (b) α-particle

(c) Neutron (d) β-particle

35. A metal surface on capable of showing photoelectric effect does not show this phenomenon on exposure to U.V. rays. The effect can be observed in exposure of surface to :

(a) IR rays (b) X-rays

(c) Radio wave (d) Micro wave

36. An electron is moving round the nucleus of a hydrogen atom in a circular orbit of radius r. The coulombic force $\vec{F}$ between the two is : $\left(K = \frac{1}{4\pi\varepsilon_0}\right)$

(a) $\frac{Ke^2}{r^2}$ (b) $-\frac{e^2}{Kr^2}$

(c) $\frac{e^2}{Kr^2}$ (d) $\frac{-Ke^2}{r^2}$

37. In which of the following systems will the radius of the first orbit is minimum?

(a) Doubly ionised lithium

(b) Singly ionised helium

(c) Deuterum atom

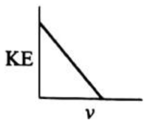
(d) Hydrogen atom

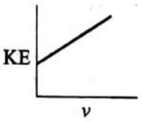
38. The mass number of nucleus is :

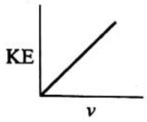
(a) always less than its atomic no.

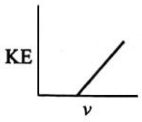
(b) always greater than its atomic no.
(c) some time equal to its atomic no.
(d) some times less than its atomic no.

39. According to Einstein photoelectric effect equation, the graph between the kinetic energy of photoelectron ejected and the frequency (ν) of incidented radiations is :

(a) 

(b) 

(c) 

(d) 

40. In India electricity is supplied for domestic use at 220V. It is supplied in USA at 110V. If the resistance of a 60W bulb for use in India is R_1, the resistance of 60W bulb in USA will be :
(a) R (b) $2R$
(c) $\frac{R}{4}$ (d) $\frac{R}{2}$

41. Ionisation potential of hydrogen atom is 13.6 eV. If ground state of H-atom is excited by monochromatic radiations of 12.1 eV, then number of spectral lines emitted by H-atom on deexcitation will be :
(a) 1 (b) 2
(c) 3 (d) 4

42. The momentum of a photon of energy 1MeV in kg-m/s will be :
(a) 5×10^{-22} (b) 0.33×10^{6}
(c) 7×10^{-24} (d) 10^{-22}

43. When photons of energy $h\nu$ fall on an aluminium plate (of work function W_0), photoelectrons of maximum kinetic energy 'K' are ejected. If the frequency of radiation is doubled, the maximum kinetic energy of the ejected photoelectrons will be :
(a) $K+h\nu$ (b) $K+W_0$
(c) $2K$ (d) K

44. The angular momentum of an electron in a H-atom is proportional to (if r is radius of orbit) :
(a) $\frac{1}{\sqrt{r}}$ (b) $\frac{1}{r}$
(c) $\sqrt{r}$ (d) r^2

45. The work function of a photosensitive surface of a metal is 6.2 eV. The wavelength of incident radiation for which stopping potential is 5eV lies in the :
(a) IR region (b) X-ray region
(c) U.V. region (d) visible region

46. Monochromatic light of wavelength 667 mm is produced by helium-neon laser. The power emitted is 9mW. The average number of photons/sec. hitting the target exposed to this beam is :
(a) 9×10^{17} (b) 3×10^{16}
(c) 9×10^{15} (d) 3×10^{19}

47. The potential difference that must be applied to stop the fastest photoelectrons emitted by a nickel surface, having work function 5.01 eV, when U.V. light of 200 nm falls in it, must be :
(a) 2.4 eV (b) – 1.2 V
(c) –2.4 V (d) 1.2 V

48. The work functions for metals A, B and C respectively are 1.92 eV, 2.00 eV and 5.0 eV. Which of them will emit photo electrons if exposed to radiations of wavelength 4100 Å.
(a) A only (b) A and B only
(c) All of these (d) None of these

49. An electron in the ground state of hydrogen has an angular momentum L_1 and electron in the first orbit of Li^{2+} has angular momentum L_2, then
(a) $L_1 = L_2$ (b) $L_1 = 3L_2$
(c) $3L_1 = L_2$ (d) $L_1 = 6L_2$

50. If magnetic quantum number of a given electron in an atom is –3, then what will be its minimum principal quantum no.?
(a) 2 (b) 3
(c) 4 (d) 5

51. Out of a photon and electron, the equation $E = p \cdot c$ (where p is momentum and c is velocity of light) is valid for :
(a) photon only (b) electron only
(c) both (a) and (b) (d) none of these

52. The total number of electrons in one molecule of CO_2 is :
(a) 22 (b) 44
(c) 66 (d) 88

53. The number of neutrons in dipositive zinc ion, with mass number 70 is :
(a) 34 (b) 36
(c) 38 (d) 40

54. Rutherford's experiment on scattering of α-particles showed for the first time that the atom has :
(a) electrons (b) protons
(c) nucleus (d) neutrons

55. The number of unpaired electrons in Ni^{2+} are :
(a) 0 (b) 2
(c) 4 (d) 8

56. Any p-orbital can accommodate upto :
(a) four electrons
(b) six electrons
(c) two electrons with parallel spins
(d) two electrons with opposite spins

57. The principal quantum number of an atom is related to the :
(a) size of the orbital
(b) spin angular momentum
(c) orientation of the orbital in space
(d) orbital angular momentum

58. Rutherford's scattering experiment is related to the size of the :
(a) nucleus (b) atom
(c) electron (d) neutron

59. The increasing order (lowest first) for the values of e/m (charge/mass) for electron (*e*), proton (*p*), neutron (*n*) and alpha particle (α) is :
(a) e, p, n, α (b) n, p, e, α
(c) n, p, α, e (d) n, α, p, e

60. Correct set of four quantum numbers for the valence (outermost) electron of rubidium (Z = 37) is :
(a) 5, 0, 0, + 1/2 (b) 5, 1, 0, + 1/2
(c) 5, 1, 1, + 1/2 (d) 6, 0, 0, + 1/2

61. Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon?
(a) 3*s* (b) 2*p*
(c) 2*s* (d) 1*s*

62. Bohr's model can explain :
(a) the spectrum of hydrogen atom only
(b) spectrum of an atom or ion containing one electron only
(c) the spectrum of hydrogen molecule
(d) the solar spectrum

63. The radius of an atomic nucleus is of the order of :
(a) 10^{-10}cm (b) 10^{-13}cm
(c) 10^{-15}cm (d) 10^{-8}cm

64. Electromagnetic radiation with maximum wavelength is :
(a) ultra violet (b) radio wave
(c) X-ray (d) infra-red

65. Rutherford's alpha particle scattering experiment eventually led to the conclusion that :
(a) mass and energy are related
(b) electrons occupy space around the nucleus
(c) neutrons are buried deep in the nucleus
(d) the point of impact with matter can be precisely determined

66. Which one of the following sets of quantum numbers represents an impossible arrangement?

	n	*l*	*m*	*s*		*n*	*l*	*m*	*s*
(a)	3	2	−2	1/2	(b)	4	0	0	1/2
(c)	3	2	−3	1/2	(d)	5	3	0	−1/2

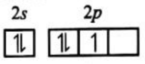
67. The ratio of the energy of a photon of 2000 Å wavelength radiation to that of 4000Å radiation is :
(a) 1/4 (b) 4
(c) 1/2 (d) 2

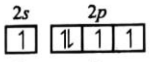
68. The sum of the numbers of neutron and proton in the isotope of hydrogen is :
(a) 6 (b) 5
(c) 4 (d) 3

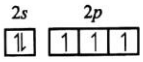
69. The triad of nuclei that are isotones is :
(a) $^{14}_{6}C$, $^{15}_{7}N$, $^{17}_{9}F$ (b) $^{12}_{6}C$, $^{14}_{7}N$, $^{19}_{9}F$
(c) $^{14}_{6}C$, $^{14}_{7}N$, $^{17}_{9}F$ (d) $^{14}_{6}C$, $^{14}_{7}N$, $^{19}_{9}F$

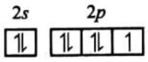
70. The wavelength of a spectral line for an electronic transition is inversely related to :
(a) the number of electrons undergoing the transition
(b) the nuclear charge of the atom
(c) the difference in the energy of the energy levels involved in the transition
(d) the velocity of the electron undergoing the transition

71. The orbital diagram in which the aufbau principle is violated :

(a) 

(b) 

(c) 

(d) 

72. The correct ground state electronic configuration of chromium atom is :
(a) $[Ar]3d^5 4s^0$ (b) $[Ar]3d^4 4s^2$
(c) $[Ar]3d^6 4s^0$ (d) $[Ar]4d^5 4s^1$

73. The correct set of quantum numbers for the unpaired electron of chlorine atom is :

	n	*l*	*m*		*n*	*l*	*m*
(a)	2	1	0	(b)	2	1	−1 or +1
(c)	3	1	−1 or +1	(d)	3	0	0

74. If the speed of electron in the Bohr's first orbit of H-atom is *X*, the speed of the electron in the third orbit is :
(a) *X*/9 (b) *X*/3
(c) 3*X* (d) 9*X*

75. Which of the following does not characterise X-rays?
(a) The radiation can ionise gases
(b) It causes ZnS to fluorescence
(c) Deflected by electric and magnetic fields
(d) Have wavelengths shorter than ultraviolet rays

76. Which of the following relates to photons both as wave motion and as a stream of particles?
(a) Interference (b) $E = mc^2$
(c) Diffraction (d) $E = h\nu$

77. The orbital angular momentum of an electron in 2*s* orbital is :
(a) $+\frac{1}{2} \cdot \frac{h}{2\pi}$ (b) zero
(c) $\frac{h}{2\pi}$ (d) $\sqrt{2} \cdot \frac{h}{2\pi}$

78. The wave no. for the shortest wavelength transition in the Balmer series of atomic hydrogen is :

(a) 27420 cm^{-1} (b) 28420 cm^{-1}
(c) 29420 cm^{-1} (d) 12186 cm^{-1}

79. The electron in He^+ ion is excited to next higher state. The ratio of area of shell of excited state to ground state is :

(a) 9 (b) 4
(c) 16 (d) 12

80. For an electron, α-particle and proton to have same de Broglie wavelength, their kinetic energy should be in the order :

(a) $E_\alpha > E_p > E_e$ (b) $E_e > E_p > E_\alpha$
(c) $E_p > E_\alpha > E_e$ (d) $E_p = E_\alpha = E_e$

81. During the transition of electron in H-atom from any lower to higher orbit, the angular momentum cannot be changed by :

(a) $\hbar$ (b) $\frac{\hbar}{2}$
(c) $2\hbar$ (d) $3\hbar$

82. The electronic configuration of an element is $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$. This represents its: **(IIT 2000)**

(a) excited state (b) ground state
(c) cationic form (d) anionic form

83. Number of nodal plane in p_x-orbital is: **(IIT 2000)**

(a) 1 (b) 2
(c) 3 (d) 0

84. The wavelength of a golf ball weighing 200 g and moving with a speed of 5 m / h is of the order: **(IIT 2001)**

(a) 10^{-10} m (b) 10^{-20} m
(c) 10^{-30} m (d) 10^{-40} m

85. If I is the intensity of absorbed light and *C* is the concentration of *AB* for the photochemical process $AB + h\nu \longrightarrow AB^*$. The rate of formation of AB^* is directly proportional to: **(IIT 2001)**

(a) C (b) I
(c) I^2 (d) CI

86. Rutherford's experiment, which established the nuclear model of the atom, used a beam of: **(IIT 2002)**

(a) β-particles, which impinged on a metal foil and got absorbed
(b) γ-rays, which impinged on a metal foil and ejected electrons
(c) helium atoms, which impinged on a metal foil and got scattered
(d) helium nuclei, which impinged on a metal foil and got scattered

87. If the nitrogen atom and electronic configuration $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^2 2s^2 2p^3$, because the electrons would be closer to the nucleus. Yet $1s^7$ is not observed because it violates: **(IIT 2002)**

(a) Heisenberg's uncertainty principle
(b) Hund's rule
(c) Pauli exclusion principle
(d) Bohr postulate of stationary orbits

88. The quantum numbers +1 / 2 and −1 / 2 for the electron spin represent: **(IIT 2001)**

(a) rotation of the electron in clockwise and anticlockwise direction respectively
(b) rotation of the electron in anticlockwise and clockwise direction respectively
(c) magnetic moment of the electron pointing up and down respectively
(d) two quantum mechanical states which have no classical analogue

89. The radius of which of the following orbit is same as that of the first Bohr's orbit of hydrogen atom? **(IIT 2004)**

(a) $He^+ (n=2)$ (b) $Li^{2+} (n=2)$
(c) $Li^{2+} (n=3)$ (d) $Be^{3+} (n=2)$

90. The number of radial nodes of 3*s* and 2*p*-orbitals are respectively: **(IIT 2005)**

(a) 2, 0 (b) 0, 2
(c) 1, 2 (d) 2, 1

91. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is : (a_0 is Bohr radius) **(IIT 2012)**

(a) $\frac{h^2}{4\pi^2 m a_0^2}$ (b) $\frac{h^2}{16\pi^2 m a_0^2}$
(c) $\frac{h^2}{32\pi^2 m a_0^2}$ (d) $\frac{h^2}{64\pi^2 m a_0^2}$

92. Energy of an electron is given by $E = -2.178 \times 10^{-18}\,J\left(\frac{Z^2}{n^2}\right)$. Wavelength of light required to excite an electron in an hydrogen atom from level $n = 1$ to $n = 2$ will be :
($h = 6.62 \times 10^{-34}$ Js and $c = 3.0 \times 10^{8}\,ms^{-1}$) **[JEE (Main) 2013]**

(a) 6.500×10^{-7} m (b) 8.500×10^{-7} m
(c) 1.214×10^{-7} m (d) 2.816×10^{-7} m

SOLUTIONS (One Answer Correct)

1. (d) $E_n = -\dfrac{Rh}{n^2}$ $\therefore n = 3$ Thus, degenerate orbitals of 3rd energy level are $3s$, $3p_x$, $3p_y$, $3p_z$, $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{z^2}$, $3d_{xy}$ and $3d_{yz}$.

2. (c) $\lambda = u$ then $\lambda = \dfrac{h}{mu}$ or $\lambda = \sqrt{\dfrac{h}{m}}$

3. (a) Electrons in atom lie in ground state.

4. (b) For Balmer series $\dfrac{1}{\lambda} = R_H\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$,

$$\frac{1}{4103\times10^{-8}} = 109678\left[\frac{1}{2^2} - \frac{1}{(m+2)^2}\right]$$

$$\therefore \qquad m = 4$$

Thus, m^{th} line represents 4^{th} line of Balmer series.

5. (a) Spin angular momentum $= \dfrac{h}{2\pi}\sqrt{m_s(m_s+1)}$

$$= \frac{h}{2\pi}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} = \frac{h}{2\pi}\times\sqrt{\frac{3}{4}} = \frac{\sqrt{3}}{4}\frac{h}{\pi}$$

6. (c) Pd has 18 electrons in 4^{th} shell whereas Cu^{2+} has 17 electrons.

7. (c) Spectrum is observed only when $\Delta l = \pm 1$ and $\Delta m = 0, \pm 1$.

8. (a) $\lambda = \dfrac{h}{mu}$ and $\dfrac{1}{2}mu^2 = eV$, $\quad \therefore u^2 = \dfrac{2eV}{m}$

$$\therefore \lambda = \frac{h}{m\times\sqrt{\dfrac{2eV}{m}}} = \frac{h}{\sqrt{2meV}}$$

$$= \frac{6.626\times10^{-34}}{\sqrt{2\times9.108\times10^{-31}\times1.602\times10^{-19}\times500}}$$

$$= 5.5\times10^{-11}\text{ m}$$

9. (c) Cr has $3d^5$ configuration.

10. (c) In absence of Pauli principle configuration of Li would have been $1s^3$.

11. (c) Spherical node $= n - l - 1 = 3 - 1 - 1 = 1$
Non-spherical node $= l = 1$

12. (d) Fe^{2+} has four unpaired electron $(1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6)$

13. (a) Angular momentum in $3d$-orbital

$$= \frac{h}{2\pi}\sqrt{l(l+1)} = \frac{h}{2\pi}\sqrt{2(2+1)}$$

$$= \sqrt{6}\frac{h}{2\pi} = \sqrt{6}\hbar\left(\hbar = \frac{h}{2\pi}\right)$$

14. (b) Bohr made use of Planck's quantum of theory to propose his model for atom.

15. (a) $E_n = \dfrac{E_1}{n^2} = \dfrac{-13.6}{2^2} = -3.4\text{ eV}$

16. (a) Higher is the value of $(n+l)$, more is the energy level of orbital. If $(n+l)$ is same, lower value of n decides lower energy level.

17. (d) Wave function ψ represents an orbital.

18. (c) $E = h\nu$ represents dual nature.

19. (b) $$\lambda = \frac{2\pi r_n}{n} = \frac{2\pi\times n^2\times r_1}{n} = 2\pi_{r_1}\times n$$

For H-atom if $n = 2$; $\lambda = 2\pi r_1 \times 2 = 4\pi r_1$

20. (d) Angular momentum in two successive orbitals are $\dfrac{nh}{2\pi}$ and $(n+1)\dfrac{h}{2\pi}$

$$\therefore \qquad a = \frac{n+1}{n} \text{ and } b = \frac{h}{2\pi}$$

$$\therefore \qquad \frac{a}{b} = \frac{n+1}{n}\cdot\frac{2\pi}{h}$$

21. (b) $\lambda = \dfrac{h}{mu} = \dfrac{h}{m\sqrt{\dfrac{3kT}{m}}} = \dfrac{h}{\sqrt{3mkT}}$ $\qquad \because \dfrac{3}{2}kT = \dfrac{1}{2}mu^2$

22. (c) $\lambda = \dfrac{h}{\sqrt{3mkT}}$ $\quad \therefore \quad \lambda \propto \dfrac{1}{\sqrt{m}}$

23. (b) $P.E. = -2\times E_{Total} = -\dfrac{2\times E_1}{n^2} = -\dfrac{2\times13.6}{3^2} = -3.02\text{ eV}$

24. (a) $\lambda = \dfrac{h}{mu_3} = \dfrac{h}{m\cdot\dfrac{u_1}{3}}$

$$= \frac{3h}{mu_1} = \frac{3h}{h/2\pi a_0} \qquad \left(\text{Also } mur = \frac{nh}{2\pi}\right)$$

$$= 6\pi a_0$$

25. (a) $\because$ $K.E. = -\dfrac{P.E.}{2}$

Let kinetic energy be initially E, then $P.E. = -2E$
New kinetic energy will be $E - \dfrac{E}{4} = \dfrac{3E}{4}$

$\therefore$ New potential energy will be $-\dfrac{3E}{2}$

$\therefore$ Change in potential energy $= 2E - \dfrac{3E}{2}$

(change is always + ve)

$$= \frac{E}{2}$$

26. (b) $E = mc^2$

$$E = mc\cdot c$$

$$\therefore \quad c = \frac{E}{mc} = \frac{E}{p}$$

27. (b) $$QV = \frac{1}{2}mu^2$$

(Q is charge, V is accelerating potential)

$$\therefore \qquad u = \sqrt{\frac{2Q.V}{m}}$$

For proton

$$u_p = \sqrt{\frac{2Q.V}{m_p}}; \quad \therefore \quad m_p\cdot u_p = \sqrt{2Q.V.m_p}$$

For α-particle

$$u_\alpha = \sqrt{\frac{2\times 2QV}{m_\alpha}}; \quad \therefore m_\alpha \cdot u_\alpha = \sqrt{4Q.V.m_\alpha}$$

$$\therefore \frac{\text{momentum of proton}}{\text{momentum of } \alpha} = \sqrt{\frac{m_p}{2m_\alpha}}$$

Now momentum ratio $= \frac{p_p}{p_\alpha} = \frac{m_p \cdot u_p}{m_\alpha \cdot u_\alpha}$

28. (d) $\frac{hc}{\lambda} = 1 + w$

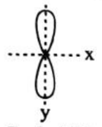
$\frac{3hc}{\lambda} = 4 + w$

$\therefore 3(1+w) = 4 + w$

$\therefore 2w = 1$

$w = 0.5$

29. (c)



Probability of finding the electron along *xz*-plane is zero.

30. (b) Frequency (F) of revolution = No. of revolution/sec

$$= \frac{u_1 \cdot Z^2}{r_1 n^3}$$

(u_1 & r_1 are velocity of H-atom and radius of I orbit)

For H-atom : $Z = 1,\ n = 2$

$$\therefore \quad F_{\text{H}} = \frac{u_1 \times 1^2}{r_1 \times 2^3} = \frac{u_1}{8}$$

For He$^+$-atom : $Z = 2,\ n = 3$

$$\therefore \quad F_{\text{He}^+} = \frac{u_1 \times 2^2}{r_1 \times 3^3} = \frac{4u_1}{27}$$

$$\frac{F_{\text{He}^+}}{F_{\text{H}}} = \frac{32}{27}$$

31. (c) Let work function of A and B be W_A and W_B respectively, then

$4.25 = W_A + T_A$

$\therefore \quad T_A = 4.25 - W_A$ ...(i)

$T_B = 4.70 - W_B$ ...(ii)

$\therefore \quad T_B - T_A = 0.45 + W_A - W_B$

$\because \quad T_B - T_A = -1.5$

$\therefore \quad W_B - W_A = 1.95\,\text{eV}$ ...(iii)

Now, $\lambda = \frac{h}{mu} = \frac{h}{\sqrt{2K \cdot m}}$ $\left(\text{KE} = \frac{1}{2}mu^2\right)$

$\therefore \quad \lambda \propto \frac{1}{\sqrt{K}}$ (K is kinetic energy)

$$\frac{\lambda_B}{\lambda_A} = \sqrt{\frac{K_A}{K_B}} = 2$$

$\therefore \quad \frac{K_A}{K_B} = 4 = \frac{T_A}{T_B}$ (KE = T)

or $\frac{T_A}{T_A - 1.5} = 4$

$\therefore \quad T_A = 2\,\text{eV}$

$T_B = 0.5\,\text{eV}$

$W_A = 2.25\,\text{eV}$

$W_B = 4.2\,\text{eV}$

32. (a) Work function $= \frac{hc}{\lambda}$ and

$$w = 4.125\,\text{eV} = 4.125 \times 1.6 \times 10^{-19}\,\text{J}$$

$$\lambda = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{4.125 \times 1.6 \times 10^{-19}}\,\text{Å} = 3011\,\text{Å}$$

33. (b) By Wien's displacement law : $\lambda_{\max} \cdot T = \text{constant}$

$\therefore \quad \lambda_1 T_1 = \lambda_2 T_2$

$\lambda \times 2000 = \lambda_2 \times 3000$

$\therefore \quad \lambda_2 = \frac{2\lambda}{3}$

34. (d) $\lambda = \frac{h}{mu} = \frac{K}{m}$ (u is same & h is a constant)

Lower is m, more will be λ.

35. (b) The light used should be of higher energy then UV region.

36. (d) $F = K\frac{Q_1 \times Q_2}{r^2}$

37. (a) $r_1 = \frac{r_{1_{\text{H}}} \times n^2}{Z} = \frac{0.529 \times n^2}{Z}$

$\therefore \quad r_1 \propto \frac{1}{Z}$

38. (c) ${}_1^1\text{H}$

39. (d) $h\upsilon = W + \text{K.E} = h\upsilon_0 + \text{K.E}$

$\therefore \text{K.E} = h\upsilon - h\upsilon_0$

$\upsilon = mx + C$ (slope $= -h$ and intercept $= h\upsilon_0$)

40. (c) Power $= \frac{V^2}{R}$

$\therefore \frac{V_1^2}{R_1} = \frac{V_2^2}{R_2}$ or $\frac{(220)^2}{R_1} = \frac{(110)^2}{R_2}$

$\therefore R_2 = \frac{R_1}{4}$

41. (c) $E_n = -\frac{13.6}{n^2}$ Also $E = E_n - E_0$

$$12.1 = -\frac{13.6}{n^2} + 13.6$$

$\therefore \quad n = 3$

Thus, deexcitation will lead spectral lines $= \Sigma\Delta n$

$= \Sigma(3-1) = 3$

42. (a) $E = mc^2$

$$E = \text{momentum} \times c$$

$$\therefore \text{momentum} = \frac{E}{c} = \frac{10^6 \times 1.6 \times 10^{-19}}{3 \times 10^8}$$

$$= 5.22 \times 10^{-22}\ \text{kg-m/s}^{-1}$$

43. (a) $h\upsilon = w_0 + K$

$2h\upsilon = w_0 + K_1$

$\therefore \quad K_1 = h\upsilon + K$

44. (c) $\frac{mu^2}{r} = \frac{ze^2}{r^2}$

$\therefore \quad u \propto \frac{1}{\sqrt{r}}$

Also angular momentum $= mur \propto m\frac{1}{\sqrt{r}} \times r \propto m\sqrt{r}$

45. (c) $h\nu = W + K_{\max} = W + eV_0$

or $\quad h\upsilon = h\nu_0 + eV_0$

$\frac{hc}{\lambda} = 6.2 + 5 = 11.2\,\text{eV}$

$\therefore \quad \lambda = \frac{6.625\times10^{-34}\times3\times10^{8}}{11.2\times1.6\times10^{-19}}$

$= 1.1\times10^{-7}$ m *i.e.*, U.V. region

46. (b) No. of photons emitted/sec $= \frac{E\cdot\lambda}{hc}$

$(\because E = nh\upsilon)$ and $E = W \times t$ (per sec.) $= W$

$= \frac{9\times10^{-3}\times6.67\times10^{-7}}{6.6\times10^{-34}\times3\times10^{8}} = 3\times10^{16}$

47. (d) $E = h\nu_0 + eV_0$

$h\nu = \frac{6.626\times10^{-34}\times3\times10^{8}}{200\times10^{-9}\times1.6\times10^{-19}}\,\text{eV}$

$= 6.2\,\text{eV}$

$\therefore \quad eV_0 = h\nu - h\nu_0 = h\nu - W$

$\therefore \quad eV_0 = 6.2 - 5.01 = 1.2$ eV

or $\quad V_s = 1.2$ V

48. (b) $E = h\nu = \frac{hc}{\lambda} = \frac{6.6\times10^{-34}\times3.0\times10^{8}}{4100\times10^{-10}\times1.6\times10^{-19}}\,\text{eV}$

$= 3\,\text{eV}$

Work function should be lower than 3eV to eject electron.

49. (a) Angular momentum in the orbit is $\frac{nh}{2\pi}$

50. (c) For $m = -3, l = 3 \;\therefore$ minimum value of $n = 4$

51. (a) For photon $E = mc^2$

52. (a) 6 of C and 16 of O; Total 22 electrons.

53. (d) ${}^{70}_{30}\text{Zn}$; $\therefore$ no. of neutrons in Zn or $\text{Zn}^{2+} = 40$

54. (c) All the positive charge concentrated in nucleus and thus scattering occurs.

55. (b) ${}_{28}\text{Ni}$: ....$3s^2 3p^6 3d^8, 4s^2$

Ni^{2+} : ....$3s^2 3p^6 3d^8$

56. (d) Pauli's exclusion principle. A p orbital contains maximum two electrons and that too with opposite spin.

57. (a) $r_1 \times n^2 = r_n$

where, r_n = radius of n^{th} shell and

n = principal quantum number.

58. (a) Rutherford α-scattering experiment led to discovery of nucleus.

59. (d) $(e/m)_n = \frac{0}{1.675\times10^{-27}\,\text{kg}}$;

$(e/m)_\alpha = \frac{2\times1.602\times10^{-19}\,\text{C}}{4\times1.675\times10^{-27}\,\text{kg}}$;

$(e/m)_p = \frac{1.602\times10^{-19}\,\text{C}}{1.675\times10^{-27}\,\text{kg}}$;

$(e/m)_e = \frac{1.602\times10^{-19}\,\text{C}}{9.108\times10^{-31}\,\text{kg}}$

60. (a) ${}_{37}\text{R}b = 2, (2, 6)\,(2, 6, 10)\,(2, 6)\,(1)$

$= 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6, 5s^1$

Valence electron is $5s^1$.

$$\overset{5s^1}{\boxed{\uparrow}}$$

$\therefore \quad n = 5, l = 0, m = 0, s = +\frac{1}{2}\left(\text{or } -\frac{1}{2}\right)$

61. (d) Ground state of hydrogen atom, *i.e.*, 1s.

62. (b) Bohr's model is based on one electron system

63. (b) $r_{\text{nucleus}} = \ldots\ldots\ldots \times10^{-13}$ cm; $r_{\text{atom}} = \ldots\ldots\ldots \times10^{-8}$ cm

64. (b)

Radiation	**Wavelength (incm)**
UV	10^{-5} to 10^{-6}
Radio Wave	1 to 10^2
X-ray	10^{-6} and above
Infra-red	10^{-3} to 10^{-4}

65. (b) Rutherford thus proposed his model.

66. (c) For a given $n, l = 0$ to $n - 1$ and $m = -1$ to $+1$

67. (d) $E_1 = \frac{hc}{\lambda_1}$ and $E_2 = \frac{hc}{\lambda_2}$

$\frac{E_1}{E_2} = \frac{hc}{\lambda_1} \times \frac{\lambda_2}{hc} = \frac{\lambda_2}{\lambda_1} = \frac{4000}{2000} = 2$

68. (d) In ${}^{3}_{1}\text{H}$

69. (a) All contain 8 neutrons. (Species containing same number of neutrons are called isotones).

70. (c) $\Delta E = \frac{hc}{\lambda_1}$ or $\Delta E \propto \frac{1}{\lambda}$

71. (b) According to aufbau's principle, electrons cannot be filled in $2p$ orbital till $2s$ orbital is incomplete.

72. (d) Half-filled sub-shells are more stable than incomplete sub-shell. Hence, $\quad \text{Cr}_{24} = [\text{Ar}]\,3d^5, 4s^1$

73. (c) ${}_{17}\text{Cl} = 1s^2, 2s^2 2p^6, 3s^2 3p^5$

$$\overset{3s}{\boxed{\uparrow\downarrow}} \quad \overset{3p}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}}$$

For unpaired electron : $n = 3, l = 1, m = -1$ or $+1$.

74. (b) $u_n = \frac{u}{n}$

75. (c) X-rays are not deflected by electric and magnetic fields.

76. (d) For photon, $E = h\nu$ (in form of particle and wave)

77. (b) Orbital angular momentum $(mvr) = \frac{h}{2\pi}\sqrt{l(l+1)}$

For $2s$ orbital, l (azimuthal quantum number) = 0

$\therefore$ orbital angular momentum $= \frac{h}{2\pi}\sqrt{0(0+1)}$

$= \frac{h}{2\pi}\sqrt{0} = 0$

78. (a) For shortest wavelength $\Delta E = \frac{hc}{\lambda}$, ΔE should be maximum. Thus $n_1 = 2$ and $n_2 = \infty$

$$\therefore \quad \bar{\nu} = \frac{1}{\lambda} R_H \left[\frac{1}{2^2} - \frac{1}{\infty^2}\right] = 109677 \times \frac{1}{4^2}$$

$$= 27419.5 \text{ cm}^{-1}$$

79. (c) $r_1 \text{ He}^+ = \frac{r_{1\text{H}}}{2}$; $r_2 \text{ He}^+ = \frac{r_{1\text{H}} \times 2^2}{2} = 2r_1\text{H}$

$$\therefore \frac{\text{Area of shell of } r_2\text{He}^+}{\text{Area of shell of } r_1\text{He}^+} = \frac{\pi \times (2r_1)^2}{\pi \times \left(\frac{r_1}{2}\right)^2} = 16$$

80. (b) $\lambda = \frac{h}{\sqrt{2E \times m}}$

To have same wavelength $E \times m$ must be same

$\because m_e < m_p < m_\alpha$

$\therefore E_{\text{electron}} > E_{\text{proton}} > E_\alpha$

81. (b) Change in angular momentum during transition

$$= (n_2 - n_1)\frac{h}{2\pi}$$

$$= (n_2 - n_1)\hbar$$

Also n_1 and n_2 are integers

82. (b, c) The given electronic configuration is for ground state of $_{24}\text{Cr}$ and of Mn^+. **This question was asked in single answer choice.**

83. (a) Nodal plane in p-orbital = $l = 1$

84. (c) $\lambda = \frac{h}{mu} = \frac{6.626 \times 10^{-27}}{200 \times 5} = 6.626 \times 10^{-30}$ m/h

85. (d) The rate of formation of excited molecule as a result of absorption of light is directly proportional to the intensity of radiations.

i.e., rate = KI (Lamberts law)

but if solution is used then

rate = K.I.C. (Beer's law)

86. (d) Because Rutherford used α-particles and one α-particle is represented as nucleus of helium with 2 protons and 2 electrons.

87. (c) Pauli proposed that s-orbitals cannot have more than two electrons.

88. (d) Spin quantum number was derived in quantum mechanics.

89. (d) $r_2\text{Be}^{3+} = \frac{r_2\text{H}}{\text{Z}} = \frac{r_1\text{H} \times 2^2}{\text{Z}} = \frac{r_2\text{H} \times 4}{4} = r_1\text{H}$

90. (a) Number of radial nodes = $n - l - 1$

For $3s$ it is 2

For $2p$ it is 0

91. (c) As per Bohr's postulate, kinetic energy in II orbit

$$= +\frac{e^2}{2r_2} = \frac{e^2}{2a_0 \times 2^2} \quad (\because r_2 = r_1 \times n^2)$$

$$= \frac{e^2}{8a_0}$$

Since, $a_0 = \frac{h^2}{4\pi^2 me^2}$

$\therefore$ Kinetic energy in II orbit $= \frac{h^2}{4\pi^2 ma_0} \times \frac{1}{8a_0} = \frac{h^2}{32\pi^2 ma_0^2}$

92. (c) $E = \frac{hc}{\lambda} = 2.178 \times 10^{-18} \times z^2\left[\frac{1}{1^2} - \frac{1}{2^2}\right]$ $(z = 1)$

$$\therefore \lambda = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{2.178 \times 10^{-18}} \times \frac{4}{3} = 1.214 \times 10^{-7} \text{ m}$$

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. If T is the time required by electron in taking one round in an orbit, n represents the number of waves in an orbit, r represents the radius of orbit, then which are correct?

(a) $\frac{r_{2(\text{H})}}{r_{4(\text{He}^+)}}=\frac{1}{2}$ (b) $\frac{T_{2(\text{H})}}{T_{4(\text{He}^+)}}=\frac{1}{2}$

(c) $\frac{n_{2(\text{H})}}{n_{4(\text{H})}}=\frac{1}{2}$ (d) $\frac{E_{2(\text{H})}}{E_{4(\text{He}^+)}}=\frac{1}{2}$

2. Select the correct sentences:

(a) An electron in an orbit can absorb only one photon and that too equivalent in energy to the energy difference between two orbits

(b) $3d$ sub-shell penetrates more towards nucleus than $4s$

(c) Green light is never emitted in black body radiations

(d) The energy change between two successive orbits increases with increasing value of n

3. A metal surface having ν_0 as threshold frequency is incidented by light of frequency ν, then which are correct?

(a) $u=\sqrt{\frac{2h\cdot c(\lambda_0-\lambda)}{m\cdot\lambda\cdot\lambda_0}}$ (b) $u=\sqrt{\frac{2h(\nu-\nu_0)}{m}}$

(c) $u=\sqrt{\frac{2h(\lambda_0-\lambda)}{m}}$ (d) $u=\sqrt{\frac{2(h\nu-w)}{m}}$

4. Select the correct statements if $\hbar=\frac{h}{2}$ and $\hbar=\frac{h}{2\pi}$:

(a) $\Delta p\cdot\Delta x=\frac{\hbar}{2\pi}$ (b) $\Delta p\cdot\Delta x=\frac{\hbar}{2}$

(c) $\Delta u_y\cdot\Delta x=\frac{\hbar}{2\pi m}$ (d) $\Delta u_x\cdot\Delta x=\frac{\hbar}{2\pi m}$

5. Which of the following are correct?

(a) Each atom has at least one orbital symmetrical about the nucleus

(b) Each orbit has at least one orbital symmetrical about the nucleus

(c) Number of electrons in Ne having their angular momentum equal to zero is four

(d) Number of waves made by an electron in an orbit is equal to number of orbit

6. Which of the following are correct?

(a) Only Lyman series is observed in emission and absorption spectrum both

(b) The continuum in line spectrum is noticed after a certain value of n

(c) The wavelength of m^{th} line of Balmer series is:

$$\frac{1}{\lambda}=R_{\text{H}}Z^2\left[\frac{1}{2^2}-\frac{1}{m^2}\right]$$

(d) The number of spectral lines given when electron drops from 5^{th} to 2^{nd} shell is six

7. Select the correct statements:

(a) The concept of shell was given by Bohr

(b) The concept of sub-shells within a shell was given by Pauli

(c) The degeneracy of orbitals exists in presence of magnetic field

(d) The splitting of a line in fine lines under the influence of magnetic field was proposed by Zeeman

8. An isotone of $^{76}_{32}\text{Ge}$ is :

(a) $^{77}_{32}\text{Ge}$ (b) $^{77}_{33}\text{As}$

(c) $^{77}_{34}\text{Se}$ (d) $^{78}_{34}\text{Se}$

9. Many elements have non-integral atomic masses because :

(a) they have isotopes

(b) their isotopes have non-integral masses

(c) their isotopes have different masses

(d) the constituents, neutrons, protons and electrons, combine to give fractional masses

10. When alpha particles are sent through a thin metal foil, most of them go straight through the foil because :

(a) alpha particles are much heavier than electrons

(b) alpha particles are positively charged

(c) most part of the atom is empty space

(d) alpha particles move with high velocity

11. The atomic nucleus contains :

(a) protons (b) neutrons

(c) electrons (d) photons

12. Which of the following statement(s) is (are) correct?

(a) the electronic configuration of Cr is [Ar] $3d^5 4s^1$. (Atomic number of Cr = 24)

(b) The magnetic quantum number may have a negative value

(c) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (Atomic number of Ag = 47)

(d) The oxidation state of nitrogen in HN_3 is -3

13. Decrease in atomic number is observed during :

(a) alpha emission (b) beta emission

(c) positron emission (d) electron capture

14. Ground state electronic configuration of nitrogen atom can be represented by :

(a) $\boxed{\uparrow\downarrow}\,\boxed{\uparrow\downarrow}\;\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ (b) $\boxed{\uparrow\downarrow}\,\boxed{\uparrow\downarrow}\;\boxed{\downarrow}\boxed{\downarrow}\boxed{\downarrow}$

(c) $\boxed{\uparrow\downarrow}\,\boxed{\uparrow\downarrow}\;\boxed{\uparrow}\boxed{\downarrow}\boxed{\downarrow}$ (d) $\boxed{\uparrow\downarrow}\,\boxed{\uparrow\downarrow}\;\boxed{\uparrow}\boxed{\uparrow}\boxed{\downarrow}$

SOLUTIONS (More Than One Answer Correct)

1. (a,c) $r_n = r_1 \times n^2$

$$r_{2(\mathrm{H})} = r_{1(\mathrm{H})} \times 2^2 = 4r_{1(\mathrm{H})}$$

$$r_{4\mathrm{He}^+} = \frac{r_{1(\mathrm{H})} \times 4^2}{Z} = \frac{r_1 \times 4^2}{2}$$

$$\therefore \frac{r_{2(\mathrm{H})}}{r_{4\mathrm{He}^+}} = \frac{1}{2}$$

No. of waves in an orbit = No. of orbit

$$\therefore \frac{n_{2\mathrm{H}}}{n_{4\mathrm{H}}} = \frac{2}{4} = \frac{1}{2}$$

$$E_n = \frac{E_1}{n^2} \times Z^2$$

$$E_{2\mathrm{H}} = \frac{E_1}{4} \times 1^2$$

$$E_{4\,\mathrm{He}^+} = \frac{E_1 \times 2^2}{4^2}$$

$$\therefore \frac{E_{2\mathrm{H}}}{E_{4\,\mathrm{He}^+}} = 1$$

Now $T_{2\mathrm{H}} = \frac{2\pi r_2}{u_2} = \frac{2\pi r_{1\mathrm{H}} \times n^2 \times n}{u_1} = \frac{2\pi r_{1\mathrm{H}} \times n^3}{2\pi e^2} \times h$

$$= \frac{r_{1\mathrm{H}}\, n^3 h}{e^2} = \frac{r_{1\mathrm{H}}\, 2^3 h}{e^2}$$

Similarly $T_{4\mathrm{He}^+} = \frac{2\pi r_{4\,\mathrm{He}^+}}{u_{4\,\mathrm{He}^+}} = \frac{2\pi r_{4\mathrm{H}} \times n^2}{Z \times u_{n\mathrm{H}} \times Z}$

$$= \frac{2\pi r_{1\mathrm{H}} \times 4^2}{Z^2 \times \frac{u_{1\mathrm{H}}}{4}} = \frac{2\pi r_{1\mathrm{H}} \times 4^3}{2^2 \times \frac{2\pi r_{1\mathrm{H}} e^2}{4 \times h}} = 4^3 \frac{r_{1\mathrm{H}} \cdot h}{e^2}$$

$$T_{4\mathrm{He}^+} = \frac{r_1 n^3 h}{e^2 z^2} \quad \therefore \quad \frac{T_{2\mathrm{H}}}{T_{4\mathrm{He}^+}} = \frac{2^3}{4^3} = \frac{1}{8}$$

2. (a,b,c) $E_2 - E_1 > E_3 - E_2 > E_4 - E_3 \ldots$

3. (a,b,d) $h\nu = h\nu_0 + \frac{1}{2}mu^2$

$$\therefore \quad u = \sqrt{\frac{2h(\nu - \nu_0)}{m}} = \sqrt{\frac{2hc[\lambda_0 - \lambda]}{m(\lambda_0 \times \lambda)}}$$

$$h\nu = w + \frac{1}{2}mu^2$$

$$\therefore \quad u = \sqrt{\frac{2(h\nu - w)}{m}}$$

4. (a,b,d) Heisenberg principle is $\Delta p \cdot \Delta x = \frac{h}{4\pi} = \frac{\hbar}{2\pi} = \frac{\hbar}{2}$

$$m \cdot \Delta u \cdot \Delta x = \frac{h}{4\pi}$$

Note that the principle loses its significance if Δu and Δx are not considered along same axis.

5. (a,b,c,d) For emission of λ; $\Delta n =$ any value, $\Delta l = \pm 1$, $\Delta m = 0, \pm 1$

Ne has 4 electrons in s-orbitals: $1s^2, 2s^2 2p^6$

For a given n, $l = 0$ to $(n-1)$

6. (a,b,d) m^{th} line, $\frac{1}{\lambda_B} = R_H \cdot Z^2 \left[\frac{1}{2^2} - \frac{1}{(m+2)^2}\right]$; ΔE of two successive orbits becomes almost constant after a certain value of n.

Number of lines $= \Sigma\Delta n = \Sigma\, 5 - 2 = \Sigma\, 3 = 6$

7. (a,d) In presence of magnetic field orbitals are non-degenerate, *i.e.*, possess different energy levels.

8. (b,d) ${}^{77}_{33}\mathrm{As}$ and ${}^{78}_{34}\mathrm{Se}$ have same number of neutrons (A–Z) as ${}^{72}_{36}\mathrm{Ge}$.

9. (d) Mass of an atom is due to masses of p, n and 'e' which are not integers. (a), (b), (c) choices are for non-integral at. wt.

10. (c,d) α-particles pass through because most part of the atom is empty.

11. (a,b) Nucleus contains protons and neutrons.

12. (a,b,c)

(a) ${}_{24}\mathrm{Cr} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$
$= [\mathrm{Ar}]\, 3d^5 4s^1$

(b) For magnetic quantum number (m) negative values are possible.
For s-sub-shell : $l = 0$, hence $m = 0$
For p-sub-shell : $l = 1$, hence $m = -1, 0, +1$

(c) ${}_{47}\mathrm{Ag} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^1$
Hence, 23 electrons have a spin of one type and 24 of the opposite type.

(d) Oxidation state of N in HN_3 is $-\frac{1}{3}$.

13. (a,c, d)

$${}^{11}_{6}\mathrm{C} \longrightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}e \quad \text{(Positron emission)}$$

$${}^{133}_{56}\mathrm{Ba} + {}^{0}_{-1}e \longrightarrow {}^{133}_{55}\mathrm{Cs} + \text{X-rays}$$

(K-electron capture)

$${}^{235}_{92}\mathrm{U} \longrightarrow {}^{231}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He} \quad (\alpha\text{-emission})$$

14. (a,b) By Hund's rule

COMPREHENSION BASED PROBLEMS

Comprehension 1 : A gas of identical H-like atom has some atoms in the lowest (ground) energy level A and some atoms in a particular upper (excited) energy level B and there are no atoms in any other energy level. The atoms of the gas make transition to a higher energy level by absorbing monochromatic light of photon energy 2.7 eV. Subsequently, the atoms emit radiation of only six different photons energies. Some of the emitted photons have energy 2.7 eV. Some have more and some have less than 2.7 eV.

[1] The principal quantum number of initially excited level B is:
(a) 2 (b) 3
(c) 4 (d) 5

[2] The ionisation energy for the gas atoms.
(a) 14.0 eV (b) 14.4 eV
(c) 13.6 eV (d) 20.2 eV

[3] Find the maximum and the minimum energies of the emitted photons.
(a) 14.4, 13.6 eV (b) 13.4, 14.6 eV
(c) 13.5, 0.7 eV (d) 0.7, 13.5 eV

Comprehension 2 : Whenever an electron falls from a higher level of energy to lower level of energy, equivalent amount of energy is given out. The jump of electron not only depends on major energy shell but also on the nature of orbital. The emission of energy is derived from Bohr's model and the possibility of jump is decided by the selection rule. According to Bohr's theory E_1 for H-atom is 2.17×10^{-18} J/atom.

[1] In which of the following jump of electron is possible?
(a) $3d$ to $1s$ (b) $4d$ to $3s$
(c) $4f$ to $2s$ (d) $3p$ to $2s$

[2] The shortest frequency which can remove 2^{nd} electron of He atom with a velocity of 10^5 m / sec :
(a) 3.28×10^{15} Hz (b) 13.45×10^{15} Hz
(c) 23.21×10^{15} Hz (d) 4.5×10^{15} Hz

[3] The angular frequency of an electron occupying the second Bohr's orbit of He^+ is:
(a) 2.07×10^{16} sec^{-1} (b) 2.07×10^{17} sec^{-1}
(c) 2.07×10^{18} sec^{-1} (d) 2.07×10^{15} sec

[4] The wavelength of H_B-line of Balmer series of H-atom is:
(a) 386 nm (b) 486 nm
(c) 586 nm (d) 686 nm

[5] The corresponding H_B-line of He^+ ion has frequency:
(a) 18.64×10^{14} (b) 9.12×10^{14}
(c) 4.56×10^{14} sec^{-1} (d) 2.46×10^{15} Hz

[6] The longest wavelength of light which can remove electron completely from 2^{nd} orbit of H-atom.
(a) 4000 Å (b) 3000 Å
(c) 5060 Å (d) 3663.6 Å

Comprehension 3 : The hydrogen like species Li^{2+} is in a spherically symmetric state S_1 with one radial node. Upon absorbing light the ion undergoes to transition to a state S_2. The state S_2 has one radial node and its energy is equal to the ground state of the H-atom. **[IIT 2010]**

[1] The state S_1 is:
(a) $1s$ (b) $2s$
(c) $2p$ (d) $3s$

[2] Energy of the state S_1 in units of H-atom ground state energy is:
(a) 0.75 (b) 1.50
(c) 2.25 (d) 4.50

[3] The orbital angular momentum quantam number of the state S_2 is:
(a) 0 (b) 1
(c) 2 (d) 3

Comprehension 4 : The letters n, l, m proposed by Bohr, Sommerfeld and Zeeman respectively for quantisation of angular momentum in classical physics were later on obtained as the results of solution of Schrödinger wave equation based on quantum mechanics. The term n, l, m were named as principal quantum number, azimuthal quantum number and magnetic quantum number respectively. The fourth quantum number s was given the name spin quantum number on the basis of two spins of electrons. The first two quantum numbers also decides the nodes of an orbital.

[1] The numerical value $\psi_{4,3,0}$ denotes :
(a) $3d$-orbitals (b) $4f$-orbitals
(c) $2s$-orbitals (d) $4d$-orbitals

[2] The angular momentum of $3p$-orbitals in terms of $\hbar \left\{\hbar = \frac{h}{2\pi}\right\}$ is :
(a) $\sqrt{2}\,\hbar$ (b) $2\,\hbar$
(c) $\frac{\hbar}{\sqrt{2}}$ (d) $\frac{\hbar}{2\pi}$

[3] Which statement about energy level in H-atom is correct?
(a) Only n and l decides energy level
(b) Only 'l' decides energy level
(c) Only n decides energy level
(d) n, l and m decides energy level

[4] Δu_x is uncertainty in velocity of electron and Δx_y is uncertainty in position, then :
(a) $\Delta u_x \cdot \Delta x_y = \frac{h}{4\pi}$ (b) $\Delta u_x \cdot \Delta x_y = \frac{h}{4\pi m}$
(c) $\Delta u_x \cdot \Delta x_y \geq \frac{h}{4\pi m}$ (d) none of these

SOLUTIONS

Comprehension 1

[1] (a) The electrons being present in I shell and another shell n_1. These are excited to higher level n_2 by absorbing 2.7 eV and on de-excitation emits six λ and thus excited state n_2 comes to be 4. $[6 = \Sigma\,\Delta n = \Sigma(n_2 - 1)\ \therefore\ n_2 = 4]$

Now $E_1 = -\dfrac{R_h \cdot c \cdot h}{1^2}$; $E_{n_1} = -\dfrac{R_h \cdot c \cdot h}{n_1^2}$;

$$E_4 = -\frac{R_h \cdot c \cdot h}{4^2}$$

Since, de-excitation leads to different λ having photon energy $\lesseqgtr 2.7\,\text{eV}$ and thus absorption of 2.7 eV energy causing excitation to IV shell and then re-emitting photons of $\lesseqgtr 2.7\,\text{eV}$ are possible only when $n_1 = 2$ (the de-excitation from IV shell occurs in I, II and III shell).

$$E_4 - E_2 = 2.7\,\text{eV}$$
$$E_4 - E_3 < 2.7\,\text{eV}$$
$$E_4 - E_1 > 2.7\,\text{eV}$$
$$\therefore\ E_{n_1} = E_2 = \frac{R_h \cdot c \cdot h}{2^2} = \frac{E_1}{2^2}$$

since $\boldsymbol{n_1} = \mathbf{2}$ (as obtained by discussion)

[2] (b) Also, $E_4 - E_2 = 2.7\,\text{eV}$

$$\therefore\quad -\frac{E_1}{4^2} + \frac{E_1}{2^2} = 2.7\,\text{eV}$$
$$\therefore\quad E_1 = -14.4\,\text{eV}$$
$$\therefore\quad \text{IP} = \mathbf{14.4\ eV}$$

[3] (c) $E_{\text{max}} = E_4 - E_1 = -\dfrac{E_1}{4^2} + \dfrac{E_1}{1^2} = -\dfrac{14.4}{16} + 14.4 = \mathbf{13.5\ eV}$

$$E_{\text{min}} = E_4 - E_3 = -\frac{E_1}{4^2} + \frac{E_1}{3^2} = \mathbf{0.7\ eV}$$

Note : It is $_1\text{H}^2$ atom.

Comprehension 2

[1] (d) For a jump $\Delta l = \pm 1$ according to selection rule

[2] (a) Total $E_{\text{needed}} = E_{\text{needed}}$ to remove 2nd electron from

$$\text{He} + \frac{1}{2}mu^2$$
$$= E_{2_{\text{He}^+}} + \frac{1}{2} \times 9.108 \times 10^{-31} \times (10^5)^2 \text{ Joule}$$
$$= E_{2\text{H}} \times Z^2 + 4.554 \times 10^{-21}$$
$$= \frac{E_1}{n^2} \times Z^2 + 4.554 \times 10^{-21}$$
$$= 2.17 \times 10^{-18} + 4.554 \times 10^{-21} \qquad (n = 2; Z = 2)$$
$$E = 2.1746 \times 10^{-18} = h\nu$$
$$\therefore\ \nu = \frac{2.1746 \times 10^{-18}}{6.626 \times 10^{-34}} = \mathbf{3.28 \times 10^{15}\ Hz}$$

[3] (a) Velocity of electron in He$^+$ ion in an orbit $(u) = \dfrac{2\pi Z e^2}{nh}$

Radius of He$^+$ ion in an orbit $(r_n) = \dfrac{n^2 h^2}{4\pi^2 m e^2 Z}$

∴ Angular frequency or angular velocity

$$\omega = \frac{u}{r_n} = \frac{2\pi Z e^2 \times 4\pi^2 m e^2 Z}{nh \times n^2 h^2} = \frac{8\pi^3 Z^2 m e^4}{n^3 h^3}$$
$$\because\quad n = 2,\ m = 9.108 \times 10^{-28}\text{ g},$$
$$Z = 2,\ h = 6.625 \times 10^{-27}$$
$$\therefore w = \frac{8 \times (22/7)^3 \times (2)^2 \times 9.108 \times 10^{-28} \times (4.803 \times 10^{-10})^4}{(2)^3 \times (6.625 \times 10^{-27})^3}$$
$$= \mathbf{2.067 \times 10^{16}\ sec^{-1}}$$

[4] (b) $\dfrac{1}{\lambda} = R_{\text{H}} \cdot Z^2 \left[\dfrac{1}{2^2} - \dfrac{1}{4^2}\right]$

$$= 109678 \times 1^2 \left[\frac{3}{16}\right]$$
$$\therefore\quad \lambda = 4.86 \times 10^{-5}\text{ cm} = 4.86 \times 10^{-7}\text{ m}$$
$$= 486 \times 10^{-9}\text{ m} = 486\text{ nm}$$

[5] (c) $\lambda_{\text{He}^+} = 1.216 \times 10^{-5}$ cm $\qquad \left(\lambda^+_{\text{He}} = \dfrac{\lambda_{\text{H}}}{Z^2}\right)$

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^{10}}{1.216 \times 10^{-5}} = \mathbf{2.467 \times 10^{15}\ Hz}$$

[6] (d) $E_n = -\dfrac{21.7 \times 10^{-12}}{n^2}$ erg

$$\therefore\quad E_2 = -\frac{21.7 \times 10^{-12}}{4} = -5.425 \times 10^{-12}\text{ erg}$$

∴ For removal of electron $E_2 = \dfrac{hc}{\lambda}$; E_2 should be given to remove electron, *i.e.*, + ve.

$$\therefore\quad \lambda = \frac{6.625 \times 10^{-27} \times 3.0 \times 10^{10}}{5.425 \times 10^{-12}}$$
$$= 3663.6 \times 10^{-8}\text{ cm} = \mathbf{3663.6\ Å}$$

So, the longest wavelength is **3663.6 Å.**

Comprehension 3

Energy in state S_2 of $\text{Li}^{2+} = E_1$ of $\text{Li}^{2+} = E_1$ of $\text{H} = -13.6\,\text{eV}$

Also, E_{S_2} of $\text{Li}^{2+} = \dfrac{E_{1\text{H}} \times z^2}{n^2} = \dfrac{-13.6 \times 3^2}{n^2}$

$$\therefore\quad n = 3$$

The state S_2 represents 3rd orbital with one radial node, *i.e.*, 3*p* radial node $= n - l - 1 = 1$

The state S_1 represents 2*s* (as $n - 1 - l = 1$). Also transition is possible from 2*s* to 3*p* $\Delta l = \pm 1$ and $E_{S_1} = \dfrac{E_{1\text{H}} \times 3^2}{2^2} = 2.25 \times E_{1\text{H}}$; For state S_2 (*i.e.*, 3*p*) $l = 1$

1. (b) 2. (c) 3. (b)

Comprehansion 4

[1] (b) ψ represents an orbital and $\psi_{4,3,0}$, has $n = 4$, $l = 3$, *i.e.*, 4*f*-orbital.

[2] (a) Angular momentum in an orbital $= \sqrt{l(l+1)} \cdot \dfrac{h}{2\pi}$

$$= \sqrt{l(l+1)} \cdot \frac{h}{2\pi} = \sqrt{2} \times \hbar$$

[3] (c) Subshells of a shell in H-atom possess same energy level, *i.e.*, *l* does not specify for the energy level of an orbital in H-atom.

[4] (d) Heisenberg principle has no significance of Δu is along *X*-axis and ΔX along *Y*-axis are given.

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement (S) and explanation (E) is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) S is correct but E is wrong

(b) S is wrong but E is correct

(c) Both S and E are correct and E is correct explanation of S

(d) Both S and E are correct but E is not correct explanation of S

1. S : Transition of electron between p_x and p_y would not lead to an spectral line.

E : *p*-orbitals are degenerate orbitals.

2. S : Number of sub-shells in a shell is equal to the number of shell.

E : According to Sommerfeld :

$$\frac{n}{k}=\frac{\text{Length of major axis}}{\text{Length of minor axis}}$$

3. S : Electronic configuration of $_{23}V^{3+}$ ion is $[Ar]^{18}\,3d^2$ and not $[Ar]^{18}\,3d^0\,4s^2$.

E : V^{3+} ion is diamagnetic in nature.

4. S : Bohr proposed that angular momentum of electron in an orbit is quantised.

E : de Broglie derived that : $mur=n\frac{h}{2\pi}$.

5. S : Number of waves in an orbit of atom is equal to number of that orbit.

E : Number of waves in an orbit is derived by $\frac{2\pi r_n}{\lambda}$.

6. S : Matter waves and electromagnetic waves differ from each other in many respect.

E : The matter waves possess lesser wave number than electromagnetic waves as well as cannot radiate in empty space.

7. S : A triply ionised Be-atom has the same radius of 2nd orbit as that of ground state of H-atom.

E : The radius of an orbit is $r_n=\frac{r_1\times n^2}{Z}$.

8. S : Wavelength of I line of Humphrey series is more than I line of Lyman series in H-atom.

E : $\Delta E=\frac{hc}{\lambda}$.

9. S : The energy radiated per unit volume, *i.e.*, energy density in black body radiation depends upon the temperature.

E : Green light is never emitted in black body radiations.

10. S : The magnetic moment of Mg-atom is more than K-atom as the former has two electrons in outermost shell.

E : The magnetic moment of N-atom is more than magnetic moment of O-atom and former has more number of unpaired electrons.

11. S : An electron in an *s*-orbital has a non-zero probability of being found right at the nucleus.

E : $l=0$ for *s*-orbitals and thus there is no orbital angular momentum to fling the electron away from the nucleus.

12. S : An electron in *s*-orbital is not circulating around the nucleus but simply as distributed around it whereas an electron in *p*-orbital can be thought of as circulating around the nucleus.

E : For *s*-orbital angular momentum is zero for a *p*-orbital angular momentum is non-zero.

13. S : All *s*-orbital in H-atom corresponds to a non-zero probability density at nucleus.

E : The probability density is given by : ψ^2 and $\psi\propto e^{-\frac{Zr}{2a_0}}$.

14. S : The location and momentum of an electron in an orbital are complementry to each other.

E : The statement is against Heisenberg uncertainty principle.

15. S : Studies on black body radiations led to Planck's hypothesis of quantisation of electromagnetic radiations.

E : Photoelectric effect provides evidence of the particle nature of electromagnetic radiation whereas diffraction provides evidence of its wave nature.

16. S : The minimum frequency of radiations to show photoelectric effect depends upon the work function.

E : The concept is used to determine identity of the metals.

17. S : The $3p$-orbital has higher energy level than $3s$ in He^+ ion.

E : The energy of an orbital depends upon *n* and *l*.

18. S : Specific charge of α-particles is twice to that of proton.

E : Specific charge is given by *e*/ *m*.

19. S : *d*-orbitals are five fold non-degenerate in presence of magnetic field.

E : In presence of magnetic field the energy of orbitals becomes altogether different.

20. S : Electromagnetic radiations will be emitted for the transition of $2p$ to $2s$-orbital in H-atom.

E : Both have same energy level and thus, no transition.

21. S : The ψ_{640} represents an orbital.

E : The orbital may be 6 g.

22. S : Monochromatic X-rays fall on lighter elements such as carbon and show scattering under the name of Compton effect.

E : $\lambda_{\text{scattered}}$ light is always lower than $\lambda_{\text{incident}}$ light.

23. S : $_{24}$Cr has more paramagnetic nature than $_{25}$Mn.

E : Cr has more number of unpaired electrons than Mn.

24. S : The possible number of orientations of a sub-shell is $(2l+1)$.

E : The possible number of electrons in a sub-shell is $(4l+2)$.

25. S : Aufbau rule is violated in writing electronic configuration of Pd.

E : Pd shows diamagnetic nature.

26. S : Humphrey series discovered in H atomic spectra has lowest energy radiations.

E : The series belongs to $n_1 = 6$.

27. S : $Cu^{+}_{(aq.)}$ has less stable nature than $Cu^{2+}_{(aq.)}$ but $Fe^{3+}_{(aq.)}$ is more stable than $Fe^{2+}_{(aq.)}$.

E : Half filled and completely filled, subshells are more stable.

28. S : $2p$-orbitals do not have any spherical node.

E : The number of spherical and angular node is equal to $(n-l-1)$ and l respectively.

29. S : Dipositive zinc ion exhibits paramagnetism due to the loss of two electrons from $3d$-orbitals of neutral atom.

E : Paramagnetism is due to the presence of unpaired electron.

30. S : As the distance of shell increases from the nucleus, its energy level increases.

E : The energy of a shell is $E_n \propto -1/n^2$.

31. S : Zn^{2+} is diamagnetic

E : The electrons are lost from $4s$ orbital from Zn^{2+}

32. S : A spectral line is seen when electron jumps from $4d$ to $3s$

E : A spectral line is seen when electron jumps from $4d$ to $3p$

33. S : H-atom has only one electron in its orbit, but several spectral lines are noticed

E : The H-spectra is observed in H_2 gas

34. S : All the d-orbitals are identical in shape.

E : All the p-orbitals are identical in shape.

35. S : Band gap in germanium is small. **(2007)**

E : The energy spread of each germanium atomic energy level is infinitesimally small.

ANSWERS (Statement Explanation Problems)

1. (c) Degenerate orbitals possess same energy and thus, transition between p_x and p_y will not radiate energy.
2. (c). $k = 1$ to n and cannot be zero
   $\therefore$ For fourth shell $k = 1, 2, 3, 4$, *i.e.*, four sub-shells.
3. (a) ${}_{23}\text{V}:[\text{Ar}]3d^3, 4s^2; \text{V}^{3+}:[\text{Ar}]3d^2$. Also it is paramagnetic due to the presence of two unpaired electrons.
4. (d) Both are facts.
5. (c) On substituting $r_n \left(mur_n = \frac{n \cdot h}{2\pi}\right)$ and $\lambda \left(\lambda = \frac{h}{mu}\right)$ in $\frac{2\pi r_n}{\lambda}$, number of waves comes equal to n.
6. (c) Explanation is correct reason for statement.
7. (c) $r_n = \frac{r_1 \times n^2}{Z}$ for $r_{2_{\text{Be}^{3+}}} = \frac{r_1 \times 2^2}{4}$ and for $r_{1\text{H}} = \frac{r_1 \times 1^2}{1}$
8. (c) $\Delta E_1 = E_6 - E_5$ in Humphrey series and $\Delta E = E_2 - E_1$ for Lyman series
   $\because \quad \Delta E > \Delta E_1$
   $\therefore \quad \lambda_{\text{Lyman}} < \lambda_{\text{Humphrey}}$
9. (d) Both are facts.
10. (b) Magnetic moment depends upon number of unpaired electrons and given by $= \sqrt{n(n+2)}$, where n is no. of unpaired electrons.

	Valence electron	Unpaired electron
K	1	1
Mg	2	0
N	3	3
O	4	2

11. (c) Explanation is correct reason for statement.
12. (c) Explanation is correct reason for statement.
13. (c) $\psi \propto e^{-\frac{Zr}{2a_0}}$ at $r = 0$; $\psi^2 \propto e^{-0} \propto 1$
14. (a) The statement belongs to Heisenberg uncertainty principle.
15. (d) Both are facts.
16. (d) Both are facts.
17. (b) Higher is the value of $(n + l)$ more is the energy level of orbital for one electron systems energy of $3s = 3p$.
18. (b) Specific charge for proton $= \frac{e}{m}$ and
    specific charge of $\alpha = \frac{2e}{4m} = \frac{e}{2m}$
19. (c) Presence of magnetic field shows different repulsions for micromagnetic character developed in d-orbitals due to different orientations.
20. (b) In H like atom energy, of an orbital is decided by 'n' only and not by 'l'.
21. (d) ψ represents an orbital ψ_{640} means $n = 6$, $l = 4$, $m = 0$, *i.e.*, $6g$ orbital.
22. (a) In Compton effect $\lambda_{\text{scattered}} > \lambda_{\text{incident}}$.
23. (c) ${}_{24}\text{Cr}$ has all six unpaired electrons whereas ${}_{25}\text{Mn}$ has five unpaired out of seven electrons. Both have 5 d-electrons.
24. (c) The values of m are $-l$ to $+l$ through zero, *i.e.*, total $(2l+1)$ orbitals and each orbital has two electrons.
25. (c) Pd being diamagnetic and thus, has $4d^{10}$ configuration rather than $4d^8 5s^2$.
26. (c) For Humphrey series $\Delta E = E_{n_2} - E_5$, .*i.e.*, very small.
27. (d) In Cu^+, no doubt outer shell has $3d^{10}$ or completely filled configuration but hydration energy of Cu^+(aq.) is more.
28. (c) Explanation is correct answer for statement.
29. (b) Zn^{2+} shows paramagnetism due to the presence of unpaired electrons but electrons are lost from Zn from $4s$ subshell.
30. (c) $E_n \propto -\frac{1}{n^2}$; thus if n increase; E_n increases.
31. (d) Zn : .....$3s^2 3p^6 3d^{10} 4s^2$
    Zn^{2+} : .....$3s^2 3p^6 3d^{10}$ (diamagnetic due to no unpaired electron)
32. (b) For spectral line to be given $\Delta l = \pm 1$
33. (c) H_2 gas has so many molecules which are dissouated to from a large no. of H-atoms having different energy levels.
34. (b) One of the d-orbital has baby soother shape.
35. (c) Germanium, semi-conductor substance, has small band gap in comparison to insulator (non-metal).

MATCHING TYPE PROBLEMS

Type I : Only One Match Possible

1.

List-A	**List-B**
A. r_n	1. n^{-2}
B. E_n	2. n^2
C. U_n	3. n^{-1}
D. Angular momentum of orbit	4. n

2. According to Bohr's concept, E_n is total energy, K_n is kinetic energy, V_n is potential energy, r_n is radius of n^{th} orbit.

List-A	**List-B**
A. $\frac{V_n}{K_n}$	1. 0
B. $r_n \propto E_n^x$, then $x =$	2. −1
C. Angular momentum in lowest orbit	3. −2
D. $(r_n)^{-1} \propto u_n^Y$, then $Y =$	4. 1

3.

List-1	**List-2**
A. Number of electrons in a *p*-orbital	a. $4l+2$
B. Number of orbitals in a shell	b. $2l+1$
C. Number of orbital in a sub-shell	c. n
D. Number of electrons in a sub-shell	d. 2

4.

List-1	**List-2**
A. Orbital angular momentum of $4f$-sub-shell	a. zero
B. Total spin of 6 electrons in *p*-sub shell	b. $\frac{3h}{\pi}$
C. Angular momentum of electron in 6th shell	c. $\frac{\sqrt{3}}{4}\frac{h}{\pi}$
D. Spin angular momentum of $3d^8$ sub-shell	d. $\sqrt{3}\frac{h}{\pi}$

5.

List-1	**List-2**
A. Mass spectrum	a. Wave function
B. X-ray spectrum	b. Unpaired electrons
C. Paramagnetism	c. Atomic number
D. Orbital	d. Isotopes

Type II : More than one match are Possible

6.

List-A	**List-B**
A. Orbital angular momentum of the electron in a H-like atom	1. Principal quantum number
B. Wave function of a H-like atom obeying Pauli principle	2. Azimuthal quantum number
C. Shape, size and orientation of H-like orbitals	3. Magnetic quantum number
D. Probability density of electron at the nucleus in H-like atom	4. Electron spin quantum number

7.

List-A	**List-B**
A. 1 B.M	1. Spin magnetic moment
B. 1 NM	2. Nuclear magnetic moment
C. Doughnut structure	3. 9.27×10^{-24} J/T
D. ψ_{320}	4. 5.051×10^{-27} J/T
E. Two nodal planes	5. $3d_{z^2}$

8.

List-1	**List-2**
A. $3d_{z^2}$	a. Two angular mode
B. $3d_{x^2-y^2}$	b. Doughnut shape
C. $5f$	c. Zero node
D. $2s$	d. Four total nodes

9.

Column-I	**Column-II**
A. Diffraction	i. Wave motion
B. Interference	ii. Mass decay
C. Photoelectric effect	iii. Particle nature
D. $E = mc^2$	iv. Planck's theory
E. $E = h\nu$	v. Threshold frequency

Type III : Only one Match from each list

10.

List-A	List-B	List-C
(A) Density of nucleus	1. $10^{-15}\ \text{m}^3$	a. Independent of mass number
(B) Nuclear radius	2. $10^{17}\ \text{kg / m}^3$	b. Dependent of mass number
(C) Higher e/m	3. $-1.76\times10^{11}\ \text{C kg}^{-1}$	c. Electron
(D) Lower e/m	4. $9.58\times10^{7}\ \text{C kg}^{-1}$	d. Proton
(E) $\lambda = 91.75\left[\frac{n^2}{n^2-1}\right]$	5. Balmer series	e. λ in Å
(F) $\lambda = 3647\left[\frac{n^2}{n^2-4}\right]$	6. Lyman series	f. λ in nm

ANSWERS

1. A–2; B–1; C–3; D–4
2. A–3; B–2; C–1; D–4
3. A–d; B–c; C–b; D–a
4. A–d; B–a; C–b; D–c
5. A–d; B–c; C–b; D–a
6. A–2; B–1; C–1, 2, 3; D–none
7. A–1, 3; B–2, 4; C–5; D–5; E–5.
8. A–b; B–a, b; C–d; D–c
9. A–i; B–i; C–iii, v; D–ii, iii; E–i, iii, iv
10. A–2– a; B–1–b; C–4–d; D–3–c; E–6–f; F–5–e

4

Radioactivity

Binding energy: The total energy given out during binding up of nucleons in nucleus is known as binding energy.

Mass defect: 1. A stable nucleus has less mass than its constituent particles. This difference is known as mass defect, *i.e.*,

Δm = sum of the masses of constituents − mass of stable nucleus

2. The difference in mass is converted into energy (known as BE) according to Einstein mass-energy relationship, *i.e.*,

$$E = mc^2 \quad ...(1)$$

3. Thus, Binding energy $= \Delta m \times c^2$ ...(2)

where, BE is in erg, Δm in g and c in cm sec^{-1}

$$\therefore \quad \text{BE} = 1.66 \times 10^{-24} \ (\Delta m') \times (3 \times 10^{10})^2 \text{ erg} \quad (\Delta m' \text{ in amu})$$

$$= 14.94 \times 10^{-4} \times \Delta m' \text{ erg}$$

$$= 14.94 \times 10^{-11} \times \Delta m' \text{ joule}$$

$$= \frac{14.94 \times 10^{-11}}{1.602 \times 10^{-19}} \times \Delta m' \text{ eV} \quad (\because 1.602 \times 10^{-19} \text{ J} = 1 \text{ eV})$$

$$= \frac{14.94 \times 10^{-11}}{1.602 \times 10^{-19} \times 10^6} \times \Delta m' \text{ MeV} \quad (\because 10^6 \text{ eV} = 1 \text{ MeV})$$

$$\text{BE} \approx 931.478 \times \Delta m' \text{ MeV} \quad ...(3)$$

$$\text{or} \quad 1 \text{ amu mass} \equiv 931.478 \text{ MeV} \quad ...(4)$$

4. $\text{BE per nucleons} = \dfrac{\text{Total BE}}{\text{No. of nucleons}}$ ...(5)

Stability of nucleus

(1) Greater is the mass defect, more is BE, Lesser is the energy level of nucleus, more is its stability.

(2) If neutron-proton ratio, *i.e.*, $n/p > 1.5$ the nucleus is unstable.

(3) The no. of stable nucleide is maximum when both at. no. and no. of neutrons are even numbers.

The radioactive emissions: The radioactive disintegrations are accompanied with α, β particles and γ rays.

α-particle emission: 1. An excited nucleus having higher energy level allows α-particles (mass 4 units, charge 2 units) to come out as energy carrier in order to bring down the lower energy level to excited nucleus.

2. α-particles are identified as ${}_2\text{He}^4$, *i.e.*, fastly moving He nucleus.

3. n/p ratio increases during α-emission.

β-particle emission: 1. After α-emission, n/p ratio increases and thus to bring it down, neutron decay occurs which results in emission of β-particles as

$${}_0n^1 \longrightarrow {}_{+1}\text{H}^1 + {}_{-1}e^0$$

2. β-particles are identified as fastly moving electrons, *i.e.*, ${}_{-1}e^0$.

3. n/p ratio decreases during β-emission.

γ-rays emission: 1. If the resultant nucleus formed after α, β emission still possesses higher energy level than required for its stability, the difference in energy comes out in the form of electromagnetic waves or γ-rays.

2. γ-rays are represented as $h\nu$.

Soddy and Fajan's Group Displacement Law

(1) A radioactive element on losing an α-particle shows a loss in its mass no. by 4 units and loss in atomic no. by 2 units.

That is why a newly formed element occupies two positions left to the parent element in periodic table.

$$\underset{\text{II group}}{{}_{88}\text{Ra}^{226}} \xrightarrow{-\alpha} \underset{\text{zero group}}{{}_{86}\text{Rn}^{222}} \xrightarrow{-\alpha} \underset{\text{VI group}}{{}_{84}\text{Po}^{218}}$$

(2) A radioactive element on decay of a β-particle shows a gain in its atomic no. by 1 unit, whereas mass no. remains the same.

That is why newly formed element occupies one position right to the parent element in periodic table.

$$\underset{\text{IV group}}{{}_{82}\text{Pb}^{214}} \xrightarrow{-\beta} \underset{\text{V group}}{{}_{83}\text{Bi}^{214}} \xrightarrow{-\beta} \underset{\text{VI group}}{{}_{84}\text{Po}^{214}}$$

Note : While reporting the position of a new element in periodic table formed after emission of α, β-particles, one should keep in mind that:

1. Elements with at. no. 89, 90 to 103 are placed in III gp.
2. Elements with at. no. 57, 58 to 71 are placed in III gp.
3. Elements with at. no. 26, 27, 28; 44, 45, 46; 76, 77, 78 are placed in VIII gp.

Rutherford's theory of rate of radioactive disintegration or rate of decay: Radioactive decays occur at their characteristic rates, following first order kinetics, independent of temperature, pressure and all external factors. The rate of decay depends upon the amount of element present. Consider, an element A undergoes decay to form B.

$$A \longrightarrow B$$

$t = 0$, no. of atoms $\quad N_0$

$t = t$, no. of atoms $\quad N$

The rate of decay $\neq \dfrac{N_0 - N}{t}$ because rate continuously decreases with time.

Suppose dN atoms are decayed in an infinitesimal small time dt, then

$$\text{Activity or rate of decay} = -\frac{dN}{dt} = \lambda\,(N) \qquad ...(6)$$

The negative sign indicates for a decrease in no. of atoms with time. K is characteristic constant for given substance known as decay constant, independent of all external factors such as P, T......, etc.

On integrating Eq. (1) $\quad -\int \dfrac{dN}{N} = \lambda \int dt$

$$-\ln N = \lambda t + c$$

at $\quad t = 0, N = N_0$

$\therefore$

$$c = -\ln N_0$$

$$-\ln N = \lambda t - \ln N_0$$

or
$$\ln \frac{N_0}{N} = \lambda t \qquad ...(7)$$

or
$$\frac{N_0}{N} = e^{\lambda t} \qquad ...(8)$$

or
$$2.303 \log_{10} \frac{N_0}{N} = \lambda t \qquad ...(9)$$

or
$$\frac{N}{N_0} = e^{-\lambda t} = 10^{-\lambda t/2.303} \qquad ...(10)$$

Characteristics of Rate of Decay

1. **Half-life period:** The time required to complete half of the decay, *i.e.*, if $t = t_{1/2}$, $N = \dfrac{N_0}{2}$;

On substituting these in Eq. (1), $\quad \lambda = \dfrac{0.693}{t_{1/2}} \qquad ...(11)$

2. **Average life:** $\quad \text{Average life } (\tau) = \dfrac{1}{\lambda} \qquad ...(12)$

Average life of a radioactive species is the time in which species reduces to 37% of its initial value.

3. The time required to disintegrate a definite fraction is independent of initial concentration, *i.e.*, $t_{1/n} \propto (N_0)^0$, where $t_{1/n}$ is time required to complete $1/n$ decay. Therefore, half decay is also written as,

$$t_{1/2} \propto (N_0)^0$$

4. $\text{Amount left after } n \text{ halves} = \dfrac{N_0}{2^n} \qquad ...(13)$

$\therefore \quad$ Amount used in n halves

$$= N_0 - \frac{N_0}{2^n} = \frac{N_0[2^n - 1]}{2^n} \qquad ...(14)$$

Also, $\quad \text{No. of halves } (n) = \dfrac{\text{total time}}{\text{half - life period}} = \dfrac{T}{t_{1/2}} \qquad ...(15)$

5. $\quad \text{Activity} = \dfrac{0.693 \times \text{Number of atoms present}}{\text{Half - life}} \qquad ...(16)$

Unit of radioactivity: The unit of radioactivity of an element is measured by the rate at which it changes into daughter element. It has been derived on the scale of disintegration of Ra.

Consider 1 g Ra ($t_{1/2} = 1600$ year) undergoes decay, then

Rate of decay $= \lambda \times$ No. of atoms of Ra in 1 g

$$= \frac{0.693}{1600 \times 365 \times 24 \times 60 \times 60} \times \frac{6.023 \times 10^{23}}{226}$$

$= 3.7 \times 10^{10}$ dps $= 3.7 \times 10^{10}$ Becquerrel (or Bq.) $\qquad$ ...(17)

$= 1$ curie $\qquad$ ($\because$ 3.7×10^{10} dps $= 1$ ci) $\qquad$ ...(18)

$= 3.7 \times 10^4$ Rutherford $\quad$ ($\because$ 10^6 dps $= 1$ rd) $\qquad$ ...(19)

The S.I. unit of radioactivity is dps or Becquerrel. The other units to express rate of decay are,

Microcurie $= 10^{-6}$ curie $= 3.7 \times 10^4$ dps

Millicurie $= 10^{-3}$ curie $= 3.7 \times 10^7$ dps

Radioactive series: A series of radioactive nucleide, each except the first being the decay product of previous one. **The three naturally occurring series are,**

(1) Thorium series or $4n$ series with parent element Th^{232}

(2) Uranium series or $(4n + 2)$ series with parent element U^{238}

(3) Actinium series or $(4n + 3)$ series with parent element U^{235}

One is Artificial Series

(4) Naptunium series or $(4n + 1)$ series with parent element Np^{237}

The significance of 'n' lies in the fact that mass number of each member of a given series is an integer multiple of n with residue 0, 1, 2, 3 respectively for $4n$, $4n + 1$, $4n + 2$ and $4n + 3$ series. In all the series except Np series, there exists an element of zero group (at. no. 86) in gaseous state.

Radioactive equilibrium: A state ultimately reached when a radioactive substance of slow decay yields a radioactive product on disintegration. This product also decays to give a further radioactive substance and so on to produce a radioactive series. The amount of any daughter radioactive product present, after equilibrium has been reached, remains constant, the loss due to decay being counter balanced by gain from the decay of immediate product.

$$A \longrightarrow B \longrightarrow C$$

At equilibrium, rate of formation of B = rate of decay of B

$$\lambda_A \cdot N_A = \lambda_B \cdot N_B$$

or

$$\frac{\lambda_A}{\lambda_B} = \frac{N_B}{N_A}$$

$\therefore$

$$\frac{\lambda_A}{\lambda_B} = \frac{N_B}{N_A} = \frac{t_{1/2B}}{t_{1/2A}} = \frac{\tau_B}{\tau_A} \qquad ...(20)$$

λ is decay constant and $\lambda \propto \frac{1}{\tau}$ and $\lambda \propto \frac{1}{t_{1/2}}$

Note:
1. Eq. (2) holds good only when $\lambda_A >>> \lambda_B$ or $t_{1/2}\, A >>> t_{1/2} B$. This is called **secular equilibrium.**
2. If $t_{1/2}\, A \simeq t_{1/2}\, B$ and $\lambda_A < \lambda_B$, then

$$\frac{N_A}{N_B} = \frac{\lambda_B - \lambda_A}{\lambda_A} \qquad ...(21)$$

   This is called **transient equilibrium.**
3. If $\lambda_A > \lambda_B$ or $t_{1/2}\, A < t_{1/2}\, B$, no state of equilibrium is attained.

Maximum yield of daughter element: A radioactive element A decays to give a daughter element B which further decays to another daughter element C and so on till a stable element is formed $(A \to B \to C)$. Also if number of daughter atoms at $t = 0$ is zero and parent atom is much more lived than daughter (*i.e.*, $\lambda_A < \lambda_B$), where λ_A and λ_B are decay constants of A and B respectively, then number of atoms of daughter element B after time t is

$$N_B = \frac{N_0 \lambda_A}{\lambda_B - \lambda_A}[e^{-\lambda_A t} - e^{-\lambda_B t}] \qquad ...(22)$$

Maximum activity of daughter element can be expressed at $t_{\max}$:

$$t_{\max} = \frac{2.303}{\lambda_B - \lambda_A} \log_{10}\left[\frac{\lambda_B}{\lambda_A}\right] \qquad ...(23)$$

Parallel path decay: A radioactive element A decays to B and C in two parallel paths as:

$$\begin{tikzcd} & B \\ A \arrow[ur, "\text{Say emission of } \alpha"] \arrow[dr, "\text{Say emission of } \beta"'] & \\ & C \end{tikzcd}$$

The average decay constant for the element A can be expressed as

$$\lambda_{\text{average}} = \lambda_{\alpha \text{ path}} + \lambda_{\beta \text{ path}} \qquad ...(24)$$

Eq. (24) can be expressed in Eq. (25) and (26) as:

$$\lambda_{\alpha \text{ path}} = [\text{Fractional yield of } B] \times \lambda_{\text{av.}} \qquad ...(25)$$

$$\lambda_{\beta \text{ path}} = [\text{Fractional yield of } C] \times \lambda_{\text{av.}} \qquad ...(26)$$

Average atomic mass $(\bar{A}) = \dfrac{\Sigma A_1 X_1}{\Sigma X_{\text{Total}}}$ ...(27)

Nuclear reactions

The phenomenon of interaction of nucleons giving rise to the formation of a new nucleus or a process in which one nuclide is converted to another by interaction with another nuclide. The **first ever nuclear reaction** in laboratory was carried out by Rutherford when he bombarded N atoms with α-particles.

$${}^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H} + Q$$

Another, method of representing this nuclear reaction is ${}^{14}_{7}\text{N}\,(\alpha : p)\,{}^{17}_{8}\text{O}$. Like chemical reactions, nuclear reactions also involve energy changes, represented by the symbol Q. If Q is negative, the reaction is endoergic, *i.e.*, energy is absorbed and if Q is positive, energy is released, *i.e.*, exoergic. The value of Q can be determind from the difference in the total mass of reactants and products of the reaction.

Types of nuclear reactions

Some of the nuclear reactions are cited below :

(i) Induced radioactivity : The phenomenon of converting stable nuclei into unstable one by the interaction of nucleons or a nuclear reaction yielding a product nuclei of radioactive nature, is known as induced or artificial radioactivity (Irene Curie and F. Joliot).

$${}^{10}_{5}\text{B} + {}^{4}_{2}\text{He} \longrightarrow {}^{13}_{6}\text{C} + {}^{1}_{1}\text{H} \text{ Nuclear reaction}$$

$$\begin{tikzcd} {}^{10}_{5}\text{B} + {}^{4}_{2}\text{He} \arrow[r] & {}^{13}_{7}\text{N} + {}^{1}_{0}n \arrow[d, "\text{Nuclear reaction, } \textit{Vis}\text{-a-}\textit{Vis}"] \\ & {}^{13}_{6}\text{C} + {}^{0}_{+1}e \text{ Artificial radioactivity} \end{tikzcd}$$

(ii) Nuclear Fission : (a) The phenomenon of splitting up of a heavy nucleus, on bombardment with slow speed neutrons, into two fragments of comparable mass, with the release of two or more fast moving neutrons and a large amount of energy, is known as nuclear fission.

$$\begin{tikzcd} & & {}^{140}_{56}\text{Ba} + {}^{93}_{36}\text{Kr} + 3{}^{1}_{0}n \\ \text{(b) } {}^{235}_{92}\text{U} + {}^{1}_{0}n \arrow[r] & {}^{236}_{92}\text{U} \arrow[ur] \arrow[r] \arrow[dr] & {}^{144}_{54}\text{Xe} + {}^{90}_{38}\text{Sr} + 2{}^{1}_{0}n \\ & & {}^{144}_{55}\text{Cs} + {}^{90}_{37}\text{Rb} + 2{}^{1}_{0}n \end{tikzcd}$$

A loss in mass occurs releasing a huge amount of energy $\simeq 2.041 \times 10^{10}$kJ per mol of ^{235}U.

(iii) Nuclear fusion : (a) The phenomenon of joining up of two light nuclei into a heavier nucleus is called fusion, *e.g.*,

$${}^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + {}^{1}_{0}n; \ (\Delta H = -17.6 \text{ MeV})$$

(b) Huge amount of energy is required to overpower the Coulombic forces of repulsion in between two nuclei which is obtained by triggering on nuclear fission.

(iv) Spallation reacton : Spallation is a reaction in which the excitation energy of the target nucleus is sufficiently high and results in the emission of several particles such as α-particles and protons, leaving behind a number of product nuclei of sufficiently smaller masses than the target, *e.g.*,

$${}^{75}_{33}\text{As} + {}^{2}_{1}\text{H} \longrightarrow {}^{56}_{25}\text{Mn} + 9{}^{1}_{1}\text{H} + 12{}^{1}_{0}n$$

• NUMERICAL PROBLEMS •

1. Calculate the binding energy for ${}_1H^2$ atom. The mass of ${}_1H^2$ atom is 2.014102 amu, where $1n$ and $1p$ have their masss 2.016490 amu. Neglect mass of electron.

2. (a) Although nucleus is a part of atom but number of electrons present in the atom has no role in deciding binding energy of nucleus. Explain.

(b) The atomic mass of ${}_8O^{16} = 15.9949$ amu. Calculate the BE/nucleon for this atom. Mass of $1n$ and $1p$ is 2.016490 amu and $m_e = 0.00055$ amu.

3. The atomic masses of Li, He and proton are 7.01823 amu, 4.00387 amu and 1.00715 amu respectively. Calculate the energy evolved in the reaction,

$$ {}_3Li^7 + {}_1p^1 \longrightarrow 2{}_2He^4 + \Delta E $$

Given 1 amu = 931 MeV.

4. Calculate the energy released in joules and MeV in the following nuclear reaction:

$$ {}_1^2H + {}_1^2H \longrightarrow {}_2^3He + {}_0^1n $$

Assume that the masses of ${}_1^2H$, ${}_2^3He$ and neutron (n) respectively are 2.0141, 3.0160 and 1.0087 in amu.

5. How much heat would be developed per hour from 1 curie of C^{14} source if all the energy of beta decay were imprisoned? Atomic masses of C^{14} and N^{14} are 14.00324 and 14.00307 amu respectively.

6. Calculate the loss in mass during the change:

$$ {}_3Li^7 + {}_1H^1 \longrightarrow 2\ {}_2He^4 + 17.25\ \text{MeV} $$

7. An isotopic species of lithium hydride ${}^6Li^2H$ is used as a potential nuclear fuel following the nuclear reaction:

$$ {}_3^6Li\ {}_1^2H \longrightarrow 2\ {}_2^4He $$

Calculate the expected power production of megawatt (Mw) associated with 1.00 g of ${}^6Li\ {}^2H$ per day assuming 100% efficiency. Given ${}_3^6Li = 6.01512$ amu; ${}_1^2H = 2.01410$ amu ; ${}_2^4He = 4.00260$ amu.

8. Calculate the mass defect and binding energy per nucleon for an alpha particle whose mass is 4.0028 amu. $m_P = 1.0073$ and $m_N = 1.0087$ amu.

9. Calculate mass no., atomic no. and group in the periodic table for RaC in the following change.

$$ {}_{88}Ra^{226} \xrightarrow{-\alpha} Rn \xrightarrow{-\alpha} RaA \xrightarrow{-\beta} RaB \xrightarrow{-\alpha} RaC $$

10. (a) Calculate no. of α and β-particles emitted when ${}_{92}U^{238}$ changes into radioactive ${}_{82}Pb^{206}$. **(IIT 2000)**

(b) Th^{234} disintegrates and emits 6β – and 7α-particles to form a stable element. Find the atomic number and mass number of the stable product. Also identify the element. **(IIT 2004)**

11. Calculate the group of elements formed in the final stage of radioactive changes given below:

(a) $\underset{\text{III group}}{{}_{92}U^{235}} \xrightarrow{-\alpha} {}_{90}Th^{231}$ (b) $\underset{\text{III group}}{{}_{90}Th^{231}} \xrightarrow{-\beta} {}_{91}X^{231}$

(c) $\underset{\text{III group}}{{}_{91}X^{231}} \xrightarrow{-\alpha} {}_{89}Ac^{227}$ (d) ${}_{90}Th^{231} \xrightarrow{-\alpha} {}_{88}Ra^{227}$

12. Calculate the number of neutrons in the remaining atom after emission of an α-particle from ${}_{92}X^{238}$ atoms. Also report the mass no. and atomic no. of resultant atom.

13. If a ${}_{92}U^{235}$ nucleus upon being struck by a neutron changes to ${}_{56}Ba^{145}$, three neutrons and an unknown product. What is the unknown product?

14. Prove that the time required for 99.9% decay of a radioactive substance is almost 10 times to its half-life period.

15. Represent and derive mathematically the half-life period of radioactive substance.

16. 1 g of ${}_{79}Au^{198}$ ($t_{1/2} = 65$ hr) decays by β-emission to produce stable Hg.

(a) Write nuclear reaction for process.

(b) How much Hg will be present after 260 hr.

17. The rate of decay of a radioactive sample is 3.02×10^6 dpm at time 10 min and 1.20×10^6 dpm at a time 20 min. Evaluate the decay constant, half-life and average life of sample.

18. A sample of ${}_{53}^{153}I$, as iodide ion, was administered to a patient in a carrier consisting of 0.10 mg of stable iodide ion. After 4 day, 67.7% of the initial activity was detected in the thyroid gland of the patient. What mass per cent of the stable iodide ion had migrated to the thyroid gland? $t_{1/2}$ for $I = 8$ day.

19. The half-life period of ${}_{53}I^{125}$ is 60 day. What % of radioactivity would be present after 180 day?

20. One of the hazards of nuclear explosion is the generation of Sr^{90} and its subsequent incorporation in bones. This nucleide has a half life of 28.1 year. Suppose one microgram was absorbed by a new-born child, how much Sr^{90} will remain in his bones after 20 year? **(IIT 1995)**

21. At a certain instant, a piece of radioactive material contains 10^{12} atoms. The half-life of material is 30 day. Calculate the no. of disintegrations in the first second.

22. The activity of a radioactive isotope falls to 12.5% in 90 day. Compute the half-life and decay constant of isotope.

23. A radioactive element ($t_{1/2} = 30$ day) is spread over a room. Its activity is 50 times the permissible value of safe working. Calculate the number of day after which the room will be available for safe working.

24. Calculate the ratio of N / N_0 after an hour has passed for a radioactive material of half-life 47.2 second.

25. Two radioactive nucleide P and Q have their decay constant in the ratio 3:2. 1 mole of each is taken separately and allowed to decay for a time interval of three times of half-life of A. If 0.2 mole of P are left, what moles of Q will be left?

26. The activity of a radioactive sample drops to 1/64th of its original value in 2 hr. Find the decay constant for sample.

27. It is known that 1 g of Ra^{226} emits 11.6×10^{17} atoms of α per year. Given the half-life of Ra^{226} be 1600 years. Compute the value of Avogadro's no.

28. The disintegration rate of a certain radioactive sample at any instant is 4750 dpm. Five minutes later, the rate becomes 2700 dpm. Calculate half-life of sample.

29. The radioactive disintegration of $_{94}Pu^{239}$ an α-emission process is accompanied by the loss of 5.24 MeV/dis. If $t_{1/2}$ of $_{94}Pu^{239}$ is 2.44×10^4 year, calculate the energy released per year from 1.0 g sample of $_{94}Pu^{239}$ in kJ.

30. 1 g Ra^{226} is placed in an evacuated tube whose volume is 5 cc. Assuming that each Ra nucleus yields four He-atoms which are retained in the tube, what will be the pressure of He produced at 27°C after the end of 1590 year? $t_{1/2}$ for Ra is 1590 year.

31. The decay constant for an α-decay of Th^{232} is 1.58×10^{-10} sec^{-1}. Find out the no. of α-decays that occur from 1 g sample in 365 day.

32. A certain radio isotope $_Z X^A$ ($t_{1/2} = 10$ day) decays to give $_{Z-2}Y^{A-4}$. If one g-atom of $_Z X^A$ is kept in a sealed vessel, how much He will accumulate in 20 day at STP?

33. 10 g-atoms of an α-active radioactive isotope are disintegrating in a sealed container. In one hour, the He gas collected at STP is 11.2 cm^3. Calculate half-life of the radioactive isotope.

34. A radioactive isotope $_Z A^m$ ($t_{1/2} = 10$ day) decays to give $_{Z-6}B^{m-12}$ stable atom along with α-particles. If m g of A are taken and kept in a sealed tube, how much He will accumulate in 20 day at STP?

35. 1 g-atom of Ra^{226} is placed in an evacuated tube of volume 5 litre. Assuming that each $_{88}Ra^{226}$ nucleus is an α-emitter and all the contents are present in tube, calculate the total pressure of gases and partial pressure of He collected in tube at 27°C after the end of 800 year. $t_{1/2}$ of Ra is 1600 year. Neglect volume occupied by undecayed Ra.

36. The activity of the hair of an egyptian mummy is 7 disintegration minute^{-1} of C^{14}. Find the age of mummy. Given $t_{0.5}$ of C^{14} is 5770 year and disintegration rate of fresh sample of C^{14} is 14 disintegration minute^{-1}.

37. What mass of C^{14} with $t_{1/2} = 5730$ year has activity equal to one curie?

38. A sample of $^{14}CO_2$ was mixed with ordinary $^{12}CO_2$ for studying a biological tracer experiment. The 10 mL of this mixture at STP possess the rate of 10^4 disintegration per minute. How many millicurie of radioactive carbon is needed to prepare 60 litre of such a mixture?

39. 0.1 g-atom of radioactive isotope $_Z X^A$ (half-life 5 day) is taken. How many number of atoms will decay during eleventh day?

40. $_{84}Po^{210}$ decays with α-particle to $_{82}Pb^{206}$ with a half-life of 138.4 day. If 1.0g of $_{84}Po^{210}$ is placed in a sealed tube, how much helium will accumulate in 69.2 day? Express the answer in cm^3 at STP. Also report the volume of He formed if 1 g of $Po^{210}O_2$ is used.
(Roorkee 1991)

41. A solution contains 1 milli curie of L-phenyl alanine C^{14} (uniformly labelled) in 2.0 mL solution. The activity of labelled sample is given as 150 milli curie/milli mole. Calculate:
- (a) the concentration of sample in the solution in mole/litre.
- (b) the activity of the solution in terms of counting per minute/mL at a counting efficiency of 80%.

42. The $_6C^{14}$ and $_6C^{12}$ ratio in a piece of wood is 1/16 part that of atmosphere. Calculate the age of wood. $t_{1/2}$ of C^{14} is 5577 years.

43. The half-life period of C^{14} is 5760 year. A piece of wood when buried in the earth had 1% C^{14}. Now as charcoal it has only 0.25% C^{14}. How long has the piece of wood been buried?

44. A sample of U^{238} (half-life = 4.5×10^9 yr) ore is found to contain 23.8g of U^{238} and 20.6 g of Pb^{206}. Calculate the age of the ore. **(Roorkee 1996)**

45. (a) On analysis a sample of uranium ore was found to contain 0.277 g of $_{82}Pb^{206}$ and 1.667 g of $_{92}U^{238}$. The half-life period of U^{238} is 4.51×10^9 year. If all the lead was assumed to have come from decay of $_{92}U^{238}$, what is the age of earth?

(b) An ore of $_{92}U^{238}$ is found to contain $_{92}U^{238}$ and $_{82}Pb^{206}$ in the mass ratio of 1:0.1. The half life period of $_{92}U^{238}$ is 4.5×10^9 year. Calculate the age of ore. **(IIT 2000)**

46. A sample of pitch blende is found to contain 50% uranium and 2.425% lead. Of this lead only 93% was Pb^{206} isotope. If the disintegration constant is 1.52×10^{-10} yr^{-1}, how old could the pitch blende deposits?

47. The isotopes U^{238} and U^{235} occur in nature in the ratio 140 : 1. Assuming that at the time of earth formation, they were present in equal ratio, make an estimation of the age of earth. The half-life period of U^{238} and U^{235} are 4.5×10^9 and 7.13×10^8 year respectively.

48. In nature a decay chain series starts with $_{90}Th^{232}$ and finally terminates at $_{82}Pb^{208}$. A thorium ore sample was found to contain 8×10^{-5} mL of He at STP and 5×10^{-7} g of Th^{232}. Find the age of ore sample assuming that source of He to be only due to decay of Th^{232}. Also assume complete retention of He within the ore. $t_{1/2} Th^{232} = 1.39 \times 10^{10}$ year. **(Roorkee 1992)**

49. The half-life of ^{32}P is 14.3 day. Calculate the specific activity of a phosphorus containing specimen having 1.0 part per million ^{32}P (Atomic mass of P = 31).

50. A mixture of Pu^{239} and Pu^{240} has a specific activity of 6×10^9 dps per g sample. The half-lives of the isotopes are 2.44×10^4 year and 6.58×10^3 year respectively. Calculate the composition of mixture.

51. In a sample of radioactive element, radium disintegrates at an average rate of 2.24×10^{13} α-particles per minute. Each α-particle takes up 2 electrons from the air and becomes a neutral helium atom. After 420 days, the He gas collected was 0.5 mL measured at 27° C and 750 nm of mercury pressure. From the above data, calculate Avogadro's no.

52. An experiment requires minimum β-activity produced at the rate of 346 β-particles per minute. The half-life period of $_{42}Mo^{99}$ which is a β-emitter is 66.6 hrs. Find the minimum amount of $_{42}Mo^{99}$ required to carry out the experiment in 6.909 hours.

53. A solution contains a mixture of isotopes of X^{A_1} ($t_{1/2} = 14$ days) and X^{A_2} ($t_{1/2} = 25$ days). Total activity is 1 curie at $t = 0$. The activity reduces by 50% in 20 days. Find:

(a) the initial activities of X^{A_1} and X^{A_2}.

(b) the ratio of their initial no. of nuclei.

54. What amount of energy is evolved by one curie of Rn (an α-emitter) in:

(a) one hour (b) its mean life?

Given that kinetic energy of one α-particle is 5.5 MeV and $\lambda = 2 \times 10^{-6}$ sec^{-1} for Rn.

55. 54.5 mg of Na_3PO_4 contains P^{32} (15.6% of sample) and P^{31} atoms. Assuming only P^{32} atoms radioactive, calculate the rate of decay for the given sample of Na_3PO_4. The half-life period for $P^{32} = 14.3$ day; molar mass of $Na_3PO_4 = 161.2$.

56. $_{19}K^{40}$ consists of 0.012% of the potassium in nature. The human body contains 0.35% potassium by mass. Calculate the total radioactivity resulting from $_{19}K^{40}$ decay in a 75 kg human. Half-life for $_{19}K^{40}$ is 1.3×10^9 year.

57. 32 mg of pure $_{94}Pu^{238}O_2$ has an activity of 6.4×10^7 dps. Calculate (i) the half-life of $_{94}Pu^{238}$. (ii) the amount PuO_2 left, if 100 mg of PuO_2 is kept for 5000 year.

58. A small amount of solution containing Na^{24} radio nucleide with activity $A = 2 \times 10^3$ dps was administered into blood of a patient in a hospital. After 5 hours, a sample of the blood drawn out from the patient showed an activity of 16 dpm per cc $t_{1/2}$ for $Na^{24} = 15$ hrs. Find:

(a) Volume of the blood in patient.

(b) Activity of blood sample drawn after a further time of 5 hrs. **(IIT 1994)**

59. There is a stream of neutrons with kinetic energy 0.0327 eV. If the half-life of neutron is 700 sec, what fraction of neutron will decay before they travel a distance of 100 metre? $m_n = 1.675 \times 10^{-27}$ kg.

60. Nuclei of a radioactive element A are being produced at a constant rate α. The element A has a decay constant λ. At time $t = 0$, there are N_0 nuclei of element A.

(a) Calculate the number of nuclei (N) of A at any time t.

(b) If $\alpha = 2\lambda N_0$, calculate the number of nuclei of A after one half-life of A and also the limiting value of N as $t \rightarrow \infty$.

61. A radionucleide of ^{32}P with half-life 14.3 day are produced in a nuclear reactor at a constant rate, $q = 2.7 \times 10^9$ nuclei per second. How soon after the beginning of production of that nucleide will its activity be equal to 1.7×10^9 dis / s?

62. At radioactive equilibrium, the ratio between two atoms of radioactive elements A and B are $3.1 \times 10^9 : 1$. If half-life period of A is 2×10^{10} year, what is half-life of B?

63. In an experiment on two radioactive isotopes of an element (which do not decay into each other), their molar ratio at a given instant is 3. The rapidly decaying isotope has larger mass and an initial activity of 1.0 μCi. The half-lives of the two isotopes are 12 and 16 hr respectively. What would be the activity of each isotope and their molar ratio after two day?

64. The nucleidic ratio of ${}_1H^3$ to ${}_1H^1$ in a sample of water is 8.0×10^{-18} : 1. Tritium undergoes decay with a half-life period of 12.3 year. How many tritium atoms would 10.0 g of such a sample contains 40 year after the original sample is collected? **(IIT 1992)**

65. The mean lives of a radioactive substance are 1620 year and 405 year for α-emission and β-emission respectively. Find out the time during which three fourth of a sample will decay if it is decaying both by α-emission and β-emission simultaneously.

66. Consider an α-particle just in contact with a ${}_{92}U^{238}$ nucleus. Calculate the coulombic repulsion energy (*i.e.*, the height of coulombic barrier between U^{238} and α-particle) assuming that the distance between them is equal to the sum of their radii.

67. With what velocity should an α-particle travel towards the nucleus of a copper atom so as to arrive at a distance 10^{-13} metre from the nucleus of the copper atom? **(IIT May 1997)**

68. α-particles accelerated by 3×10^5 volt bombarded a boron target. This results in the nuclear reaction.

$$ {}_2He^4 + {}_5B^{10} \longrightarrow {}_6C^{13} + {}_1H^1 + \gamma $$

If the combined energy of ${}^{13}C$ and H^1 is 5×10^5 eV, calculate the energy, frequency and wavelength of γ-rays. 1×10^5 eV energy is used in penetrating the nucleus.

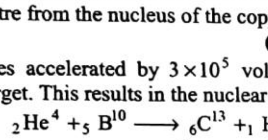
(He = 4.0026 amu, B = 10.0129 amu, C = 13.0036 amu)

69. A positron and an electron collide and annihilated to emit two gamma photons of same energy. Calculate the wavelengths corresponding to this gamma emission.

70. Ac^{227} has a half-life of 22 year in its radioactive decay. The decay follows two parallel paths, one leading the Th^{227} and the other leading to Fr^{223}. The percentage yields of these two daughters nucleides are 2% and 98% respectively. What is the rate constant in yr^{-1}, for each of the separate paths? **(IIT 1996)**

71. ${}^{64}Cu$ (half-life = 12.8 hr) decays by β^--emission (38%), β^+-emission (19%) and electron capture (43%). Write the decay products and calculate partial half lives for each of the decay processes.

72. A follows parallel path I order reactions giving *B* and *C* as:



If initial concentration of *A* is 0.25 *M*, calculate the concentration of *C* after 5 hour of reaction.

Given, $\lambda_1 = 1.5\times10^{-5}\ s^{-1}$, $\lambda_2 = 5\times10^{-6}\ s^{-1}$

73. There is a stream of neutrons with a kinetic energy of 0.0327 eV. If the half-life of neutrons is 700 second, what fraction of neutrons will decay before they travel a distance of 10 km? (Mass of neutron $= 1.675\times10^{-27}$ kg).

74. The isotopic masses of ${}_1H^2$ and ${}_2He^4$ are 2.0141 and 4.0026 amu respectively. Calculate the quantity of energy liberated when two mole of ${}_1H^2$ undergo fission to form 1 mole of ${}_2He^4$. The velocity of light in vacuum is 2.998×10^8 m / sec.

75. The half-life of Pb^{212} is 10.6 hour. It undergoes decay to its daughter (unstable) element Bi^{212} of half-life 60.5 minute. Calculate the time at which daughter element will have maximum activity.

76. Match the following:

1. Isotopes	A. ${}_8O^{16}$ and ${}_8O^{17}$
2. Isobars	B. Na^+, Mg^{2+}, F^-
3. Nuclear isomers	C. ${}_1H^2$ and ${}_2H^3$
4. Isosters	D. U_A and U_Z
5. Isotones	E. CO_2 and N_2O
6. Isoelectronics	F. ${}_AX^Z$, ${}_{A-2}X^{Z-4}$
7. Isodiaphers	G. ${}_{20}Ca^{40}$ and ${}_{19}K^{40}$

77. Naturally occurring *B* consists of two isotopes, whose atomic masss are 10.01 and 11.01. The atomic mass of natural boron is 10.81. Calculate the % of each isotope in natural boron.

78. Cl^{35} and Cl^{37} are the naturally occurring Cl isotopes, what % of Cl^{35} accounts for the atomic mass of 35.453 in mixture?

79. The abundance of three isotopes of oxygen, each containing 8, 9 and 10 neutrons respectively has the % of one isotope (containing 8 neutrons) 90%. What are the other % if the atomic mass of oxygen is 16.12?

80. Write equations for the following transformations:

(a) ${}_7N^{14}$ (*n*, *p*) (b) ${}_{19}K^{39}$ (*p*, α)

(c) K-electron capture (d) β^+-decay by ${}_{11}Na^{22}$

81. Complete the following:

(1) ${}_{92}U^{235} + {}_0n^1 \longrightarrow {}_{55}A^{142} + {}_{37}B^{92} + \ldots$ **(IIT 2005)**

(2) $2\,{}_1H^3 \longrightarrow {}_2He^4 + \ldots$

(3) ${}_{34}Se^{82} \longrightarrow \ldots + 2\,{}_{-1}e^0$ **(IIT 2005)**

82. Name the process represented below:

(a) ${}_{13}Al^{27} + {}_2He^4 \longrightarrow {}_{15}P^{30} + {}_0n^1$
$\quad\quad\quad\quad\quad\quad\quad\hookrightarrow {}_{14}Si^{30} + {}_{+1}e^0$

(b) ${}_5B^{10} + {}_2He^4 \longrightarrow {}_6C^{13} + {}_1H^1$

(c) ${}_5B^{10} + {}_2He^4 \longrightarrow {}_7N^{13} + {}_0n^1$
$\quad\quad\quad\quad\quad\quad\quad\hookrightarrow {}_6C^{13} + {}_{+1}e^0$

(d) ${}_{33}As^{75} + {}_1H^2 \longrightarrow {}_{25}Mn^{56} + 9\,{}_1H^1 + 12\,{}_0n^1$

83. To which radioactive series the following appears during disintegrations:

$$ {}_{89}Ac^{228};\ {}_{89}Ac^{227} $$

84. Following reactions are given. Which one is more hazardous for civilization?

Fission :

$$ {}_{92}U^{235} + {}_0n^1 \longrightarrow {}_{56}Ba^{141} + {}_{36}Kr^{92} + 2 \sim 3\,{}_0n^1 + 200\ \text{MeV} $$

Fusion : ${}_1H^2 + {}_1H^3 \longrightarrow {}_2He^4 + {}_0n^1 + 17.6\ \text{MeV}$

SOLUTIONS (Numerical Problems)

1. Mass of neutron and proton in $_1H^2 = 2.016490$ amu

Actual mass of $_1H^2 = 2.014102$ amu

$\therefore$ Mass defect $= 2.388 \times 10^{-3}$ amu

$\therefore$ Binding energy $= 2.388 \times 10^{-3} \times 931$ MeV

$= \mathbf{2.2232\ MeV}$

2. (a) Although binding energy is referred to nucleus, it is more convenient to use the mass of whole atom (nuclide) in calculation. If m_a is the atomic mass of atom X and m_e is mass of electron

$$m_{\text{nucleus}} = m_a - Z \times m_e \quad \text{...(i)}$$

Also for $^1_1$H atom, $m_{\text{H-atom}} = m_p$

$$m_{^1_1\text{H}_{\text{nucleus}}} = m_p - m_e \quad \text{...(ii)}$$

where m_p is mass of proton

Now for a nucleus having Z protons and $(A-Z)$ neutrons where Z and A are atomic number and mass number of given atom

Mass decay $= Z \times m_{^1_1\text{H}_{\text{nucleus}}} + (A-Z) \times m_n = m_{\text{nucleus}}$ ...(iii)

By (i), (ii) and (iii)

Mass decay

$= Z \times m_p - Z \times m_e + (A-Z) \times m_n - m_a + Z \times m_e$

$= Z \times m_p + (A-Z) \times m_n - m_a$ ...(iv)

$\therefore$ B.E. $= [Z \times m_p + (A-Z)m_n - m_a] \times c^2$ ...(v)

It is thus evident that electron's mass has no role in calculating binding energy.

(b) Mass of $1n + 1p = 2.016490$ amu

$\therefore$ Mass of $8n + 8p = 8 \times (2.016490)$ amu

$\therefore$ Total mass of O^{16} nucleus $= m(p+n)$

$= 8 \times (2.016490) = 16.13192$ amu

$\therefore$ Mass defect $= 16.13192 - 15.9949 = 0.13702$ amu

$\therefore$ BE = Mass defect × 931.478 MeV

$\therefore$ $= 0.13702 \times 931.478 = 127.63$ MeV

$\therefore$ BE/nucleon $= \dfrac{\text{Total BE}}{\text{No. of nucleons}}$

$= \dfrac{127.63}{16} = \mathbf{7.977\ MeV}$

3. Mass of reactants = mass of Li + mass of p

$= 7.01823 + 1.00715 = 8.02538$ amu

Mass of products $= 2 \times$ mass of He $= 2 \times 4.00387$

$= 8.00774$ amu

$\therefore$ Mass loss during change $= 8.02538 - 8.00774$

$= 0.01764$ amu

$\therefore$ Energy evolved during reaction

$= 0.01764 \times 931 = \mathbf{16.423\ MeV}$

4. $\Delta m = [2 \times 2.0141] - 3.0160 - 1.0087$

$= 3.5 \times 10^{-3}$ amu

$\therefore$ $\Delta E = \Delta m \times 931.478$

$\Delta E = 3.5 \times 10^{-3} \times 931.478$

$= \mathbf{3.260\ MeV}$

Also $\Delta E = \mathbf{5.223 \times 10^{-13}\ J}$

5. $_6C^{14} \longrightarrow {_7N^{14}} + {_{-1}e^0}$

$\Delta m = 14.00324 - 14.00307 = 0.00017$ amu

$\therefore$ Energy produced during this decay of 1 atom

$= \Delta m \times 931.478$ MeV

$= 0.00017 \times 931.478$ MeV

$= 0.158$ MeV

$= 0.158 \times 10^6$ eV

$= 0.158 \times 10^6 \times 1.602 \times 10^{-19}$ J

$= 2.53 \times 10^{-14}$ J

Now, 1 curie of C^{14} means decay of 3.70×10^{10} dps

Thus, energy produced during decay of 1 curie mass of C^{14}

$= 3.70 \times 10^{10} \times 2.53 \times 10^{-14}$ J s^{-1}

$= 9.36 \times 10^{-4}$ J

$\therefore$ Energy produced during 1 hr

$= 9.36 \times 10^{-4} \times 60 \times 60 = \mathbf{3.37\ J}$

6. Total energy change during reaction $= 17.25$ MeV

Energy = mass defect × 931

Now, $\Delta E = \Delta m \times 931$

$\therefore$ $\Delta m = \dfrac{\Delta E}{931} = \dfrac{17.25}{931} = 0.0185$ amu

$= \mathbf{0.0185\ amu = 3.07 \times 10^{-26}\ g}$

7. Mass decay, Δm per molecule of LiH

$= m(^6_3\text{Li}\ ^2_1\text{H}) - 2 \times m_2\text{He}^4$

$= (6.01512 + 2.01410) - 2 \times 4.0026$

$= 0.02402$ amu

Thus, energy produced during this mass decay

$= \Delta m \times 931.478$

$= 0.02402 \times 931.478 = 22.35$ MeV

$= 22.35 \times 10^6$ eV

$= 22.35 \times 10^6 \times 1.602 \times 10^{-19}$ J

$= 3.58 \times 10^{-12}$ J

Now energy produced for 1 mole of LiH

$= 3.58 \times 10^{-12} \times 6.023 \times 10^{23}$

$= 21.55 \times 10^{11}$ J mol^{-1}

$\therefore$ Energy produced for 1 g of

$^6\text{Li}\ ^2\text{H} = \dfrac{21.55 \times 10^{11}}{8}$ J g^{-1} per day

$\therefore$ Energy produced for 1 g of $^6\text{Li}\ ^2\text{H}$ per sec

$= \dfrac{21.55 \times 10^{11}}{8 \times 24 \times 3600}$ J g^{-1}s^{-1}

$= 3.12 \times 10^6$ wg^{-1} (Js^{-1} = 1 w)

$= \mathbf{3.12\ Mwg^{-1}}$

8. α-particle has $2P$ and $2N$

$\therefore$ Mass of $2P + 2N$ in α-particle

$$= 2\times 1.0073 + 2\times 1.0087 = 4.032\,\text{amu}$$

Actual mass of α-particle (given) $= 4.0028\,\text{amu}$

$\therefore$ Mass defect $= 4.032 - 4.0028 = \mathbf{0.0292\ amu}$

Now, $\text{BE} = \text{Mass defect} \times 931$

$$= 0.0292 \times 931$$
$$= 27.1852\ \text{MeV}$$

$\therefore$ $\text{BE/nucleon} = \dfrac{27.1852}{4} = \mathbf{6.7963\ MeV}$

9. Emission of an α shows a loss in mass no. by 4 units and loss in at. no. by 2 units.

Emission of a β shows a gain in at. no. by one unit; mass no. remains same.

Thus, for change

$$\underset{\text{II group}}{{}_{88}\text{Ra}^{226}} \xrightarrow{-_2\text{He}^4} \underset{\text{zero group}}{{}_{86}\text{Rn}^{222}} \xrightarrow{-_2\text{He}^4} \underset{\text{VI group}}{{}_{84}\text{Ra}A^{218}} \xrightarrow{-_{-1}e^0}$$

$$\underset{\text{VII group}}{{}_{85}\text{Ra}B^{218}} \xrightarrow{-_2\text{He}^4} \underset{\text{V group}}{{}_{83}\text{Ra}C^{214}}$$

At. no. of $\text{Ra}C = 83$

Mass no. of $\text{Ra}C = 214$

Group of element RaC is V from configuration 2, 8, 18, 32, 18, 5.

The no. of electrons in outer shell of an element suggest for its group.

10. (a) Let x α and y β-particles be given out during the change.

$\therefore$ ${}_{92}\text{U}^{238} \longrightarrow {}_{82}\text{Pb}^{206} + x\,{}_2\text{He}^4 + y\,{}_{-1}e^0$

Equating mass no. on both sides,

$\therefore$ $238 = 206 + 4x + y \times 0$

$$x = 8$$

Equating atomic no. on both sides

$$92 = 82 + 2x + y(-1) = 82 + 2\times 8 + y(-1)$$

$\therefore$ $\mathbf{y = 6}$

$\therefore$ No. of α-particles $= \mathbf{8}$

No. of β-particles $= \mathbf{6}$

(b) ${}_{90}\text{Th}^{234} \longrightarrow 7\,{}_2\text{He}^4 + 6\,{}_{-1}e^0 + {}_Z A^m$

Equating atomic number

$$90 = 14 + 6\times(-1) + Z$$

$\therefore$ $Z = 82$

Equating mass number

$$234 = 28 + m$$

$\therefore$ $m = 206$

Thus, the element with atomic number 82 and mass number 206 is ${}_{82}\text{Pb}^{206}$.

11. (a) ${}_{92}\text{U}^{235} \longrightarrow {}_{90}\text{Th}^{231} + {}_2\text{He}^4$

$\because$ Elements 89 and 90 to 103 are in III gp. known as actinides.

$\therefore$ **Th is in III gp.**

(b) ${}_{91}X^{231}$ is also in **III gp.**

(c) ${}_{89}\text{Ac}^{227}$ is also in **III gp.**

(d) ${}_{88}\text{Ra}^{227}$ is in **II gp.**

12. ${}_{92}X^{238} \longrightarrow {}_AX^m + {}_2\text{He}^4$

Equating mass no. on both sides

$$238 = m + 4$$

$\therefore$ $m = 234$

Equating at. no. on both sides

$$92 = A + 2$$

$\therefore$ $A = 90$

$\therefore$ X has at no. $= 90$

Mass no. $= 234$

$\therefore$ No. of neutrons $= 234 - 90 = \mathbf{144}$

13. ${}_{92}\text{U}^{235} + {}_0n^1 \longrightarrow {}_{56}\text{Ba}^{145} + {}_AX^m + 3\,{}_0n^1$

Equating mass no. on both sides

$$235 + 1 = 145 + m + 3\times 1$$

$\therefore$ $m = 88$

Equating at. no. on both sides

$$92 + 0 = 56 + A + 3\times 0$$

$\therefore$ $A = 36$

$\therefore$ Unknown product is ${}_{36}X^{88}$, *i.e.*, ${}_{36}\mathbf{Kr}^{88}$.

14. We have $t = \dfrac{2.303}{\lambda}\log\dfrac{N_0}{N}$

For 99.9% decay $N_0 = 100$

$$N = 100 - 99.9 = 0.1$$

$\therefore$ $t_{99.9\%} = \dfrac{2.303}{\lambda}\log\dfrac{100}{0.1}$

$$t_{99.9\%} = \frac{2.303}{\lambda}\times 3 \qquad \text{...(1)}$$

For 50% decay $N_0 = 100$; $N = 50$

$\therefore$ $t_{50\%} = \dfrac{2.303}{\lambda}\log\dfrac{100}{50} = \dfrac{2.303}{\lambda}\times 0.3010$ ...(2)

By Eqs. (1) and (2) $t_{99.9\%} = t_{50\%} \times \mathbf{10}$

15. For half life, $t = t_{1/2}$ then $N = N_0/2$

$\because$ $t = \dfrac{2.303}{\lambda}\log_{10}\dfrac{N_0}{N}$

or $t_{1/2} = \dfrac{2.303}{\lambda}\log_{10}\dfrac{N_0}{N_0/2} = \dfrac{2.303}{\lambda}\log 2$

$$= \frac{2.303}{\lambda}\times 0.3010$$

$$t_{1/2} = \frac{\mathbf{0.693}}{\lambda}$$

16. (a) ${}_{79}\text{Au}^{198} \longrightarrow {}_{80}\text{Hg}^{198} + {}_{-1}e^0$

(b) $t_{1/2} = 65\ \text{hr}$

$$T = 260\ \text{hr}$$

$\because$ $T = t_{1/2} \times n$

$\therefore$ No. of halves $(n) = \dfrac{260}{65} = 4$

Now Au left undecayed $(N) = \dfrac{N_0}{2^4} = \dfrac{1}{2^4} = \dfrac{1}{16}\,\text{g}$

$\therefore$ Au decayed $= \dfrac{15}{16}\,\text{g}$

$\because$ 198 g Au gives 198 g Hg

$\therefore$ 15/16 g Au gives **15/16 g Hg**

17. $r_1 = \lambda \cdot N_1, \quad r_2 = \lambda \cdot N_2$

$$\because \quad \frac{r_1}{r_2} = \frac{N_1}{N_2} = \frac{3.02 \times 10^6}{1.20 \times 10^6} = 2.52$$

Also,
$$10 = \frac{2.303}{\lambda} \log \frac{N_0}{N_1} \quad ...(1)$$

$$20 = \frac{2.303}{\lambda} \log \frac{N_0}{N_2} \quad ...(2)$$

By Eqs. (2) – (1)

$$\therefore \quad 20 - 10 = \frac{2.303}{\lambda}\left[\log \frac{N_0}{N_2} - \log \frac{N_0}{N_1}\right]$$

$$10 = \frac{2.303}{\lambda}\left[\log \frac{N_1}{N_2}\right] = \frac{2.303}{\lambda} \log 2.52$$

$$\therefore \quad \lambda = \mathbf{0.092\ min^{-1}}$$

$$t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{0.092} = \mathbf{7.50\ min}$$

$$T_{av} = \frac{1}{\lambda} = \frac{1}{0.092} = \mathbf{10.87\ min}$$

18.
$$t = \frac{2.303}{\lambda} \log_{10} \frac{A_0}{A} \qquad \left(t = 4; \lambda = \frac{0.693}{8}\right)$$

$$\therefore \quad \frac{A}{A_0} = 0.707 \quad \text{or} \quad 70.7\%$$

Now after 4 day $\frac{A}{A_0}$ in thyroid gland is 67.7%; Thus, unstable iodide present in thyroid $= \frac{67.7}{70.7} \times 100 = \mathbf{95.8\%}$.

Since, it is carried by stable iodide ion and thus same per cent of stable iodide is present in thyroid gland.

19.
$$t_{1/2} = 60\,\text{day}, \quad T = 180\,\text{day}$$

$$\therefore \quad n = \frac{T}{t_{1/2}} = \frac{180}{60} = 3$$

$\therefore$ % of radioactivity left after 3 halves

$$= \frac{N_0}{2^3} = \frac{100}{2^3} = \mathbf{12.5\%}$$

20. Given, $t_{1/2} = 28.1$ year, $N_0 = 10^{-6}$ g, $t = 20$ year, $N = ?$

$$\because \quad t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N}$$

$$\therefore \quad 20 = \frac{2.303 \times 28.1}{0.693} \log_{10} \frac{10^{-6}}{N}$$

$$\therefore \quad N = \mathbf{6.1 \times 10^{-7}\ g}$$

21. Given, $t_{1/2} = 30$ day, $N_0 = 10^{12}$ atoms

The disintegration in first second means initial rate of disintegration

$$\text{rate} = \frac{-dN}{dt} = \lambda . N_0 = \frac{0.693}{30 \times 24 \times 60 \times 60} \times 10^{12}$$

$$= \mathbf{2.674 \times 10^5}\ \textbf{disintegrations in first second}$$

22. Given, if $r_0 = 100; \quad r = 12.5; \quad t = 90$ day;

$$\frac{r_0}{r} = \frac{N_0}{N} = \frac{100}{12.5}$$

$$\because \quad \lambda = \frac{2.303}{t} \log_{10} \frac{N_0}{N} = \frac{2.303}{90} \log_{10} \frac{100}{12.5}$$

$$= \mathbf{2.31 \times 10^{-2}\ day^{-1}}$$

$$\therefore \quad t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{2.31 \times 10^{-2}} = \mathbf{30\ day}$$

Alternate solution
$$\frac{N_0}{N} = \frac{100}{12.5} = 8$$

$$\therefore \quad N = \frac{N_0}{8} = \frac{N_0}{2^3} = \frac{N_0}{2^n}$$

Now, No. of halves $(n) = 3$

$$\because \quad T = t_{1/2} \times n$$

$$90 = t_{1/2} \times 3$$

$$\therefore \quad t_{1/2} = \mathbf{30\ day}$$

23. Given, $r_0 = 50r$ where r is activity for safe working

Now,
$$t = \frac{2.303}{\lambda} \log_{10} \frac{r_0}{r} \qquad (\because r_0 \propto N_0 \text{ and } r \propto N)$$

$$\therefore \quad t = \frac{2.303 \times 30}{0.693} \log_{10} \frac{50r}{r} = \mathbf{169.38\ day}$$

24. We have
$$\lambda = \frac{2.303}{t} \log_{10} \frac{N_0}{N}$$

$$\lambda = \frac{0.693}{47.2} \sec^{-1}$$

$$t = 1 \times 60 \times 60 \sec$$

$$\therefore \quad \frac{0.693}{47.2} = \frac{2.303}{60 \times 60} \log_{10} \frac{N_0}{N}$$

$$\therefore \quad \frac{N}{N_0} = \mathbf{1.12 \times 10^{-23}}$$

25. Let the decay constant λ_P and λ_Q be $3a$ and $2a$ respectively.

$$t_{1/2} \text{ of } P = \frac{0.693}{3a}; \quad t_{1/2} \text{ of } Q = \frac{0.693}{2a};$$

at
$$T = 3 \times t_{1/2} \text{ of } P = \frac{3 \times 0.693}{3a} = \frac{0.693}{a}$$

$$\because \quad T = \frac{2.303}{\lambda} \log \frac{a}{a - x}$$

For P:
$$\frac{0.693}{a} = \frac{2.303}{3a} \log \frac{1}{n_P}$$

For Q:
$$\frac{0.693}{a} = \frac{2.303}{2a} \log \frac{1}{n_Q} = \frac{\log \frac{1}{n_P}}{\log \frac{1}{n_Q}} = \frac{3}{2}$$

or
$$\log \frac{1}{n_P} = \frac{3}{2} \log \frac{1}{n_Q}$$

$$\log \frac{1}{n_P} = \log \left(\frac{1}{n_Q}\right)^{3/2} \quad \text{or} \quad n_P = (n_Q)^{2/3}$$

if $n_P = 0.2$, then $n_Q = \mathbf{0.09}$.

26.
$$\underset{(r_t)}{\text{Rate at time } t} = \frac{1}{64} \times \underset{(r_0)}{\text{rate at } t = 0}$$

$$\therefore \quad \frac{r_0}{r_t} = 64$$

Since,
$$r_0 \propto N_0; \quad r_t \propto N_t$$

$$\therefore \quad \frac{r_0}{r_t} = \frac{N_0}{N_t} = 64 \quad \text{or} \quad N_t = \frac{N_0}{64} = \frac{N_0}{2^6}$$

$\therefore$ No. of halves, *i.e.*, $n = 6$

$$\text{Time} = t_{1/2} \times n \qquad (\because t = 2\,\text{hr})$$

$$2 \times 60 \times 60 = t_{1/2} \times 6 \quad \text{or} \quad t_{1/2} = 1200 \sec$$

$$\therefore \quad \lambda = \frac{0.693}{1200} = \mathbf{5.775 \times 10^{-4}\ sec^{-1}}$$

27. $\because$ Rate $= \lambda \cdot N_0$

$\because$ 226 g Ra has atoms $= N_A$ (N_A is Avogadro's number)

$\therefore$ 1 g Ra has $= \frac{\text{Av. no.}}{226}$ atoms $= N_0$

$$11.6 \times 10^{17} = \frac{0.693}{1600} \times \frac{\text{Av. No.}}{226}$$

$\therefore$ Av. No. $= \mathbf{6.052 \times 10^{23}}$

28. $r_0 = 4750 \text{dpm}$ at $t = 0$

$r_t = 2700 \text{dpm}$, at $t = 5 \text{min}$

$\therefore$ $\frac{r_0}{r_t} = \frac{4750}{2700}$

Also, Rate $\propto$ No. of atoms

$\therefore$ $\frac{r_0}{r_t} = \frac{N_0}{N_t} = \frac{4750}{2700}$

$\therefore$ $t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N_t}$

$$5 = \frac{2.303}{\lambda} \log_{10} \frac{4750}{2700}$$

$\lambda = \mathbf{0.113\ minute^{-1}}$

$\therefore$ $t_{1/2} = \frac{0.693}{0.113} = \mathbf{6.13\ minute}$

29. Rate $= \lambda \cdot N$

$$= \frac{0.693 \times 6.023 \times 10^{23}}{2.44 \times 10^4 \times 239} = 7.157 \times 10^{16} \text{ dis./year}$$

$\therefore$ Loss in energy per year $= 5.24 \times 7.157 \times 10^{16}$ MeV

$= 5.24 \times 7.157 \times 10^{16} \times 10^6$ eV

$= 5.24 \times 7.157 \times 10^{16} \times 10^6 \times 1.602 \times 10^{-19}$ J

$= 5.24 \times 7.157 \times 10^{16} \times 10^6 \times 1.602 \times 10^{-19} \times 10^{-3}$ kJ

$= \mathbf{60.08\ kJ}$

30. $N_0 = \frac{1}{226}$ or $N = \frac{1}{226} - x$

where x is the mole of Ra disintegrated in time $t = 1590$ year

$\because$ $\lambda = \frac{2.303}{t} \log_{10} \frac{N_0}{N}$

$$\frac{0.693}{1590} = \frac{2.303}{1590} \log_{10} \frac{1/226}{\frac{1}{226} - x} = \frac{2.303}{1590} \log_{10} \frac{1}{(1 - 226x)}$$

$\therefore$ $x = 2.21 \times 10^{-3}$

$\because$ 1 atom of Ra on decay gives 4 atoms of He

Mole of He formed $= 4 \times 2.21 \times 10^{-3}$

Now for pressure, $PV = nRT$

$$P \times \frac{5}{1000} = 4 \times 2.21 \times 10^{-3} \times 0.0821 \times 300$$

$\therefore$ $P = \mathbf{43.54\ atm}$

31. $t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N}$

$\because$ $\frac{N_0}{N}$ is ratio and thus taken in atoms, mass or mole as desired

$\therefore$ $365 \times 24 \times 60 \times 60 = \frac{2.303}{1.58 \times 10^{-10}} \log_{10} \frac{1}{N}$

$\therefore$ $N = 0.995 \text{g}$

$\therefore$ Mass of Th^{232} undergoing decay

$= N_0 - N = 1 - 0.995 \text{g} = 0.005 \text{g}$

$\because$ 232 g Th on decay produces 6.023×10^{23} α-particles

$\therefore$ 0.005 g Th on decay produces

$= \frac{6.023 \times 10^{23} \times 0.005}{232}$ α-particles

$= \mathbf{1.298 \times 10^{19}}$ **α-particles**

32. The decay equation is,

$${}_Z X^A \longrightarrow {}_{Z-2}Y^{A-4} + {}_2\text{He}^4$$

$t_{1/2} = 10 \text{day}$ $N_0 = 1 \text{g-atom}$

$T = 20 \text{day}$

$\therefore$ $n = 2$ $(\because n = T / t_{1/2})$

$\therefore$ Amount of X left after 2 halves $= \frac{1}{2^2}$ g-atom

$\therefore$ Amount of X used in 2 halves $= 1 - \frac{1}{2^2} = \frac{3}{4}$ g-atom

$\because$ 1 g-atom of X gives 1 mole of He or 22400 mL He

$\therefore$ $\frac{3}{4}$ g-atom of X gives $\frac{3}{4}$ mole of He or $\frac{22400 \times 3}{4}$ mL He

$= \mathbf{16800\ mL\ He}$

33. $N_0 = 10 \text{g-atoms} = 10 \times 6.023 \times 10^{23} = 6.023 \times 10^{24}$ atoms

Volume of He collected $= 11.2 \text{ mL} = \frac{11.2}{22400}$ mole

$= 5 \times 10^{-4}$ mole

$= 5 \times 10^{-4} \times 6.023 \times 10^{23}$ atoms

$= 3.01 \times 10^{20}$ atoms

The helium atoms formed = No. of atoms of radioactive substance decayed

$\therefore$ No. of atoms of radioactive substance left

$= (N) = 6.023 \times 10^{24} - 3.01 \times 10^{20} = 6.0227 \times 10^{24}$ atoms

$\because$ $\lambda = \frac{2.303}{t} \log_{10} \frac{N_0}{N}$

$$\lambda = \frac{2.303}{1} \log_{10} \frac{6.023 \times 10^{24}}{6.0227 \times 10^{24}}$$

$\lambda = 4.982 \times 10^{-5} \text{ hr}^{-1}$

$\therefore$ $t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{4.982 \times 10^{-5}} = \mathbf{13910.29\ hour}$

Note : N_0 and N can be put directly in terms of mole or g-atoms but in this problem it will lead to a problem in solving log values.

Alternate solution

Rate $= \lambda \cdot N$

mole formed/hr = rate $= \frac{11.2}{22400}$

$\therefore$ $\frac{11.2}{22400} = \frac{0.693}{t_{1/2}} \times 10$

$\therefore$ $t_{1/2} = \frac{0.693 \times 10 \times 22400}{11.2} = \mathbf{13860\ hour}$

34. $_ZA^m \longrightarrow {}_{Z-6}B^{m-12} + 3\ {}_2\text{He}^4$

Given, Mass of $A = m g$

$\therefore$ Mole of A $(N_0) = 1$ mole

Also, $t = 20$ day; $t_{1/2} = 10$ day

$\therefore$ $n = 2$ $(\because\ t = t_{1/2} \times n)$

$\therefore$ $_ZA^m$ left in 2 halves $= \frac{1}{2^2}$ mole $= \frac{1}{4}$ mol

$\therefore$ $_ZA^m$ decayed in 2 halves $= 1 - \frac{1}{4} = \frac{3}{4}$ mol

$\therefore$ He formed $= 3 \times \frac{3}{4}$ mole $= \frac{9}{4}$ mol

$(\because$ decay of 1 mole gives 3 mole He)

$\therefore$ Volume of He at STP $= \frac{22.4 \times 9}{4} =$ **50.4 litre**

35. $_{88}\text{Ra}^{226} \longrightarrow {}_{86}\text{Rn}^{222} + {}_2\text{He}^4$

$N_0 = 1$ g-atom, $t_{1/2}$ Ra $= 1600$ year, $t = 800$ year

Now, $t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N}$

$800 = \frac{2.303 \times 1600}{0.693} \log_{10} \frac{1}{N}$

$\therefore$ $N = 0.707$ g-atom

$\therefore$ Amount of Ra decayed $= 1 - 0.707 = 0.293$ g-atom

$\therefore$ Rn formed $= 0.293$ mol

and Mole of He formed $= 0.293$ mol

Total mole of gases $= 0.293 + 0.293 = 0.586$

$\because$ $PV = nRT$

$\therefore$ Total pressure of He and Rn is,

$P = \frac{0.586}{5} \times 0.0821 \times 300 =$ **2.887 atm**

$\therefore$ $P'_{\text{He}} = P \times$ mole fraction of He $= 2.887 \times \frac{1}{2}$

= 1.443 atm

36. $r_0 = 14$ dpm, $r = 7$ dpm

$\therefore$ $\frac{r_0}{r} = 2$

Also, Rate at any time $\propto$ no. of atoms

$\therefore$ $\frac{r_0}{r} = \frac{N_0}{N} = 2$

Now, $t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N} = \frac{2.303 \times 5770}{0.693} \log_{10} 2$

t = 5770 year

37. 1 curie $= 3.7 \times 10^{10}$ disintegration sec^{-1}

i.e., Rate $= 3.7 \times 10^{10}$ dps

Now, Rate $= \lambda \times$ no. of atoms

$3.7 \times 10^{10} = \frac{0.693}{5730 \times 365 \times 24 \times 60 \times 60} \times$ no. of atoms

$\therefore$ No. of atoms $= 9.65 \times 10^{21}$

Now, 6.023×10^{23} atoms of $\text{C}^{14} = 14$ g

$\therefore$ 9.65×10^{21} atoms of $\text{C}^{14} = \frac{14 \times 9.65 \times 10^{21}}{6.023 \times 10^{23}} =$ **0.2243 g**

38. Rate of decay of 10 mL gas $= 10^4$ dis/min

$= \frac{10^4}{60}$ dis/sec or dps

Thus, rate of decay of 60 litre gas

$= \frac{10^4 \times 60 \times 1000}{60 \times 10} = 10^6$ dps

Now, $\because$ 3.7×10^{10} dps is shown by 1 curie of C^{14}

$\therefore$ 10^6 dps is shown by $\frac{10^6}{3\ 7 \times 10^{10}}$ curie of C^{14}

$\therefore$ milli curie of carbon $= \frac{10^6}{3.7 \times 10^{10}} \times 10^3$

$(\because\ 10^3$ millicurie $= 1$ curie)

= 0.027 mCi

39. $N_0 = 0.1$ g-atom

$t = 10$ day and $t_{1/2} = 5$ day

$\lambda = \frac{2.303}{t} \log_{10} \frac{N_0}{N}$

$\frac{0.693}{5} = \frac{2.303}{10} \log_{10} \frac{0.1}{N}$

$\therefore$ N_{10}, *i.e.*, species left after 10 day $= 0.0250$ g-atom

Similarly if $t = 11$ day

$\frac{0.693}{5} = \frac{2.303}{11} \log_{10} \frac{0.1}{N}$

$\therefore$ N_{11}, *i.e.*, species left after 11 day $= 0.0218$ g-atom

$\therefore$ Species decayed in 11th day $= N_{10} - N_{11}$

$= 0.0250 - 0.0218 = 3.2 \times 10^{-3}$ g-atoms

$= 3.2 \times 6.023 \times 10^{23} \times 10^{-3}$ atoms

= 1.93 × 10^{21} atoms

40. $t_{1/2} = 138.4$ day, $t = 69.2$ day

$\therefore$ No. of halves $n = \frac{t}{t_{1/2}} = \frac{69.2}{138.4} = \frac{1}{2}$

$\therefore$ Po left after $\frac{1}{2}$ halves $= \frac{1}{(2)^{1/2}}$ g $= 0.707$ g

$\therefore$ Po used in $\frac{1}{2}$ halves $= 1 - 0.707 = 0.293$ g

Now, $_{84}\text{Po}^{210} \longrightarrow {}_{82}\text{Pb}^{206} + {}_2\text{He}^4$

$\because$ 210 g Po on decay will produce $= 4$ g He

$\therefore$ 0.293 g Po on decay will produce $= \frac{4 \times 0.293}{210}$

$= 5.581 \times 10^{-3}$ g He

$\therefore$ Volume of He at STP $= \frac{5.581 \times 10^{-3} \times 22400}{4}$

= 31.25 mL = 31.25 cm^3

Also Po^{210} in 1 g $\text{PoO}_2 = \frac{210}{242} = 0.868$

$\therefore$ Po^{210} left after 1/2 halves

$= \left[\frac{210}{242}\right] \times \frac{1}{2^{1/2}} = 0.614$ g

$\therefore$ Po^{210} used after 1/2 halves

$= 0.868 - 0.614 = 0.254$ g

$\therefore$ Mass of He formed $= \dfrac{4\times 0.254}{210} = 4.84\times 10^{-3}$ g

$\therefore$ Volume of He at STP $= \dfrac{4.84\times 10^{-3}\times 22400}{4}$

$$= \mathbf{27.104\ cm^3}$$

41. (a) 1 m mole $\equiv 150$ m curie

$\therefore$ 1 m curie $\equiv \dfrac{1}{150}$ m mole

Now, concentration $= \dfrac{\text{m mole}}{\text{V in mL}} = \dfrac{1}{150\times 2}$

$$= \mathbf{3.33\times 10^{-2}\ M}$$

(b) 1 curie $= 3.7\times 10^{10}$ dps $= 3.7\times 10^{10}\times 60$ dpm

$= 3.7\times 10^{10}\times 60\times \dfrac{80}{100}$ counting per minute

$\therefore$ 1 millicurie $= 3.7\times 10^{10}\times 60\times \dfrac{80}{100}\times 10^{-3}$ cpm

$\therefore$ cpm/mL $= 3.7\times 10^{10}\times 60\times \dfrac{80}{100}\times \dfrac{10^{-3}}{2}$

$$= \mathbf{88.8\times 10^{7}\ cpm/mL}$$

42. Given, $\dfrac{N_{C^{14}}}{N_{C^{12}}} = \dfrac{1}{16}\dfrac{N_{0C^{14}}}{N_{0C^{12}}}$

Since, only C^{14} undergoes decay

$\therefore$ $N_{C^{12}} = N_{0C^{12}}$

or $\dfrac{N_{0C^{14}}}{N_{C^{14}}} = \dfrac{16}{1}$

$\therefore$ $t = \dfrac{2.303}{\lambda}\log_{10}\dfrac{16}{1} = \dfrac{2.303}{0.693}\times 5577\log_{10}2^4$

$t = 5577\times 4 = \mathbf{22308\ year}$

43. $t_{1/2}$ of $C^{14} = 5760$ year

$\therefore$ $\lambda = \dfrac{0.693}{5760}\ \text{yr}^{-1}$

$N_{0C^{14}} = 1\%$

$N_{C^{14}} = 0.25\%$

$\therefore$ $t = \dfrac{2.303}{\lambda}\log_{10}\dfrac{N_0}{N}$

$= \dfrac{2.303\times 5760}{0.693}\log_{10}\dfrac{1}{0.25} = \dfrac{2.303\times 5760}{0.693}\log_{10}2^2$

$t = \mathbf{11520\ year}$

Note : Always cancel $2.303\log_{10}2$ with 0.693. Otherwise the answer will be approximate.

44. $_{92}U^{238} \longrightarrow {}_{82}Pb^{206} + 8\,{}_2He^4 + 6\,{}_{-1}e^0$

Pb present $= \dfrac{20.6}{206} = 0.1$ g-atom $=$ U decayed

U present $= \dfrac{23.8}{238} = 0.1$ g-atom

Thus, $N = 0.1$ g-atom

$N_0 =$ U present $+$ U decayed

$= 0.1 + 0.1 = 0.2$ g-atom

Now, $t = \dfrac{2.303}{\lambda}\log_{10}\dfrac{N_0}{N}$

$t = \dfrac{2.303\times 4.5\times 10^9}{0.693}\log_{10}\dfrac{0.2}{0.1}$

$t = \mathbf{4.5\times 10^{9}\ year}$

45. (a) Let, Time $= t$ year

$_{92}U^{238} = 1.667\,\text{g} = \dfrac{1.667}{238}$ mole

$_{82}Pb^{206} = 0.277\,\text{g} = \dfrac{0.277}{206}$ mole

$\because$ All the lead has come from decay of U. Therefore,

Pb formed $= \dfrac{0.277}{206}$ mol

$\therefore$ U decayed $= \dfrac{0.277}{206}$ mol

$\therefore$ Total mole of uranium before decay, *i.e.*,

$N_0 = \dfrac{1.667}{238} + \dfrac{0.277}{206}$

Also, N for $U^{238} = \dfrac{1.667}{238}$

$\because$ For U^{238} $t = \dfrac{2.303}{\lambda}\log_{10}\dfrac{N_0}{N}$

$$= \frac{2.303\times 4.51\times 10^9}{0.693}\log_{10}\frac{\frac{1.667}{238}+\frac{0.277}{206}}{\frac{1.667}{238}}$$

$t = \mathbf{1.143\times 10^{9}\ year}$

[Ans. (b) 7.097×10^{8} year]

46. Uranium present $= \dfrac{50}{100}\,\text{g} = \dfrac{0.50}{238}$ g-atom

$= 2.10\times 10^{-3}$ g-atom

Pb present $= \dfrac{2.425}{100}\,\text{g} = \dfrac{2.425}{100\times 206}$ g-atom

Pb formed from uranium decay $= \dfrac{2.425\times 93}{100\times 206\times 100}$

$= 0.109\times 10^{-3}$ g-atom

$N = 2.10\times 10^{-3}$ g-atom

$N_0 = (2.10 + 0.109)\times 10^{-3} = 2.209\times 10^{-3}$ g-atom

Now $t = \dfrac{2.303}{\lambda}\log_{10}\dfrac{N_0}{N}$

$= \dfrac{2.303}{1.52\times 10^{-10}}\log_{10}\dfrac{2.209\times 10^{-3}}{2.10\times 10^{-3}}$

$t = \mathbf{3.3\times 10^{8}\ years}$

47. In nature $\dfrac{N_{U^{238}}}{N_{U^{235}}} = \dfrac{140}{1}$ at $t = t$

At the time of earth formation,

$\dfrac{N_{0U^{238}}}{N_{0U^{235}}} = \dfrac{1}{1}$ at $t = 0$

$\therefore$ $\dfrac{N_{0U^{238}}}{N_{0U^{235}}}\times\dfrac{N_{U^{235}}}{N_{U^{238}}} = \dfrac{1}{140}$

$\therefore$ For U^{238}: $\dfrac{N_{0U^{238}}}{N_{U^{238}}} = e^{\lambda_{238}\cdot t}$ ...(1)

For U^{235}: $$\frac{N_{0U^{235}}}{N_{U^{235}}} = e^{\lambda^{235}.t} \quad ...(2)$$

$\therefore$ $$\frac{N_{0U^{238}}}{N_{0U^{235}}} \times \frac{N_{U^{235}}}{N_{U^{238}}} = e^{(\lambda^{238} - \lambda^{235})t}$$

or $$\frac{1}{140} = e^{(\lambda^{238} - \lambda^{235})t}$$

$$(\lambda^{238} - \lambda^{235})t = \log_e 1 - \log_e 140$$

or $$\left[\frac{0.693}{4.5 \times 10^9} - \frac{0.693}{7.13 \times 10^8}\right] t = -2.303 \log_{10} 140$$

$$= -4.9416$$

$\therefore$ $$t = \mathbf{6.04 \times 10^9 \text{ year}}$$

48. $${}_{90}\text{Th}^{232} \longrightarrow {}_{82}\text{Pb}^{208} + 6\ {}_2\text{He}^4 + 4\ {}_{-1}e^0$$

$\because$ 6×22400 mL He is formed by 232 g Th decay

$\therefore$ 8×10^{-5} mL He is formed by

$$= \frac{232 \times 8 \times 10^{-5}}{6 \times 22400} \text{ g Th decay}$$

$$= 1.38 \times 10^{-7} \text{ g Th decay}$$

At $t = t$, sample has Th $= 5 \times 10^{-7}$ g $\propto N$

At $t = 0$, sample had Th $= 5 \times 10^{-7} + 1.38 \times 10^{-7} \propto N_0$

$$= 6.38 \times 10^{-7} \text{ g}$$

For Th decay $\because$ $$t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N}$$

$$= \frac{2.303 \times 1.39 \times 10^{10}}{0.693} \log_{10} \frac{6.38 \times 10^{-7}}{5 \times 10^{-7}}$$

$$= \mathbf{4.89 \times 10^9 \text{ year}}$$

49. The specific activity of a radioactive nucleus is its activity of disintegration rate per g of specimen.

1 g of ^{31}P has $\frac{N}{31}$ atoms of ^{31}P

The sample contains 10^6 part of it as ^{32}P

Thus, ^{32}P in 1 g specimen

$$= \frac{N}{31 \times 10^6} \text{ atoms of } ^{32}\text{P}$$

Thus, $$\text{rate} = \lambda \cdot N$$

$$= \frac{0.693}{14.3 \times 24 \times 60 \times 60} \times \frac{N}{31 \times 10^6}$$

$$= \frac{0.693 \times 6.023 \times 10^{23}}{14.3 \times 24 \times 60 \times 60 \times 31 \times 10^6}$$

Rate $= 1.09 \times 10^{10}$ dps per g specimen

or specific activity $= 1.09 \times 10^{10}$ dps per g

$$= \frac{1.09 \times 10^{10}}{3.7 \times 10^{10}} \text{ curie per g}$$

$$= \mathbf{0.295 \text{ Ci per g}}$$

50. Given,

Specific activity of sample $= 6 \times 10^9$ dps per g of mixture

Let the masses of Pu^{239} and Pu^{240} are a and b g respectively, then

$$a + b = 1 \quad ...(1)$$

For Pu^{239}: $$r_1 = \lambda \cdot N_1$$

$$r_1 = \frac{0.693 \times 6.023 \times 10^{23} \times a}{2.44 \times 10^4 \times 365 \times 24 \times 60 \times 60 \times 239} \text{ dps g}^{-1}$$

$$= 2.77 \times 10^9 \times a \text{ dps g}^{-1}$$

For Pu^{240}: $$r_1 = \frac{0.693 \times 6.023 \times 10^{23} \times b}{6.58 \times 10^3 \times 365 \times 24 \times 60 \times 60 \times 240}$$

$$= 8.38 \times 10^9 \times b \text{ dps g}^{-1}$$

$\therefore$ $$2.27 \times 10^9 \times a + 8.38 \times 10^9 \times b = 6 \times 10^9$$

or $$2.27a + 8.38b = 6 \quad ...(2)$$

By Eqs. (1) and (2)

$a = \mathbf{0.3895}$ or **38.95%**

$b = \mathbf{0.6105}$ or **61.05%**

51. No. of α-particles or He formed $= 2.24 \times 10^{13}$ min^{-1}

$\therefore$ No. of He particles formed in 420 day

$$= 2.24 \times 10^{13} \times 420 \times 24 \times 60 = 1.355 \times 10^{19}$$

Also at 27° C and 750 mm of P, He $= 0.5$ mL

From $$PV = nRT$$

$$\frac{750}{760} \times \frac{0.5}{1000} = n \times 0.0821 \times 300$$

$\therefore$ $$n = 2.0 \times 10^{-5} \text{ mole}$$

Given, 2.0×10^{-5} mole He $= 1.355 \times 10^{19}$ particles He

$\therefore$ 1 mole He $= \frac{1.355 \times 10^{19}}{2.0 \times 10^{-5}} = 6.775 \times 10^{23}$ particles

Therefore, Avogadro's no. $= \mathbf{6.775 \times 10^{23}}$ **particle / mol**

52. To carry out experiment,

Rate of β-emission required $= 346$ particle min^{-1}

$\therefore$ $$\text{Rate} = \lambda . N$$

or desired no. of atoms to carry out experiment after 6.909 hr

$$= \frac{\text{rate}}{\lambda} = \frac{346 \times 66.6 \times 60}{0.693} = 1.995 \times 10^6 \text{ atoms}$$

Now, when $N = 1.995 \times 10^6$ atoms of Mo at $t = 6.909$ hrs

N_0 can be evaluated as

$$t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N}$$

$$6.909 = \frac{2.303 \times 66.6}{0.693} \log_{10} \frac{N_0}{N}$$

$\therefore$ $$\frac{N_0}{N} = 1.0745$$

$\therefore$ $$N_0 = N \times 1.0745 = 1.995 \times 10^6 \times 1.0745$$

$$= 2.1436 \times 10^6 \text{ atoms of Mo}^{99}$$

$\therefore$ Mass of Mo required to carry out experiment in 6.909 hour

$$= \frac{2.1436 \times 10^6 \times 99}{6.023 \times 10^{23}} \text{ g} = \mathbf{3.56 \times 10^{-16} \text{ g}}$$

53. Let activity of X^{A_1} and X^{A_2} are a and b curie respectively at $t = 0$

$\therefore$ $$a + b = 1 \text{ curie} \quad ...(1)$$

Now, Rate $\propto$ No. of atoms

$\therefore$ For X^{A_1} $t = \frac{2.303}{\lambda}\log_{10}\frac{N_0}{N} = \frac{2.303}{\lambda}\log_{10}\frac{r_0}{r}$

$$20 = \frac{2.303\times 14}{0.693}\log_{10}\frac{a}{r_1}$$

$\therefore$ $r_1 = 0.3716a$

For X^{A_2} $t = \frac{2.303}{\lambda}\log_{10}\frac{N_0}{N} = \frac{2.303}{\lambda}\log_{10}\frac{r_0}{r}$

$$20 = \frac{2.303\times 25}{0.693}\log_{10}\frac{b}{r_2}$$

$$r_2 = 0.5744b$$

Given activity after 20 day $= \frac{1}{2}$ curie

$$0.3716a + 0.5744b = \frac{1}{2}$$

or $0.7432a + 1.1488b = 1$ ...(2)

By Eqs. (1) and (2)

$$a = \mathbf{0.3669\ Ci} = 0.3669\times 3.7\times 10^{10}\ \text{dps}$$

$$b = \mathbf{0.6331\ Ci} = 0.6331\times 3.7\times 10^{10}\ \text{dps}$$

Now, $\text{Rate} = \lambda\cdot N$ $(\because a = 0.3669\,\text{curie})$

For X^{A_1} $0.3669\times 10^{10}\times 3.7 = \frac{0.693}{14\times 24\times 60\times 60}N_0^{A_1}$

For X^{A_2} $0.6331\times 10^{10}\times 3.7 = \frac{0.693}{25\times 24\times 60\times 60}N_0^{A_2}$

$\therefore$ $\frac{N_0^{A_1}}{N_0^{A_2}} = \mathbf{0.3245}$

54. $${}_{86}\text{Rn} \longrightarrow {}_{2}\text{He}^4 + {}_{84}X \qquad (\text{an } \alpha\text{-emitter})$$

$$\text{Rate} = \lambda\cdot N_0$$

$$3.7\times 10^{10} = 2\times 10^{-6}\times N_0$$

$\therefore$ N_0, *i.e.*, number of atoms of Rn at $(t = 0)$

$= 1.85\times 10^{16}$ atoms

(a) Rn left after 1 hr is calculated by

$$t = \frac{2.303}{\lambda}\log_{10}\frac{N_0}{N}$$

$$60\times 60 = \frac{2.303}{2\times 10^{-6}}\log_{10}\frac{N_0}{N}$$

$\therefore$ $\frac{N_0}{N} = 1.0072$

$\therefore$ $N = \frac{1.85\times 10^{16}}{1.0072} = 1.837\times 10^{16}$ atoms

$\therefore$ No. of α-particles formed = No. of Rn atoms decayed

$= 1.85\times 10^{16} - 1.837\times 10^{16} = 0.013\times 10^{16}$ atoms

$\therefore$ Energy $= 0.013\times 10^{16}\times 5.5 = 0.0715\times 10^{16}$ MeV

$= 0.0715\times 10^{22}$ eV

$= 0.0715\times 10^{22}\times 1.602\times 10^{-19}\ \text{J} = \mathbf{114.5\ J}$

(b) Rn left after $t = \frac{1}{\lambda}$

$$\frac{1}{\lambda} = \frac{2.303}{\lambda}\log_{10}\frac{N_0}{N}$$

$$\frac{N_0}{N} = 2.718$$

$\therefore$ $N = \frac{1.85\times 10^{16}}{2.718} = 0.6806\times 10^{16}$

$\therefore$ No. of α-particles formed

$= 1.85\times 10^{16} - 0.6806\times 10^{16}$

$= 1.1694\times 10^{16}$

$\therefore$ Energy $= 1.1694\times 10^{16}\times 5.5$

$= 6.4317\times 10^{16}$ MeV $= 6.4317\times 10^{16}\times 10^{6}$ eV

$= 6.4317\times 10^{22}\times 1.602\times 10^{-19}$ J

$= \mathbf{1.03\times 10^4\ J}$

55. $\text{Na}_3\text{PO}_4 = \frac{54.5\times 10^{-3}}{161.2}$ mol

$\therefore$ P atoms $= \frac{54.5\times 10^{-3}}{161.2}$ mol

$\therefore$ g-atoms P^{32} atoms $= \frac{54.5\times 10^{-3}}{161.2}\times\frac{15.6}{100} = 5.27\times 10^{-5}$

$\therefore$ Atoms of $\text{P}^{32} = 5.27\times 10^{-5}\times 6.023\times 10^{23}$

Now, Rate

$$= \lambda\cdot N = \frac{0.693}{14.3\times 24\times 60\times 60}\times 5.27\times 10^{-5}\times 6.023\times 10^{23}$$

Rate $= \mathbf{1.78\times 10^{13}\ dps}$

56. Total mass of ${}_{19}\text{K}^{40} = \frac{0.012}{100}\times\frac{0.35}{100}\times 75\times 10^3$ g

$= 3.15\times 10^{-2}$ g

$= \frac{3.15\times 10^{-2}\times 6.023\times 10^{23}}{40}$ atoms

$\therefore$ Rate $= \lambda\times$ No. of atoms

$$= \frac{0.693}{1.3\times 10^9\times 365\times 24\times 60}\times\frac{3.15\times 10^{-2}\times 6.023\times 10^{23}}{40}$$

Rate $= \mathbf{4.81\times 10^5\ dpm}$

57. (i) $\text{PuO}_2 = \frac{32\times 10^{-3}}{270}$ mol

$\therefore$ $\text{Pu} = \frac{32\times 10^{-3}}{270}$ mol

$\therefore$ Atoms (N) of Pu $= \frac{32\times 10^{-3}}{270}\times 6.023\times 10^{23}$

Now, $\text{rate} = \lambda\cdot N$

$\therefore$ $6.4\times 10^7 = \lambda\times\frac{32\times 10^{-3}\times 6.023\times 10^{23}}{270}$

$\therefore$ $\lambda = 8.97\times 10^{-13}\ \text{sec}^{-1}$

$\therefore$ $t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{8.97\times 10^{-13}} = \mathbf{7.73\times 10^{11}\ sec}$

(ii) Also, $\text{PuO}_2 = \frac{100\times 10^{-3}}{270}$ mol

$\therefore$ $\text{Pu} = \frac{100\times 10^{-3}}{270}$ mol

Now, $t = \frac{2.303}{\lambda}\log_{10}\frac{N_0}{N}$

$5000\times 365\times 24\times 60\times 60$

$$= \frac{2.303\times 7.73\times 10^{11}}{0.693}\log_{10}\frac{100\times 10^{-3}}{270\times N}$$

$$\therefore \quad N = \mathbf{3.21 \times 10^{-4}}$$

$$\therefore \quad \text{Pu left} = 3.21 \times 10^{-4} \text{ mol}$$

$$\therefore \quad PuO_2 \text{ left} = 3.21 \times 10^{-4} \text{ mol}$$

or $\text{Mass of } PuO_2 \text{ left} = 3.21 \times 10^{-4} \times 270\,g$

$$= \mathbf{86.67\ mg}$$

58. Let V mL blood is present in patient

(a) r_0 of $Na^{24} = 2 \times 10^3$ dps $= 2 \times 10^3 \times 60$ dpm

$$= 120 \times 10^3 \text{ dpm for } V \text{ mL blood}$$

r of $Na^{24} = 16$ dpm/mL at $t = 5$ hr $= 16 \times V$ dpm/V mL

$$\because \quad \frac{r_0}{r} = \frac{N_0}{N}$$

$$\therefore \quad \frac{N_0}{N} = \frac{120 \times 10^3}{16V}$$

$$\because \quad t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N}$$

$$5 = \frac{2.303 \times 15}{0.693} \log_{10} \frac{120 \times 10^3}{16V}$$

$$\therefore \quad V = \mathbf{5.95 \times 10^3\ mL}$$

(b) Activity of blood sample after 5 hr more, *i.e.*, $t = 10$ hr

$$t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N}$$

$$10 = \frac{2.303 \times 15}{0.693} \log_{10} \frac{120 \times 10^3}{A}$$

$$\therefore \quad A = 75.6 \times 10^3 \text{ dpm per } 5.95 \times 10^3 \text{ mL}$$

$$= \frac{75.6 \times 10^3}{5.95 \times 10^3} \text{ dpm per mL}$$

$$= 12.71 \text{ dpm per mL}$$

$$= \mathbf{0.2118\ dps\ per\ mL}$$

59. $$\frac{1}{2} mu^2 = 0.0327 \times 1.6 \times 10^{-19} \text{ J}$$

$$\therefore \quad u^2 = \frac{2 \times 0.0327 \times 1.6 \times 10^{-19}}{1.675 \times 10^{-27}} = 625 \times 10^4$$

$$\therefore \quad u = 2500 \text{ m/s}$$

Time taken to travel 100 metre $= \frac{100}{2500} = 0.04$ sec

Thus, $$\frac{dN}{N} = \lambda \cdot dt$$

$$\therefore \quad \frac{dN}{N} = \frac{0.693}{700} \times 0.04 = \mathbf{3.96 \times 10^{-5}}$$

60. (a) $$\begin{array}{lll} & A & \longrightarrow \text{Decay product} \\ t=0 & N_0 & \end{array}$$

Since, α is the number of A atoms produced at constant rate. Note that N is the number of nuclei left at time t then $-\frac{dN}{dt} = \lambda \cdot N$. Hence, rate of accumulation of radionuclide $\left(\frac{dN}{dt}\right)$;

$$\therefore \quad \frac{dN}{dt} = (\alpha - \lambda N) \quad \text{or} \quad \frac{dN}{(\alpha - \lambda N)} = dt$$

on integrating N_0 to N and time 0 to t.

$$\int_{N_0}^{N} \frac{dN}{(\alpha - \lambda N)} = \int_0^t dt$$

$$-\frac{1}{\lambda} \log_e [\alpha - \lambda N]_{N_0}^{N} = t$$

or $$(\alpha - \lambda N) = (\alpha - \lambda N_0) e^{-\lambda t}$$

$$\therefore \quad N = \frac{1}{\lambda}[\alpha - (\alpha - \lambda N_0)_e^{-\lambda t}]$$

(b) If $\alpha = 2\lambda N_0$, then

$$N = 2N_0 - N_0 e^{-\lambda t}$$

at $$t = t_{1/2} = 0.693/\lambda$$

$$N = 2N_0 - N_0 e^{\left(\frac{-\lambda \times 0.693}{\lambda}\right)}$$

$$= 2N_0 - N_0/2 = 3N_0/2$$

If $t \to \infty$, then $N = \lim_{t \to \infty} [2N_0 - N_0 e^{-\lambda t}]$

$$= 2N_0 - N_0 e^{-\infty} = \mathbf{2N_0} \qquad (e^{-\infty} \to 0)$$

61. The radio nuclide is formed at a constant rate q.

The decay rate $-\frac{dN}{dt} = \lambda \cdot N$

The rate of accumulation $\frac{dN}{dt} = (q - \lambda N)$

or $$\int_0^N \frac{dN}{(q - \lambda N)} = \int_0^t dt$$

or $$-\frac{1}{\lambda}[\log_e (q - \lambda N)]_0^N = t$$

or $$t = -\frac{1}{\lambda}[\log_e (q - \lambda N) - \log_e q]$$

or $$t = -\frac{1}{\lambda} \log_e \frac{q - \lambda N}{q} = \frac{1}{\lambda} \log_e \left[\frac{q}{q - \lambda N}\right]$$

$$\therefore \quad t = \frac{2.303}{\lambda} \log \left[\frac{q}{q - \lambda N}\right]$$

$$t = \frac{2.303}{\lambda} \log \left[\frac{q}{q - A}\right] \qquad (\because\ A = \lambda N)$$

$$= \frac{2.303 \times 14.3}{0.693} \log \frac{2.7 \times 10^9}{1.7 \times 10^9} = \mathbf{9.5\ day}$$

62. At radioactive equilibrium $A \longrightarrow B$

$$\frac{N_A}{N_B} = \frac{\lambda_B}{\lambda_A} = \frac{t_{1/2A}}{t_{1/2B}}$$

$$\therefore \quad \frac{3.1 \times 10^9}{1} = \frac{2 \times 10^{10}}{t_{1/2B}}$$

$$\therefore \quad t_{1/2B} = \mathbf{6.45\ year}$$

63. Isotope A:

Mole of $A = a$; $t_{1/2} = 12$ hr

(rapidly decaying has more mass)

$$[r_A]_0 = 1.0\mu\text{Ci} = 1.0 \times 10^{-6} \text{ Ci}$$

$$= 1.0 \times 10^{-6} \times 3.7 \times 10^{10} \text{ dps}$$

Isotope B:

Mole of $B = b$; $t_{1/2} = 16$ hr

$\therefore$ Given $\frac{a}{b} = 3$

For A: $[r_A]_0 = \lambda_A \times a \times N_A$ (N_A is Av. no.)

$$1.0 \times 10^{-6} \times 3.7 \times 10^{10} = \frac{0.693}{12 \times 60 \times 60} \times a \times 6.023 \times 10^{23}$$

$\therefore \quad a = 3.82\times10^{-15}$ mole of A

$\therefore \quad b = \frac{a}{3} = \frac{3.82\times10^{-15}}{3} = 1.28\times10^{-15}$ mole of B

For B:

$$[r_B]_0\, \lambda\cdot N_B = \frac{0.693}{16\times60\times60}\times1.28\times10^{-15}\times6.023\times10^{23}$$

$$[r_B]_0 = 9.275\times10^3 \text{ dps}$$

For A: $\quad t = \frac{2.303}{\lambda}\log\frac{r_0}{r} \qquad \left(\because \frac{r_0}{r} = \frac{N_0}{N}\right)$

$t = 2\times24$ hr; $\lambda = \frac{0.693}{12}$;

$r_0 = 1.0\times10^{-6}\times3.7\times10^{10} = 3.7\times10^4$ dps

$$2\times24 = \frac{2.303\times12}{0.693}\log\frac{3.7\times10^4}{r_A}$$

$\therefore \quad r_A = \mathbf{2315.40\ dps = 6.26\times10^{-8}\ Ci = 0.0626\,\mu Ci}$

For B: $\quad t = \frac{2.303}{\lambda}\log\frac{r_0}{r}$

$$2\times24 = \frac{2.303\times16}{0.693}\log\frac{9.275\times10^3}{r_B}$$

$\therefore \quad r_B = \mathbf{1.159\times10^3\ dps = 3.13\times10^{-8}\ Ci = 0.0313\,\mu Ci}$

Also, after 2 day $r_A = \lambda_A\cdot N_A$; $\quad r_B = \lambda_B\cdot N_B$

$\therefore \quad \frac{r_A}{r_B} = \frac{N_A}{N_B}\times\frac{\lambda_A}{\lambda_B}$

or $\quad \frac{N_A}{N_B} = \frac{r_A}{r_B}\times\frac{\lambda_B}{\lambda_A}$

$$= \frac{0.0626}{0.0313}\times\frac{0.693}{16}\times\frac{12}{0.693} = \mathbf{1.5}$$

64. $\therefore$ 18 g H_2O has $2N$ H atoms in it and $H^3 : H^1 :: 8\times10^{-18} : 1$

$\therefore$ 18 g H_2O has ${}_1H^3$ atoms $= 8\times10^{-18}\times6.023\times10^{23}\times2$

$\therefore$ 10 g H_2O has ${}_1H^3$ atoms

$$= \frac{8\times10^{-18}\times6.023\times10^{23}\times2\times10}{18}$$

i.e., $\quad N_0$ of ${}_1H^3 = 5.354\times10^6$ atoms

Now, $\quad t = \frac{2.303}{\lambda}\log_{10}\frac{N_0}{N}$

$$40 = \frac{2.303\times12.3}{0.693}\log_{10}\frac{5.354\times10^6}{N}$$

$\therefore \quad N = \mathbf{5.624\times10^5}$ **atoms.**

65. For successive α, β-emissions in parallel paths,

$$\lambda_{\text{average}} = \lambda_\alpha + \lambda_\beta = \frac{1}{1620} + \frac{1}{405} = \frac{5}{1620}\text{ year}^{-1}$$

Given at $t = t \quad N = \frac{1}{4}N_0 \qquad$ (since 3/4 part decays)

$\because \quad t = \frac{2.303}{\lambda_{\text{average}}}\log_{10}\frac{N_0}{N}$

$$t = \frac{2.303\times1620}{5}\log 4 = \mathbf{449.24\ year}$$

66. $r_{\text{nucleus}} = 1.3\times10^{-13}\times(A)^{1/3}$; $\qquad$ where A is mass number

$r_{U^{238}} = 1.3\times10^{-13}\times(238)^{1/3} = 8.06\times10^{-13}$ cm

$r_{He^4} = 1.3\times10^{-13}\times(4)^{1/3} = 2.06\times10^{-13}$ cm

$\therefore$ Total distance in between uranium and α-nuclei

$= 8.06\times10^{-13} + 2.06\times10^{-13} = 10.12\times10^{-13}$ cm

Now repulsion energy

$$= \frac{Q_1Q_2}{r} = \frac{92\times4.8\times10^{-10}\times2\times4.8\times10^{-10}}{10.12\times10^{-13}}\text{ erg}$$

$$= 418.9\times10^{-7}\text{ erg} = 418.9\times10^{-7}\times6.242\times10^{11}\text{ eV}$$

$$= \frac{418.9\times10^{-7}\times6.242\times10^{11}}{10^6}\text{ MeV} = \mathbf{26.14\ MeV}$$

67. At closest distance kinetic energy should be equal to repulsion energy

$$\frac{1}{2}mu^2 = \frac{1}{4\pi\varepsilon_0}\times\frac{2Ze^2}{r}$$

where repulsion term is given by

$$\frac{q_1\cdot q_2}{r} = \frac{2e.Z.e}{r} = \frac{2Ze^2}{r}$$

$\therefore \quad u^2 = \frac{Ze^2}{\pi\varepsilon_0 mr}$

$$u = \sqrt{\frac{29\times(1.6\times10^{-19})^2}{3.14\times8.85\times10^{-12}\times(4\times1.672\times10^{-27})\times10^{-13}}}$$

$u = \mathbf{6.3\times10^6\ m\ sec^{-1}}$

68. Total mass before reaction

$= 4.0026 + 10.0129 = 14.0155$ amu

Total mass after reaction

$= 13.0036 + 1.008 = 14.0116$ amu

$\therefore$ Mass decay during reaction

$= 14.0155 - 14.0116 = 0.0039$ amu

$\therefore$ Total energy given out

$= 0.0039\times931\text{MeV} = 3.6309\times10^6\text{eV}$

$= 3.6309\times10^6\times1.602\times10^{-19}$ J

$= \mathbf{5.816\times10^{-13}\ J}$

Now, $\quad E = h\nu$

$5.816\times10^{-13} = 6.625\times10^{-34}\,\nu$

$\therefore \quad$ Frequency, $\nu = \mathbf{8.77\times10^{20}\ Hz}$

and $\quad \nu = \frac{c}{\lambda}$

$\therefore \quad \lambda = \frac{c}{\nu} = \frac{3.0\times10^8}{8.77\times10^{20}} = \mathbf{3.4\times10^{-13}\ m}$

Note : Energy supplied to α-particle $= q\times\nu$

$= 2\times1.602\times10^{-19}\times3\times10^5$ J

$= \frac{2\times1.602\times10^{-19}\times3\times10^5}{1.602\times10^{-19}}\text{ eV} = \mathbf{6\times10^5\ eV}$

This energy is used up to over power the penetration of nucleus and imparting energy to C and H atoms, *i.e.*,

$1\times10^5\text{ eV} + 5\times10^5\text{ eV} = \mathbf{6\times10^5\ eV}$

69. $\quad {}_{+1}e^0 + {}_{-1}e^0 \longrightarrow 2\gamma$ $\quad$ (photons of same energy)

The mass of two electrons is converted into energy

The energy produced during emission of two photons

$= 2\times m_e\times c^2$

$$= 2\times 9.108\times 10^{-31}\times (3.0\times 10^{8})^{2}$$
$$= 163.9\times 10^{-15}\text{ J}$$

$\therefore$ Energy of one photon $= \frac{16.39\times 10^{-14}}{2} = 8.195\times 10^{-14}$ J

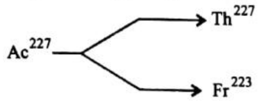
Now, $E = \frac{hc}{\lambda}$

or $8.195\times 10^{-14} = \frac{6.625\times 10^{-34}\times 3.0\times 10^{8}}{\lambda}$

or $\lambda = 2.425\times 10^{-12}\text{ m} = \mathbf{2.425\ pm}$

70. $\lambda_{\text{Ac}} = \frac{0.693}{22} = 3.15\times 10^{-2}\text{ year}^{-1}$

For the decay involving two parallel paths,



We have $\lambda_{\text{Ac}} = \lambda_{\text{Th path}} + \lambda_{\text{Fr path}}$

$\therefore$ $\lambda_{\text{Ac}}\times \text{Fraction of Th} = \lambda_{\text{Th path}}$ ...(1)

$\lambda_{\text{Ac}}\times \text{Fraction of Fr} = \lambda_{\text{Fr path}}$ ...(2)

or $\lambda_{\text{Ac}}\times (1-\text{Fraction of Th}) = \lambda_{\text{Fr path}}$ ...(3)

Thus, by Eqs. (1) and (3), we get

$$\lambda_{\text{Ac}} = \lambda_{\text{Th path}} + \lambda_{\text{Fr path}}$$

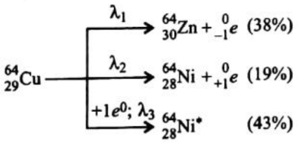
Thus, Fractional yield of Th $= \frac{\lambda_{\text{Th path}}}{\lambda_{\text{Ac path}}}$

or $\lambda_{\text{Th path}} = 3.15\times 10^{-2}\times \frac{2}{100} = \mathbf{6.30\times 10^{-4}\ yr^{-1}}$

Also, Fractional yield of Fr $= \frac{\lambda_{\text{Fr path}}}{\lambda_{\text{Ac path}}}$

$\therefore$ $\lambda_{\text{Fr}} = 3.15\times 10^{-2}\times \frac{98}{100} = \mathbf{3.087\times 10^{-2}\ yr^{-1}}$

71.



Given, $\lambda_{\text{av}} = \frac{0.693}{128}\text{ hr}^{-1}$

$\therefore$ $\lambda_1 + \lambda_2 + \lambda_3 = \lambda_{\text{av}} = \frac{0.693}{12.8}$

$= 5.41\times 10^{-2}\text{ hr}^{-1}$ ...(1)

Also for parallel path decay

$\lambda_1 = \text{Fractional yield of } {}^{64}_{30}\text{Zn}\times \lambda_{\text{av}}$

$\lambda_2 = \text{Fractional yield of } {}^{64}_{28}\text{Ni}\times \lambda_{\text{av}}$

$\lambda_3 = \text{Fractional yield of } {}^{64}_{28}\text{Ni}^{*}\times \lambda_{\text{av}}$

$\therefore$ $\frac{\lambda_1}{\lambda_2} = \frac{38}{19}$ ...(2)

and $\frac{\lambda_1}{\lambda_3} = \frac{38}{43}$ ...(3)

From Eqs. (1), (2) and (3) $\lambda_1 = 2.056\times 10^{-2}\text{ hr}^{-1}$;
$\lambda_2 = 1.028\times 10^{-2}\text{ hr}^{-1}$; $\lambda_3 = 2.327\times 10^{-2}\text{ hr}^{-1}$

$\therefore$ $t_{1/2}$ for β^{-}-emission $= \frac{0.693}{2.056\times 10^{-2}} = \mathbf{33.70\ hr}$

$t_{1/2}$ for β^{+}-emission $= \frac{0.693}{1.028\times 10^{-2}} = \mathbf{67.41\ hr}$

$t_{1/2}$ for electron capture $= \frac{0.693}{2.327\times 10^{-2}} = \mathbf{29.78\ hr}$

72. $\lambda_A = \lambda_1 + \lambda_2 = 1.5\times 10^{-5} + 5\times 10^{-6}$

$= 20\times 10^{-6}\text{ s}^{-1}$

Also, $2.303\log\frac{[A]_0}{[A]_t} = \lambda\times t$

$\therefore$ $2.303\log\frac{0.25}{[A]_t} = 20\times 10^{-6}\times 5\times 60\times 60$

$\therefore$ $[A]_t = 0.1744\,M$

$\therefore$ $[A]$ decomposed $= [A]_0 - [A]_t$

$= 0.25 - 0.1744 = 0.0756\,M$

Fraction of C formed $= \left[\frac{\lambda_2}{\lambda_1+\lambda_2}\right]\times [A]_{\text{decomposed}}\times \frac{2}{5}$

$= 0.0756\times \frac{5\times 10^{-6}}{20\times 10^{-6}}\times \frac{2}{5}$

$= \mathbf{7.56\times 10^{-3}}\ \boldsymbol{M}$

Note that 5 mole of A are used to give 2 mole of C.

73. Kinetic energy $= \frac{1}{2}mu^2$

$0.0327\times 1.602\times 10^{-19} = \frac{1}{2}\times 1.675\times 10^{-27}\times u^2$

($1\text{eV} = 1.602\times 10^{-19}$ J)

$\therefore$ $u = 2500.0\text{ m/sec} = 2.50\text{ km/sec}$

Thus, time taken to move 10 km $= \frac{10}{2.5} = 4.0$sec

Now, neutrons left (N) after 4.0 sec can be obtained by

$$\lambda = \frac{2.303}{t}\log\frac{N_0}{N}$$

$$\frac{0.693}{700} = \frac{2.303}{4}\log\frac{N_0}{N}$$

$$\frac{N_0}{N} = 1.004$$

$\therefore$ $N = 99.60\%$ $(N_0 = 100)$

$\therefore$ No. of neutrons decayed $= \mathbf{0.4\%}$ or $\mathbf{0.004}$

74. Fusion reaction is $2\,{}_1\text{H}^2 \longrightarrow {}_2\text{He}^4 + \text{energy}$

Mass defect $= 2\times$ mass of ${}_1\text{H}^2$ − mass of ${}_2\text{He}^4$

$= 2\times 2.0141 - 4.0026 = 0.0256\text{amu}$

$\therefore$ Energy liberated during fusion of 2 atoms of ${}_1\text{H}^2 = \Delta mc^2$

$= 0.0256\times 1.66\times 10^{-27}\times (2.998\times 10^{8})^{2}$

$= 3.8\times 10^{-12}$ J

$\therefore$ Energy liberated during fusion of $2N$ atoms of ${}_1\text{H}^2$ to give

N atoms (or 1 mole ${}_2\text{He}^4$) $= 3.8\times 10^{-12}\times 6.023\times 10^{23}$

$= \mathbf{2.3\times 10^{12}\ J}$

75.
$$\lambda_{\text{Pb}} = \frac{0.693}{10.6 \times 60} = 1.0896 \times 10^{-3}$$
$$\lambda_{\text{Bi}} = \frac{0.693}{60.5} = 11.45 \times 10^{-3}$$
$$t_{\max} = \frac{2.303}{\lambda_{\text{Bi}} - \lambda_{\text{Pb}}} \log_{10} \frac{\lambda_{\text{Bi}}}{\lambda_{\text{Pb}}}$$
$$= \frac{2.303}{10.3604 \times 10^{-3}} \log_{10} \frac{11.45 \times 10^{-3}}{1.0896 \times 10^{-3}}$$
$$= \mathbf{227.1\ minute}$$

76. **Isotopes:** 1. Atoms of same element having same at. no. but different mass no. are known as isotopes.

2. Nucleides and its decay product after one α and two β-particles are isotopes.

3. *e.g.*, ${}_1H^1$, ${}_1H^2$ and ${}_1H^3$; each has same at. no.

∴ Correct choice **1 – A**

Isobars: 1. Atoms of different elements having same mass no. are isobars.

2. Nucleide and its decay product after β-emission are isobars.

3. *e.g.*, ${}_1H^3$ and ${}_2He^3$; each has same mass no.

∴ Correct choice **2 – G**

Nuclear isomers: 1. Atoms of an element of the same atomic mass but possessing different rate of decay as a result of being in different quantum states.

2. *e.g.*, U_A and U_Z; Co^{60m} and Co; Br^{80} and Br^{80m}

∴ Correct choice **3 – D**

Isosters: 1. Molecules having same no. of atoms and same no. of electrons are isosters.

2. *e.g.*, CO_2 and N_2O each has three atoms and 22 electrons.

∴ Correct choice **4 – E**

Isotones: 1. Nucleide containing same no. of neutrons but different no. of protons.

2. *e.g.*, ${}_1H^2$ and ${}_2H^3$; each has one neutron.

∴ Correct choice **5 – C**

Isoelectronics: 1. Atom and ions having same no. of electrons are isoelectronics.

2. *e.g.*, N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, Al^{3+}; each has 10 electrons.

∴ Correct choice **6 – B**

Isodiaphers: 1. Atoms having the same difference of neutrons and protons or same isotopic no.

2. Nucleide and its decay product after α-emission are isodiaphers.

3. *e.g.*, ${}_Z A^m \xrightarrow{-\alpha} {}_{Z-2}B^{m-4}$; each has the same difference of n and p, *i.e.*, $(n-p) = m - 2Z$.

∴ Correct choice **7 – F**

77. Average atomic mass $(\overline{A}) = \Sigma A_1 X_1 / \Sigma X_{\text{Total}}$.

$$= \frac{\%\text{ of one isotope} \times \text{its relative atomic mass} + \%\text{ of other} \times \text{its relative atomic mass}}{100}$$

Let % of isotope of mass 10.01 be a.

$$\therefore \quad 10.81 = \frac{10.01 \times a + 11.01\,(100 - a)}{100}$$

∴ $a = 20$

∴ % of isotope of mass 10.01 = **20**

∴ % of isotope of mass 11.01 = **80**

78. Average atomic mass $(\overline{A}) = \Sigma A_1 X_1 / \Sigma X_{\text{Total}}$.

$$= \frac{\%\text{ of one isotope} \times \text{its relative at. mass} + \%\text{ of other} \times \text{its relative at. mass}}{100}$$

Let % of Cl^{35} be 'a'.

$$\therefore \quad 35.453 = \frac{35 \times a + 37(100 - a)}{100}$$

∴ $a = \mathbf{77.35\%}$

79. Mass number of isotope of O with 8 neutrons = 16 and is 90%.

Mass number of isotope of O with 9 neutrons = 17 Let a %

Mass number of isotope of O with 10 neutrons = 18

∴ $(10 - a)\%$

∴ Average atomic mass of O $(\overline{A}) = \Sigma A_1 X_1 / \Sigma X_{\text{Total}}$

$$= \frac{\%\text{ of } O^{16} \times \text{its mass} + \%\text{ of } O^{17} \times \text{its mass} + \%\text{ of } O^{18} \times \text{its mass}}{100}$$

$$\therefore \quad 16.12 = \frac{90 \times 16 + 17(a) + 18(10 - a)}{100}$$

∴ $a = 8$

∴ % of O^{17} = **8%**

% of O^{18} = 10 − 8 = **2%**

80. (a) ${}_7N^{14}$ (n, p) indicates that N^{14} on bombardment with neutrons gives proton.

$$\therefore \quad {}_7N^{14} + {}_0n^1 \longrightarrow {}_ZX^m + {}_1p^1$$

on equating at. no. and mass no. on both sides, we get

$$\mathbf{{}_7N^{14} + {}_0n^1 \longrightarrow {}_6C^{14} + {}_1p^1}$$

(b)
$$\mathbf{{}_{19}K^{39} + {}_1H^1 \longrightarrow {}_{18}Ar^{36} + {}_2He^4}$$

(c) In some nucleus, the nucleus may capture an electron from the *K* shell. The vacancy created is filled by electrons from higher levels giving rise to characteristics X-rays. This is called as *K*-electron capture or simply *K*-capture.

$$\mathbf{{}_{56}Ba^{133} + {}_{-1}e^0 \longrightarrow {}_{55}Cs^{133} + X\text{-rays}}$$

(d)
$$\mathbf{{}_{11}Na^{22} \longrightarrow {}_{10}Ne^{22} + {}_{+1}e^0}$$

(β^+ or positron)

81. (1)
$${}_{92}U^{235} + {}_0n^1 \longrightarrow {}_{55}A^{142} + {}_{37}B^{92} + \ldots\ldots$$

Equation is

$$\mathbf{{}_{92}U^{235} + {}_0n^1 \longrightarrow {}_{55}Cs^{142} + {}_{37}Rb^{92} + 2\,{}_0n^1}$$

(2)
$$2\,{}_1H^3 \longrightarrow {}_2He^4 + {}_ZX^m$$

Equating at. no. on both sides and mass no. on both sides

$$Z = 0 \qquad m = 2$$

$$\therefore \quad \mathbf{2\,{}_1H^3 \longrightarrow {}_2He^4 + 2\,{}_0n^1}$$

(3) Equating at. no. and mass no. on both sides

$$_{34}\mathbf{Se}^{82} \longrightarrow {}_{36}\mathbf{Kr}^{82} + 2\,_{-1}e^{0}$$

82. (a) It is an example of **induced radioactivity** or **artificial radioactivity,** *i.e.*, conversion of a naturally stable element into radioactive element by bombarding it with high energy particles.

(b) It is an example of **nuclear reaction.** A reaction that involves a change in the nucleus of an atom due to interaction of nucleons.

(c) It is an example of **induced radioactivity** or **artificial radioactivity.**

(d) It is an example of **spallation reaction.** A nuclear reaction in which a high energy incident particle causes several particles or fragments to be emitted out from target nucleus. The mass no. and at. no. of target nucleus are reduced by several units.

83. For $_{89}\text{Ac}^{228}$: $\dfrac{\text{Mass No.}}{4} = \dfrac{228}{4} = 57.0$

i.e., 228 is completely divisible by 4 and therefore, $_{89}\text{Ac}^{228}$ is a member of **4*n* series.**

For $_{89}\text{Ac}^{227}$: $\dfrac{\text{Mass No.}}{4} = \dfrac{227}{4} = 56\dfrac{3}{4}$

$\therefore$ Ac^{227} is a member of **(4*n* + 3) series.**

84. **Nuclear fission:** A nuclear reaction in which a heavy atomic nucleus splits up into two approximately equal parts, at the same time emitting neutrons and releasing very large amount of energy.

Nuclear fusion: A nuclear reaction between light atomic nuclei as a result of which a heavier nucleus is formed and a large quantity of nuclear energy is released.

As given:

In fission 200 MeV is formed and mass involved = 236 g

In fusion 17.6 MeV is formed and mass involved = 2 + 3 = 5 g

$\therefore$ Energy released/g mass is more in fusion and thus fusion is more hazardous for civilization.

• SINGLE INTEGER ANSWER PROBLEMS •

1. $^{232}_{90}\mathrm{Th}$ belongs to III gp. It forms a new element after emission of an α-particle belonging to gp.
2. n/p ratio of $^{12}\mathrm{C}$ is .....
3. $_1\mathrm{H}^3$ on decays forms a new element with mass number ......
4. Pair annihilation involves how much particles to produce γ-rays.
5. No. of α-particles emitted during the emission :
$$^{238}_{92}\mathrm{U} \longrightarrow {}^{206}_{82}\mathrm{Pb} + a\,^{4}_{2}\mathrm{He} + b\,^{0}_{-1}e$$
6. Time required to complete 99% decay is how much to time required to complete 90% decay?
7. If $1\,Rd = 10^a\ dps$, then a is ......
8. Total number of α-particles emitted in Actinium series is ......
9. Ratio of atoms of B and A left after the process of decay at secular equilibrium if their average life are 12 year and 3 year for A and B respectively.
$$\underset{T\ \ 12\text{ yr.}}{A} \longrightarrow \underset{3\text{ yr.}}{B} \longrightarrow C$$
10. The number of known isotopes of iron are ......
11. Nucleodic masses of $^{14}_{7}\mathrm{N}$ and $^{15}_{7}\mathrm{N}$ are mixed to give average atomic mass of 14.1. The ratio of $^{14}\mathrm{N}$ and $^{15}\mathrm{N}$ mixed is ......
12. The radius of nucleus varies with mass no. as $A^{1/n}$. The value of n is .....
13. If $t_{3/4}$ and $t_{1/2}$ are time required for completetion of 3/4 decay and 1/4 decay then $t_{3/4} = t_{1/2} \times n$, than n is ......
14. Nuclear fusion occurs at 10^n K. The value of n is ......
15. Atoms $_7A$, $_8B$ and $_9C$ are such that $_8B$ is an isobar of $_7A$ and atom $^{17}_{9}C$ is isotone to $_8B$. The number of neutrons in A are ......
16. Isotopic number of $^{58}_{26}\mathrm{Fe}$ is ......
17. In a nuclear reaction : $\underset{(\text{E.S.})}{^{19}_{8}\mathrm{O}} \longrightarrow \underset{(\text{G.S.})}{^{19}_{8}\mathrm{O}}$;
$\Delta E = 4.5 \times 10^8$ kJ mol^{-1}. The mass difference in mg of excited state and ground state of $^{19}\mathrm{O}$ is ......
18. The minimum number of particles required to show pair annihilation process.
19. The total number of α-and β-particles emitted in the nuclear reaction $^{238}_{92}\mathrm{U} \longrightarrow {}^{214}_{82}\mathrm{Pb}$. **(IIT 2009)**
20. The number of neutrons emitted when $^{235}_{92}\mathrm{U}$ undergoes controlled nuclear fission to $^{142}_{54}\mathrm{Xe}$ and $^{90}_{38}\mathrm{Sr}$.
21. In a certain type of nuclear reaction, one neutron is a projectile (a reactant) and two neutrons are produced. Assume that each process takes 1 s. Suppose that half of all the product neutrons cause another event each, and the other half escape from the sample. How many neutrons will be produced in the third second ?
22. In the abundance of three isotopes of H, one of mass 2 is 6%. Calculate the % of other respective isotopes of $^3\mathrm{H}$ in a mixture when the mean atomic mass of H is 1.12 at any time.
23. Number of neutrons in lighter isotope of $_8\mathrm{O}$ is.....
24. Atoms $_7A$, $_8B$ and $^{17}_{9}C$ are such that $_8B$ is an isobar of $_7A$ and atom $^{17}_{9}C$ is isotone to $_8B$. The number of neutrons in $_7A$ are.....
25. A certain radio-isotope shows the change $^{A}_{Z}X \rightarrow {}^{A-8}_{Z-4}Y + 2\,^{4}_{2}\mathrm{He}$ ($t_{1/2} = 10$ day). If 2g-atom of $^{A}_{Z}X$ are taken, pressure of He (in atm) accumulated in a sealed tube of 12 litre in 20 day at 300K is..... ($R = 0.08$ litre atm K^{-1} mol^{-1})
26. The n/p ratio in the daughter element formed after exposure of $^{24}_{12}\mathrm{Mg}$ to deuterium which as a result loose an α-particle is.....
27. In the nuclear chain reaction
$$^{235}_{92}\mathrm{U} \longrightarrow {}^{140}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3\,^{1}_{0}\mathrm{n} + E$$
The number of neutrons given out after three steps is.....
28. In the problem 27 energy released in Three steps is nE, the value of n is.....
29. In a nuclear fission caused by the impact of a single neutron, two neutrons are produced in one step. The number of neutrons produced in 3rd step will be.....
30. 10 g of a radioactive sample has a half life of 4 hour. The half life of 5 g of the same substance is.....
31. The ratio of radii of the atom to the nucleus is 10^a. The value of a is.....
32. An element has a half life of 2 day. The time taken for seven by eight of a sample to decay is.....
33. Two radioactive nuclides A and B have half lives in the ratio 2 : 3 respectively. An experiment is started with one mole of each A and B. The molar ratio n_B/n_A left after three half lives of A is.....
34. In a nuclear reaction $^{19}_{8}\mathrm{O} \longrightarrow {}^{19}_{8}\mathrm{O}$; $\Delta E = 4.5 \times 10^8$ k J mol^{-1}. The mass difference in excited state of ^{19} O and ground state of $^{19}\mathrm{O}$ per mol in mg is....
35. Number of neutrons in parent nucleus after two successive β emission giving $^{14}_{7}\mathrm{N}$ is.....
36. Area of cross section of nucleus is about 10^{-24} cm^2 or........ barn.
37. Two radioactive species A and B have their decay constant 10 : 1 respectively. Both have initially the same number of nuclei. After time t, the ratio of nuclei of A and B becomes $\frac{1}{e}$. The average life of A will be $a \times t$. What is a ?
38. If $t_{99.6} = n \times t_{1/2}$, then n is equal to ......

39. Assuming the nuclear chain reaction:

$$^{235}_{92}\text{U} \rightarrow {}^{140}_{56}\text{Ba} + {}^{92}_{36}\text{Kr} + 3\,^{1}_{0}n + E,$$

The number of neutrons released in three successive steps is ......

40. Packing fraction of element $^{12}_{6}\text{C}$ is ......

41. If $1u = 1.492 \times 10^{-a}$ erg ; the value of a is ......

42. The ratio of ^{35}Cl and ^{37}Cl isotope in Cl_2 gas is ......

43. $^{209}_{83}\text{Bi}$ is last product of series $(4n + a)$, the value of a is ......

44. The ratio of nuclear radius of two elements ^{64}A and ^{8}B is ....

45. $_{90}\text{Th}$ a member of 3rd group on loosing one α-particles forms the daughter element. The group of this element is ...... in periodic table.

46. The number of neutrons in lightest radioisotope is ......

47. The degree of decay in time t is equal to ...... if t is equal to zero.

48. The number of radioactive atom of a radioisotope falls to 12.5% in nine days. What is its half-life period in day?

49. The half-life of $^{90}_{38}\text{Sr}$ is 20 year. If a sample of this nucleide has activity of 8000 disintegration per minute, its activity after 80 year will be 5×10^{a} dpm. What is a?

50. In the abundance of three isotopes of H, one of mass 2 is 6%, the % of $^{3}_{1}\text{H}$ isotope of H in a mixture when the average atomic mass of H is 1.12 at any time ......

51. The half-life of a radioactive element is 100 minute. The time interval required between the two stages of decay, *i.e.*, 50% and 87.5% is $a \times 10^{2}$ minute. The value of a is ....

52. The periodic table consists of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element X as shown below. To which group, element X belongs in the periodic table?

$$^{63}_{29}\text{Cu} + {}^{1}_{1}\text{H} \longrightarrow 6\,^{1}_{0}n + \alpha + 2\,^{1}_{1}\text{H} + X$$ **(IIT 2012)**

ANSWERS

1. Two **2.** One **3.** Three **4.** Two **5.** Eight **6.** Two **7.** Six **8.** Seven **9.** Four **10.** Four **11.** Nine **12.** Three
13. Two **14.** Seven **15.** Nine **16.** Six **17.** Five **18.** Two **19.** Eight **20.** Four (one neutron is to be used to bring in fission)
21. Two **22.** Three **23.** Eight **24.** Nine **25.** Six **26.** One **27.** Nine **28.** Three **29.** Eight **30.** Four **31.** Five **32.** Six
33. Two **34.** Five **35.** Nine **36.** One **37.** Nine **38.** Eight **39.** Nine **40.** Zero **41.** Three **42.** Three **43.** One **44.** Two
45. Two **46.** Two **47.** Zero **48.** Three **49.** Two **50.** Three **51.** Two **52.** Eight

18×0.0

+ 15.68 = 16.12
n = 0.08

16 17 18

OBJECTIVE PROBLEMS (One Answer Correct)

1. $^{60m}Co \longrightarrow {}^{60}Co$ emits γ-radiations of wavelength 3×10^{-10} m. Assuming each nuclei emits one wavelength, with what mass per mole of two nuclei differ?
(a) 4.43×10^{-9} g [✓ (b) 4.43×10^{-6} g]
(c) 4.43×10^{-3} g (d) 4.43 g

2. A drug has radioactivity 80 dpm and after 20 minutes after its activity is 40 dpm. The number of atoms present initially were:
(a) 2375 [✓ (b) 2309] $k = \frac{\ln 2}{20}$
(c) 2409 (d) 2475

3. 1 g sample of ^{152}Sm has 27% purity and emits α-particles with half-life 10^{12} year. Calculate the number of α-particles approximately emitted in 1 sec:
[✓ (a) 24] (b) 48
(c) 16 (d) 32

4. The degree of decay of a radioactive species ($t_{1/2}$ = 12 years) after six years is:
[✓ (a) 0.30] (b) 0.60
(c) 0.20 (d) 0.45

$kt = \ln 2$
$k = \frac{\ln 2}{12} \times 4$

5. A radioactive element decays as:

$$\underset{t_{1/2} = 2\ \text{yrs}}{A} \longrightarrow \underset{t_{1/2} = 4\ \text{yrs}}{B} \longrightarrow C.$$

If 100 atoms of A present initially undergoes decay then at radioactive equilibrium:
(a) $N_B / N_A = 2$
(b) $\frac{N_B}{N_A} = 4$
(c) $\frac{N_B}{N_A} = \frac{0.693}{\ln 2}$
[✓ (d) the equilibrium does not exist]

6. Emission of α-particle from a radioactive species produces its:
(a) Isotope (b) Isotone
(c) Isobar [✓ (d) Isodiapher]

7. The activity of a radioactive sample reduces by 10% in 12.5 yr. The half-life of this radioactivity species when it is reduced to 90%:
(a) 28.20 yr [✓ (b) 82.20 yr]
(c) 2.5 yr (d) 12.5 yr

$\frac{0.9}{12.5} = \frac{0.9}{x}$

8. The activity of ^{131}I is reduced to 60% in 4 yr. How much time it would require to reduce its amount by 40%?
(a) 6 yr (b) 0.2303 yr
(c) 2.2 yr [✓ (d) 4 yr]

$100 = 60 e^{-k4}$

9. Specific activity of ^{226}Ra is:
(a) 10 curie (b) 226 curie
(c) 223 curie [✓ (d) 1000 millicurie]

10. The abundance of three isotopes of oxygen (atomic mass 16.12) contains 8, 9, 10 neutrons respectively. One of the heaviest isotopes has 2% abundance. The other two are:
[✓ (a) 90, 8] (b) 80, 18
(c) 60, 38 (d) 18, 80

11. $^{232}_{90}Th$ belongs to III gp. It emits an α-particle. The daughter element belongs to:
(a) I gp. (b) II gp.
[✓ (c) III gp.] (d) IV gp.

12. An heavier element continuously emits α- and β-particles. The finally stable element may belong to:
[✓ (a) 14th gp.] (b) 16th gp.
(c) 10th gp. (d) 12th gp.

13. Conversion of energy to mass occurs in:
(a) α-emission (b) β-emission
(c) γ-emission [✓ (d) pair production]

14. Two radioactive elements A and B (decay constant $= 10\lambda$ and λ respectively), initially have the same number of nuclei. The ratio of nuclei of A and B left will be $1/e$ after time:
(a) $(10\lambda)^{-1}$ (b) $(11\lambda)^{-1}$
(c) $11 \times (10\lambda)^{-1}$ [✓ (d) $(9\lambda)^{-1}$]

$\frac{e^{-10\lambda t}}{e^{-\lambda t}}$

15. A sample of radioactive element has rate R_1 at time t_1 and R_2 at time t_2 ($t_2 > t_1$). Which one is not correct if λ is rate constant and τ is average life?
(a) $R_1 > R_2$
[✓ (b) No. of atoms decayed in time $(t_2 - t_1) = \frac{R_1 - R_2}{\lambda}$]
(c) No. of atoms decayed in time $(t_2 - t_1) = (R_1 - R_2) \times \tau$
(d) No. of atoms decayed in time $(t_2 - t_1) = \frac{R_2 - R_1}{\lambda}$

16. The number of neutrons accompanying the formation of $^{139}_{54}Xe$ and $^{94}_{38}Sr$ from the absorption of a slow neutron by $^{235}_{92}U$ followed by nuclear reaction is:
(a) 0 (b) 2
(c) 1 [✓ (d) 3]

17. Select the incorrect statement:
(a) The adsorption of H_2 by Pd is known as occlusion.
[✓ (b) The number of electrons in the parent nucleus of $^{14}_{7}N$ after β-emission is 8.]
(c) In electric field β-particles are deflected more than α-particles inspite of α-particles carry more charge.
(d) Nucleides having odd number of protons and neutrons are fairly stable.

18. The charge mass ratio for an alpha particle is about ...... coulombs/kg.
[✓ (a) 4.8×10^{7}] (b) 2.41×10^{6}
(c) 2.41×10^{-7} (d) 2.41×10^{-6}

19. The activity of a radioactive substance is A_1 and A_2 at time t_1 and t_2 respectively. If $t_2 > t_1$, then the ratio of $\frac{A_2}{A_1}$ is:

(a) $e^{-\lambda(t_1+t_2)}$
[✓ (b) $e^{\lambda(t_1-t_2)}$]
[✓ (c) $e^{\lambda(t_2-t_1)}$]
(d) e^{t_2/t_1}

20. The time required for a radioactive species to decay $\frac{2}{3}$ of its initial amount is t. The fraction of radioactive species left after $0.5t$ is:

[✓ (a) $\frac{1}{\sqrt{3}}$]
(b) $\frac{1}{\sqrt{5}}$
[✓ (c) $\sqrt{\frac{2}{3}}$]
(d) $\frac{1}{3}$

$\ln 3/2 = \lambda t$

$4t_{1/2} = t$

21. A radioactive species involves four half life period in time t. The time t is related to mean life (T) by:

(a) $2T\ln 2$
(b) $2T^3\ln 2$
(c) $2T^4\ln 2$
[✓ (d) $4T\ln 2$]

$t_{1/2} = \frac{\ln 2}{\lambda}$

$\frac{1}{\lambda} = T$

$t_{1/2} = T\ln 2$

22. A radionuclide having decay constant λ is produced at a constant rate of α per sec. If N_0 be the number of nuclei at $t = 0$, then maximum number of nuclide possible are:

[✓ (a) $N_0 + \frac{\alpha}{\lambda}$]
(b) $N_0 + \frac{\lambda}{\alpha}$
[✓ (c) $\frac{\alpha}{\lambda}$]
(d) N_0

23. Two radioactive species A and B having half life in the ratio 3 : 2. If A goes to 25% decay in time t_1 and B goes to 75% decay in time t_2. The ratio of t_1 and t_2 is:

(a) 0.311 : 1
(b) 0.420 : 1
(c) 0.119 : 1
(d) 0.273 : 1

24. Half life period of lead is equal to:

(a) Zero
(b) 0.693
(c) 1/0.693
[✓ (d) Infinity]

25. N_0 atoms of a radioactive nuclide are decayed having decay constant λ. The degree of decay after t time is given by:

(a) $e^{-\lambda t}$
[✓ (b) $1-e^{-\lambda t}$]
(c) $e^{\lambda t}$
(d) $\frac{1}{1-e^{\lambda t}}$

26. 5 g of radioactive species having molar mass 200 undergoes decay with decay constant of λ. The initial specific activity can be given by:

$\frac{\lambda N_A}{M}$

(a) 3×10^{23} λ dps
(b) 3×10^{24} λ dps
[✓ (c) 3×10^{21} λ dps]
(d) 3×10^{20} λ dps

27. If E_i and E_n are the energy to remove an electron from shell and a nucleon from the nucleus respectively, then:

[✓ (a) $E_n > E_i$]
(b) $E_i > E_n$
(c) $E_n = E_i$
(d) $E_n \geq E_i$

28. 4.0 mg of a β-emitter (^{210}X) has half life of 5 days and the average energy of emitted β-particles is 0.34 MeV. The rate of emission of energy in watt is:

(a) 2.0
[✓ (b) 1.0]
(c) 1.5
(d) 1.0

29. The nucleus $^{115}_{48}$Cd, after two successive β-decay will give:

(a) $^{115}_{40}$Pa
(b) $^{114}_{49}$In
(c) $^{113}_{50}$Sn
[✓ (d) $^{115}_{50}$Sn]

30. Nuclear-Fission is best explained by:

[✓ (a) Liquid droplet theory]
[✓ (b) Yukawa π-meson theory]
(c) Independent particle model of the nucleus
(d) Proton-proton cycle

31. M_n and M_p represents mass of neutron and proton respectively. An element having atomic mass M has n neutrons and Z protons, then:

[✓ (a) $M < [N \cdot M_n + Z \cdot M_p]$]
(b) $M > [N \cdot M_n + Z \cdot M_p]$
(c) $M = [N \cdot M_n + Z \cdot M_p]$
(d) $M = N[M_n + M_p]$

32. Energy released in nuclear fission is due to:

[✓ (a) Few mass is converted into energy]
(b) Total binding energy of fragments is more than the binding energy of parental element
(c) Total binding energy of fragments is less than the binding energy of parental element
(d) Total binding energy of fragments is equal to the binding energy of parental element

33. A 10 g sample of radioactive sample is present at $t = 0$. The approximate mass of this element in the sample after two mean life is:

[✓ (a) 1.35 g]
(b) 2.50 g
(c) 3.70 g
(d) 6.30 g

$\frac{10}{e^2}$ [illegible]

34. In a nuclear fusion process masses of the fusing nuclei be m_1 and m_2 and the mass of resultant nucleus is m, then:

(a) $m = m_1 + m_2$
(b) $m = m_1 - m_2$
[✓ (c) $m < m_1 + m_2$]
(d) $m > m_1 + m_2$

35. If M_p and M_n are masses of proton and neutron respectively. For a nucleus it binding energy is B and it contains Z protons and N neutrons, the correct relation for this nucleus it C is velocity of light is:

(a) $M(N,Z) = NM_n + ZM_p - BC^2$
(b) $M(N,Z) = NM_n + ZM_p + BC^2$
[✓ (c) $M(N,Z) = NM_n + ZM_p - \frac{B}{C^2}$]
[✓ (d) $M(N,Z) = NM_n + ZM_p + \frac{B}{C^2}$]

36. In the reaction $^2_1H + ^3_1H \rightarrow ^4_2He + ^1_0n$, if binding energies of ^2_1H, ^3_1H and ^4_2He are respectively a, b and c (in MeV), then the energy released in this reaction is:

(a) $a+b+c$
[✓ (b) $a+b-c$]
[✓ (c) $c-(a+b)$]
(d) $c+a-b$

37. Fission of nuclide is possible because the binding energy per nucleon in them:
(a) increases with mass no. at low mass number
(b) decreases with mass no. at low mass number
(c) increases with mass no. at high mass number
(d) decreases with mass no. at high mass number

38. $^{238}_{92}U$ emits 8α- and 6β-particles. The ratio of neutron /proton in product nuclei is:
(a) 60/41
(b) 62/41
(c) 61/62
(d) 61/40

39. The radius of Germanium nuclide is measured to be twice of the radius of $^{9}_{4}Be$. the number of nucleons in Ge are:
$r = K(9)^{1/3}$ $2K(9)^{1/3}$
(a) 72
(b) 73
(c) 74
(d) 75

40. Two radioactive materials A_1 and A_2 have decay constant 5λ and λ respectively. If initially they have the same number of nuclei than ratio of nuclei of A_1 to A_2 will be $\frac{1}{e}$ after a time:
$-5\lambda/e + \lambda/e$
(a) $\frac{1}{4\lambda}$
(b) $\frac{e}{\lambda}$
(c) λ
(d) $\frac{\lambda}{2}$

41. An α-particle of energy $\frac{1}{2}mu^2$ bombarded a heavy target of charge ze. The distance of closest approach for α-nucleus will be proportional to:
$\frac{1}{2}mu^2 = \frac{Kze^2}{r}$
(a) $\frac{1}{ze}$
(b) u^2
(c) $\frac{1}{m}$
(d) $\frac{1}{u^4}$

42. The activity of a radioactive sample is A_0 at $t = 0$ and $\frac{A_0}{e}$ at $t = 5$ minute. The time in which activity is reduced to half of initial value is:
$\frac{1}{e} = e^{-k5}$ $1 = +k5$ $k = 1/5$ $\frac{\ln 2}{1/5} =$
(a) $\ln\frac{2}{5}$
(b) $\frac{5}{\ln 2}$
(c) $5\log_{10}2$
(d) $5\ln 2$

43. In nuclear reactions, we have conservation of :
(a) mass only
(b) energy only
(c) momentum only
(d) charge, total energy and momentum

44. Two nuclei have their mass no. in the ratio 1 : 3, the ratio of their nuclear densities is:
(a) $3^{1/3}:1$
(b) 1 : 1
(c) 1 : 3
(d) 3 : 1

45. In a nuclear fission, 0.1% mass is converted into energy. The energy released by fission of 1kg mass is:
$.1 \times 9 \times 10^{16}$ 9×10^{15}
(a) 9×10^{19} J
(b) 9×10^{17} J
(c) 9×10^{16} J
(d) 9×10^{13} J

46. A nuclide A undergoes α-decay and another nuclide undergoes β-decay, then :
(a) The α-particles emitted by A may have widely different speed
(b) All the β-particles emitted by B will have same speed
(c) The β-particles emitted by B have widely different speeds
(d) In both cases α- and β- have almost same speed.

47. If $^{238}_{92}U$ emits an α-particle, the product has mass no. and at. no.:
(a) 236, 92
(b) 234, 90
(c) 238, 90
(d) 236, 90

48. The radiations from a naturally occurring radioactive substance, as seen after deflection by a magnet in one direction, are:
(a) definitely alpha rays
(b) definitely beta rays
(c) both alpha and beta rays
(d) either alpha or beta rays

49. The radius of an atomic nucleus is of the order of:
(a) 10^{-10} cm
(b) 10^{-13} cm
(c) 10^{-15} cm
(d) 10^{-8} cm

50. The half-life period of a radioactive element is 140 days. After 560 days, one gram of element will reduce to:
(a) 1/2 g
(b) 1/4 g
(c) 1/8 g
(d) 1/16 g

51. $^{27}_{13}Al$ is a stable isotope, $^{29}_{13}Al$ is expected to disintegrate by:
(a) α emission
(b) β emission
(c) positron emission
(d) proton emission

52. The number of neutrons accompanying the formation of $^{139}_{54}Xe$ and $^{94}_{38}Sr$ from the absorption of a slow neutron by $^{235}_{92}U$, followed by nuclear fission is:
(a) 0
(b) 2
(c) 1
(d) 3

53. The decay constant of a radioactive species is λ for the process in which a parent element showing formation of a daughter element. After time t, P atoms of parent element are left and D atoms of daughter elements are formed. If $t_{1/2}$ is half life then which expression correctly represents decay of parent element :
(a) $t = \frac{t_{1/2}}{0.693}\ln\left(1+\frac{D}{P}\right)$
(b) $t = \frac{t_{1/2}}{0.693}\ln\left(1-\frac{D}{P}\right)$
(c) $t = \frac{t_{1/2}}{0.693}\ln\left(\frac{D}{P}\right)$
(d) $t = \frac{t_{1/2}}{0.693}\ln\left(\frac{P}{D}\right)$

54. Which is correct for a graph plotted between $\log\frac{r_n}{r_o}$. vs $\log A$ (where r_n is radius of nucleus and A is its mass no).
(a) a straight line with a slope 0.5
(b) a circle with radius 1.3×10^{-13}cm
(c) a straight line with slope 0.333
(d) an ellipse with minor and major axis in the ratio $\frac{1}{3}$

$\ln r = \frac{1}{3}\ln A + \ln k$

no. of neutron
− no. of proton

55. Isotopic number of $^{235}_{92}U$ is :

(a) 235   143 − 92   (b) 92
(c) 143   (d) 51

56. Total time (T) required for a species to reduce it to $\frac{1}{16}$ is correctly represented with its average life, by the relation :

(a) $\tau^2 \ln 2$ (b) $2\tau \ln 2$
(c) $\tau^4 \ln 2$ (d) $4\tau \ln 2$

$4t_{1/2} = T$
$4\tau \ln 2$

57. $^{23}_{11}Na$ is the most stable isotope of Na. Find the process by which $^{24}_{11}Na$ can undergo radioactive decay:
(IIT 2003)

[✓ (a)] β^--emission   (b) α-emission
(c) β^+-emission   (d) K-electron capture

58. A positron is emitted by $^{23}_{11}Na$. The ratio of the atomic mass and atomic number of the resulting nuclide is:
(IIT 2007)

(a) 22/10   (b) 22/11
(c) 23/10   (d) 23/12

59. Given that the abundances of isotopes ^{54}Fe, ^{56}Fe and ^{57}Fe are 5%, 90% and 5% respectively, the atomic mass of Fe is:
(IIT 2009)

$\times 0.9 + 57 \times 0.05$

(a) 55.85   (b) 55.95
(c) 55.75   (d) 56.65

60. The total no. of α- and β-particles emitted in the nuclear reaction: $^{238}_{92}U \rightarrow ^{214}_{82}Pb$ 24 ⑥
(IIT 2009)

(a) 8   (b) 6
(c) 4   (d) 2

61. Bombardment of aluminium by α-particles leads to the artificial disintegration in two ways (i) and (ii) as shown Products X, Y and Z respectively are
(IIT 2011)

$$\begin{tikzcd}
^{27}_{13}Al \arrow[r, "+^{4}_{2}He\ (ii)"] \arrow[d, "(i)"', "^{4}_{2}He"'] & ^{30}_{15}P + Y \arrow[d] \\
^{30}_{14}Si + X & ^{30}_{14}Si + Z
\end{tikzcd}$$

(a) Proton, neutron, positron
(b) Neutron, positron, proton
(c) Proton positron neutron
(d) Positron, proton neutron

SOLUTIONS (One Answer Correct)

1. (b) $E/\text{photon} = \frac{N \cdot hc}{\lambda}$ Also, $E = mc^2$

$\therefore \quad \frac{N \cdot hc}{\lambda} = mc^2$

$\therefore \quad m = \frac{N \cdot h}{c \cdot \lambda} = \frac{6.023 \times 10^{23} \times 6.626 \times 10^{-34}}{3 \times 10^8 \times 3 \times 10^{-10}}$

$= 4.43 \times 10^{-9}\ \text{kg} = 4.43 \times 10^{-6}\ \text{g}$

2. (b) $t = \frac{2.303}{\lambda} \log \frac{N_0}{N} = \frac{2.303}{\lambda} \log \frac{\gamma_0}{\gamma}$

$\therefore \quad 20 = \frac{2.303}{\lambda} \log \frac{80}{40}$

$\therefore \quad \lambda = \frac{2.303 \times 0.3010}{20}$, Now, $\gamma_0 = \lambda \cdot N_0$

$\therefore \quad 80 = \frac{2.303 \times 0.3010}{20} \times N_0$

$\therefore \quad N_0 = 2309$

3. (a) $\lambda = \frac{0.693}{10^{12} \times 365 \times 24 \times 60 \times 60} = 2.2 \times 10^{-20}\ \text{sec}^{-1}$

$\therefore \quad \gamma = \lambda \times N = 2.2 \times 10^{-20} \times \frac{1 \times 27 \times 6.023 \times 10^{23}}{100 \times 152}$

$= 24\ \alpha\text{-per sec}^{-1}$

4. (a) $\frac{N_0}{N} = e^{\lambda t}; \quad \therefore N = N_0 e^{-\lambda t},$

Now, $\alpha = \frac{N_0 - N}{N_0} = \frac{N_0 - N_0 e^{-\lambda t}}{N_0} = 1 - e^{-\lambda t}$

$\therefore \quad \alpha = 1 - e^{-\frac{0.693}{12} \times 6} = 0.29$

5. (d) If $t_{1/2}$ of daughter element is higher than parent element, radioactive equilibrium is not noticed.

6. (d) Emission of α-particles always leads to formation of isodiapher, *i.e.*, $(n - P)$ remains constant.

7. (b) Half-life of a species remains constant. $N = \frac{N_0 \times 90}{100}$,

Now $\quad \lambda = \frac{2.303}{12.5} \log \frac{100}{90} = 8.43 \times 10^{-3}$

$\therefore \quad t_{1/2} = \frac{0.693}{8.43 \times 10^{-3}} = 82.20\ \text{yrs}$

8. (d) Time required to reduce activity by $40\% =$ time required to reduce activity to 60%, *i.e.*, 40% is decayed.

9. (d) Specific activity $^{226}\text{Ra} =$ rate of decay of 1 g of $^{226}\text{Ra} = 1\ \text{curie} = 1000$ millicurie

It is the unit of radioactivity derived by assuming rate of decay of 1 g of Ra.

10. (a) $16.12 = \frac{16 \times a + 17 \times (98 - a) + 18 \times 2}{100}$

$\therefore \quad a = 90\%$ for ^{16}O and 2% for ^{17}O.

11. (b) $^{232}_{90}\text{Th} \longrightarrow {}^{228}_{88}\text{Ra} + {}^{4}_{2}\text{He}$; Note elements from 89 to 103 are placed in gp. III.

12. (a) Naptunium series ends at Bi (15th gp.) and rest all series terminates at Pb (14th gp.).

13. (d) Energy of photon can be converted entirely into an electron and a positron when the photon passes through matter. This is pair production $(h\nu = {}^{0}_{-1}e + {}^{0}_{+1}e)$

14. (d) $N_A = N_0 e^{-\lambda t}, \quad N_B = N_0 e^{-\lambda t}$

$\therefore \quad \frac{N_A}{N_B} = e^{-9\lambda t}$ Given, $\frac{N_A}{N_B} = e^{-1}$

$\therefore \quad 9\lambda t = 1$ or $t = \frac{1}{9\lambda}$

15. (d) Rate decreases with time : $R_1 = \lambda N_1, \quad R_2 = \lambda N_2$

$\therefore \quad R_1 - R_2 = \lambda (N_1 - N_2)$

∴ No. of atoms decayed in time

$t_2 - t_1 = N_1 - N_2 = \frac{R_1 - R_2}{\lambda}$

$= (R_1 - R_2) \cdot \tau$

16. (d) $^{235}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{139}_{54}\text{Xe} + {}^{94}_{38}\text{Sr} + 3\,{}^{1}_{0}n$

17. (d) Nuclides with odd number of neutrons and protons are unstable.

18. (a) $\frac{e}{m} = \frac{2 \times 1.602 \times 10^{-19}}{4 \times 1.66 \times 10^{-27}} = 4.8 \times 10^7$

19. (b) $\frac{A_1}{A_0} = e^{-\lambda t_1}$ and $\frac{A_2}{A_0} = e^{-\lambda t_2}$

$\therefore \quad \frac{A_2}{A_1} = e^{\lambda(t_1 - t_2)}$

20. (a) $\lambda t = 2.303 \log \frac{1}{1/3}$

$\lambda \times \frac{1}{2} t = 2.303 \log \frac{1}{a}$

$\therefore \quad 2 = \frac{\log 3}{\log \frac{1}{a}}$

$\log \frac{1}{a} = \frac{0.477}{2} = 0.2385$

$\frac{1}{a} = 1.7318$

$\therefore \quad a = 0.5774 = \frac{1}{\sqrt{3}}$

21. (d) $t_{1/2} \times 4 = t$

Also $T = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693} = \frac{t_{1/2}}{\ln 2}$

$\therefore \quad T = \frac{t/4}{\ln 2}$ or $t = 4T \ln 2$

22. (c) Rate of formation of nuclide, $\frac{dN}{dt} = \alpha - \lambda N$

(where λN is its rate of decay)

For maximum number, $\frac{dN}{dt} = 0$

$\therefore \quad \alpha - \lambda N = 0$

or $\quad N = \frac{\alpha}{\lambda}$

23. (a) $\frac{t_{1/2}A}{t_{1/2}B} = \frac{3}{2}$

For A: $t_1 = \frac{2.303 \times t_{1/2}A}{0.693} \log \frac{4}{3}$

For B: $t_2 = \frac{2.303 \times t_{1/2}B}{0.693} \log 4$

$\therefore \quad \frac{t_1}{t_2} = \frac{t_{1/2}A}{t_{1/2}B} \times \frac{\log 4/3}{\log 4}$

$= \frac{3}{2} \times 0.2075 = 0.311$

24. (d) Pb is not radioactive and thus $\lambda = 0$

or $t_{1/2} = \frac{0.693}{\lambda}$, $\quad \therefore \quad t_{1/2} = \infty$

25. (b) $N = N_0 \cdot e^{-\lambda t}$

$\therefore \quad N_0 - N = N_0 - N_0 \cdot e^{-\lambda t}$

$= N_0[1 - e^{-\lambda t}]$

degree of decay $= \frac{N_0 - N}{N_0} = 1 - e^{-\lambda t}$.

26. (c) Specific activity = activity shown by 1 g species = rate shown per g by species

Activity $= \lambda \cdot N = \frac{\lambda \cdot N_A}{M} = \frac{6 \times 10^{23} \times \lambda}{200}$

$= \lambda \times 3 \times 10^{21}$ dps

where N is no. of atoms in 1 g

27. (a) $E_n > E_e$ as binding energy responsible for holding nucleons in nucleus is very high.

28. (b) Power = Energy of 1β (in J) × No. of β particles emitted/sec

No. of β particles emitted $= -\frac{dN}{dt} = \lambda \cdot N$

$= \frac{0.693}{5 \times 24 \times 60 \times 60} \times \frac{4 \times 10^{-3} \times 6.023 \times 10^{23}}{210}$

$= 1.84 \times 10^{13}$

$\therefore \quad$ Power $= 0.34 \times 10^{6} \times 1.6 \times 10^{-19} \times 1.84 \times 10^{13}$

= 1 watt

29. (d) ${}^{115}_{48}\text{Cd} \rightarrow {}^{115}_{50}\text{Sn} + 2\,{}^{0}_{-1}e$

30. (a) Nuclear fission has been explained in terms of liquid droplet theory.

31. (a) Total mass of atom is always less than sum of the masses of its constituent elements and this difference is given out in form of binding energy of nucleus.

32. (a) The decay releases energy due to mass decay, *i.e.*, $E = mc^2$.

33. (a) mean life $= \frac{1}{\lambda}$ $\quad \therefore t = \frac{2}{\lambda}$

$N = N_0 e^{-\lambda t} = N_0 e^{\frac{-2\lambda}{\lambda}} = N_0 e^{-2}$

$\therefore \quad N = 10 \times 0.135 = 1.35$ g

34. (c) During fusion, mass decay also occurs to release huge amount of energy.

35. (c) Mass decay $= N \cdot M_n + Z \cdot M_p - M(N,Z)$

B.E. = Mass decay $\times C^2$

$\therefore \quad$ Mass decay $= \frac{B}{C^2}$

$\frac{B}{C^2} = NM_n + ZM_p - M(N,Z)$

$\therefore M(N,Z) = NM_n + ZM_p - \frac{B}{C^2}$

36. (c) Mass decay = (mass of ${}^{4}_{2}\text{He}$ + mass of ${}^{1}_{0}n$)

− (mass of ${}^{2}_{1}\text{H}$ + mass of ${}^{3}_{1}\text{H}$)

$(\because \; \Delta m = E \times u^2)$

$= \frac{\text{B.E. of } {}^{4}_{2}\text{He} + 0 - \text{B.E. of } {}^{2}_{1}\text{H} - \text{B.E. of } {}^{3}_{1}\text{H}}{u^2}$

mass decay $= \frac{c - a - b}{u^2}$

Now E = mass decay $\times u^2 = \frac{c - a - b}{u^2} \times u^2 = c - a - b$

37. (d) It is a fact and therefore heavier nuclei show fission.

38. (b) ${}^{238}_{92}\text{U} \rightarrow {}^{206}_{82}\text{Pb} + 8\,{}^{4}_{2}\text{He} + 6\,{}^{0}_{-1}e$

$p = 82, n = 124$

$\therefore \quad n/p = 124/82 = 62/41$

39. (a) $R = R_0 (A)^{1/3}$

$\therefore \quad \frac{R_B}{R_{\text{Ge}}} = \left(\frac{9}{m}\right)^{1/3}$

$\left[\frac{R_B}{R_{\text{Ge}}}\right]^3 = \frac{9}{m} = \left(\frac{1}{2}\right)^3$

$\therefore \quad m = 9 \times 2^3 = 72$

40. (a) $N_A = N_0 e^{-\lambda_1 t} = N_0 e^{-5\lambda t}$

$N_B = N_0 e^{-\lambda_2 t} = N_0 e^{-\lambda t}$

$\therefore \quad \frac{N_A}{N_B} = e^{-4\lambda t} = e^{-1}$ $\quad \left(\text{Given } \frac{N_A}{N_B} = \frac{1}{e}\right)$

$\therefore \quad 4\lambda t = 1$

$t = \frac{1}{4\lambda}$

41. (c) For the closest approach

Final P.E. = Initial K.E.

$\frac{K \cdot ze \cdot 2e}{r_0} = \frac{1}{2} mu^2$

$\therefore \quad r_0 = \frac{4Kze^2}{mu^2}$

42. (d) $A = A_0 e^{-\lambda t}$

$\frac{A_0}{e} = A_0 e^{-\lambda 5}$

$\therefore \quad e^{-1} = e^{-5\lambda}$

$$\therefore \quad \lambda = \frac{1}{5}$$

$$t_{1/2} = \frac{\ln 2}{\lambda} = 5 \ln 2$$

43. (d) All are conserved.

44. (b) Densities of nucleus are independent of mass no.

45. (d) $E = \Delta m \cdot c^2 = \frac{0.1 \times 1 \times (3 \times 10^8)^2}{100}$

$$= 9 \times 10^{13} \text{ J}$$

46. (c) During β-decay, the energy is distributed among β-particles and antineutrino

$$_0^1 n \rightarrow {}_{-1}^{0} e + {}_{+1}^{1} p + \overline{\nu}$$

47. (b) $_{92}^{238}\text{U} \xrightarrow{-\alpha} {}_{90}^{234}\text{Th}$

48. (d) A naturally occurring substance may emit alpha- or beta-rays.

49. (b) It is an experimental fact $[r_n = 1.33 \times 10^{-13} \text{ A cm}^{1/3}]$

50. (d) $T = n \times t_{1/2}$

$$\therefore \quad n = \frac{T}{t_{1/2}} = \frac{560}{140} = 4$$

Now, $N_t = N_0 \left(\frac{1}{2}\right)^n = 1 \times \left(\frac{1}{2}\right)^4 = \frac{1}{16} \text{g}$

51. (b) The species $_{13}^{29}\text{Al}$ (No. of neutrons = 16) contains more neutrons than the stable isotope $_{13}^{27}\text{Al}$ (No. of neutrons = 14) due to higher n/p ratio. Neutron decays to show β emission.

$$_0^1 n \rightarrow {}_{+1}^{1} p + \underset{\beta-\text{particle}}{{}_{-1}^{0} e}$$

52. (d) $_{92}^{235}\text{U} + {}_0 n^1 \rightarrow {}_{54}^{139}\text{Xe} + {}_{38}^{94}\text{Sr} + 3\,{}_0 n^1$

53. (a) For $I \rightarrow D$

$$t = \frac{1}{\lambda} \ln \frac{N_0}{N}$$

$$N_0 = P + D$$

$$N = P$$

$$t = \frac{1}{\lambda} \ln \left[\frac{P+D}{P}\right]$$

$$t = \frac{t_{1/2}}{0.693} \ln \left[1 + \frac{D}{P}\right]$$

54. (c) $r_n = r_o \times A^{1/3}$ (where $r_o = 1.3 \times 10^{-13}$ cm)

$$\frac{r_n}{r_o} = A^{1/3}$$

$\log \frac{r_n}{r_o} = \frac{1}{3} \log A$ *i.e.*, a straight line with slope $\frac{1}{3}$

55. (d) Isotopic number = No. of neutron – no. of protons

56. (d) $N = \frac{N_0}{16} = \frac{N_0}{2^4}$ $\therefore$ No. of half lives = 4

$$\therefore T = 4 \times t_{1/2}$$

Also $t_{1/2} = \frac{\ln 2}{\lambda} = \tau \times \ln 2$ (τ is average life)

$$\therefore T = 4\tau \ln 2$$

57. (a) n/p of $_{11}^{24}\text{Na} > {}_{11}^{23}\text{Na}$

58. (c) $_{11}^{23}\text{Na} \longrightarrow {}_{10}^{23}\text{Ne} + {}_{+1}^{0}e$

59. (b) At. mass $= \frac{54 \times 5 + 56 \times 90 + 57 \times 5}{5 + 90 + 5} = 55.95$

60. (a) $_{92}^{238}\text{U} \longrightarrow {}_{82}^{214}\text{Pb} + 6\,{}_2^4\text{He} + 2\,{}_{-1}^{0}e$

61. (a) $_{13}^{27}\text{Al} + {}_2^4\text{He} \longrightarrow {}_{14}^{30}\text{Si} + {}_1^1 p$

$$_{13}^{27}\text{Al} + {}_2^4\text{He} \longrightarrow {}_{15}^{30}\text{P} + {}_0^1 n$$

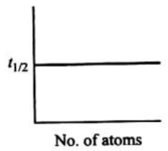
$$\downarrow$$

$$_{15}^{30}\text{P} + {}_{+1}^{0}e$$

OBJECTIVE PROBLEMS (More Than One Answer Correct)

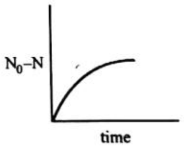
1. Decrease in atomic number is observed in:
   (a) α-emission (b) β-emission
   (c) positron emission (d) electron capture
2. Which of the following statements are correct?
   (a) *K*-electron capture always release X-rays
   (b) Gaseous emenation is not observed in neptunium series
   (c) γ-emissions are secondary emissions
   (d) Elements placed above the belt of stability show β-emission.
3. In which of the following decays n/p increases?
   (a) α-emission (b) *K*-electron capture
   (c) Positron emission (d) γ-emission
4. Select the correct statements:
   (a) α-decay produces isodiaphers
   (b) β-decay produces isobars
   (c) ${}_{6}^{11}\mathrm{C}$ shows positron emission
   (d) ${}_{11}^{24}\mathrm{Na}$ shows β-emission
5. Select the correct statements. Fusion in stars:
   (a) occurs at temperature 10^7 K through proton-proton cycle
   (b) occurs at temperature 10^8 K through proton-carbon cycle
   (c) is uncontrolled nuclear reaction
   (d) is thermonuclear reaction
6. Radioisotopes are used in:
   (a) deciding basicity of H_3PO_4 and H_3PO_3
   (b) deciding mechanism of photosynthesis
   (c) deciding mechanism of ester hydrolysis
   (d) calculating age of animal or vegetable objects by carbon dating technique
7. Select the correct statements:
   (a) Relative stabilities of radioactive isotopes are expressed in terms of their average life
   (b) The complete decay of radioactive species takes place in infinite time
   (c) The half-life of $^{14}\mathrm{C}$ in charcoal or in cellulose is same
   (d) Average life is defined as the time to reduce rate of decay by 63%
8. Select the correct statements:
   (a) Mass of a stable nucleus can never be less than twice of its atomic number
   (b) Shorter the life of a radio element, longer is its range and greater the energy of the α-particles that it expels
   (c) Tritium dating is used for determining ages of comparatively recent dates
   (d) The first example of true artificial transmutation was ${}_{3}^{7}\mathrm{Li} + {}_{1}^{1}\mathrm{H} \longrightarrow 2\,{}_{2}^{4}\mathrm{He}$
9. The nuclear reactions accompanied with emission of neutron(s) are:
   (a) ${}_{13}^{27}\mathrm{Al} + {}_{2}^{4}\mathrm{He} \rightarrow {}_{15}^{30}\mathrm{P}$
   (b) ${}_{6}^{12}\mathrm{C} + {}_{1}^{2}\mathrm{H} \rightarrow {}_{7}^{14}\mathrm{N}$
   (c) ${}_{15}^{30}\mathrm{P} \rightarrow {}_{14}^{30}\mathrm{Si} + {}_{+1}^{0}e$
   (d) ${}_{95}^{241}Am + {}_{2}^{4}\mathrm{He} \rightarrow {}_{97}^{244}Bk$
10. Decrease in atomic number is observed during:
    (a) alpha emmission (b) beta emission
    (c) positron emission (d) electron capture
11. For a radioactive species decaying with rate *r*, N is the number of atoms left after time *t*, *D* being the no. of daughter element formed and $t_{1/2}$ be the half-life period. Select the correct graphical representations :

(a)

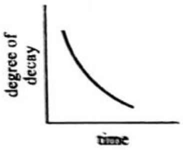


(b)

(c)



(d)



12. Which of the following are used as moderator in nuclear reactor :
    (a) Graphite (b) Lithium
    (c) Beryllium (d) Heavy water
13. Which of the following emissions do not emit X-rays ?
    (a) β^+-decay (b) β^--decay
    (c) K-electron capture (d) α-decay
14. In which of the following radioactive process, electrical neutrality is maintained in daughter element.
    (a) α-decay (b) K-electron capture
    (c) γ-decay (d) β^--decay
15. In the nuclear transmutation
    ${}_{4}^{9}\mathrm{Be} + X \longrightarrow {}_{4}^{8}\mathrm{Be} + Y$ (X, Y) is (are) :
    [JEE (Advanced) II 2013]
    (a) (γ, n) (b) (p, D)
    (c) (n, D) (d) (γ, p)

SOLUTIONS (More Than One Answer Correct)

1. (a,c,d) α-emission : ${}_{z}^{m}A \longrightarrow {}_{z-2}^{m-4}B + {}_{2}^{4}\text{He}$ (z decreases)

   β-emission : ${}_{z}^{m}A \longrightarrow {}_{z+1}^{m}B + {}_{-1}^{0}e$

   Positron emission : ${}_{1}^{1}p \longrightarrow {}_{0}^{1}n + {}_{+1}^{-0}e$ (z decreases)

   K-electron capture :

   ${}_{1}^{1}p + {}_{-1}^{0}e \longrightarrow {}_{0}^{1}n + \text{X-ray}$ (z decreases)

2. (a,b,c,d) For concepts follow Concepts of physical chemistry by P. Bahadur, Prakash Publications, Muzaffarnagar. Naptunium series does not produces Rn isotope as intermediate.
3. (a,b,c) In γ-emission n/p remains constant.
4. (a,b,c,d) ${}_{92}\text{U}^{235} \longrightarrow {}_{90}^{231}\text{Th} + {}_{2}^{4}\text{He}$ $(n-p) = \text{constant}$

   ${}_{1}^{3}\text{H} \longrightarrow {}_{2}^{3}\text{He} + {}_{-1}^{0}e$ (${}_{1}^{3}\text{H}$ and ${}_{2}^{3}\text{He}$ have same mass number)

   ${}_{6}^{11}\text{C} \longrightarrow {}_{5}^{11}\text{B} + {}_{+1}^{0}e$ (n/p below the belt of stability)

   ${}_{11}^{24}\text{Na} \longrightarrow {}_{12}^{24}\text{Mg} + {}_{-1}^{0}e$ (n/p above the belt of stability)

5. (a,b,c,d) All are facts.
6. (a,b,c,d) —do—.
7. (a,b,c,d) —do—.
8. (b,c,d) ${}_{1}^{1}\text{H}$ is stable nucleus.
9. (a,d) ${}_{13}^{27}\text{Al} + {}_{2}^{4}\text{He} \rightarrow {}_{15}^{30}\text{P} + {}_{0}^{1}n$

   ${}_{95}^{241}Am + {}_{2}^{4}\text{He} \rightarrow {}_{97}^{244}Bk + {}_{0}^{1}n$

10. (a,c,d) ${}_{Z}X^{A} \xrightarrow{-\alpha} {}_{Z-2}Y^{A-4}$ (α-emission)

    ${}_{Z}X^{A} \xrightarrow{-\beta} {}_{Z+1}Y^{A}$ (β-emission)

    ${}_{Z}X^{A} \longrightarrow {}_{Z-1}Y^{A} - {}_{+1}^{0}e$ (positron-emission)

    ${}_{Z}X^{A} + {}_{-1}^{0}e \longrightarrow {}_{Z-1}Y^{A}$ (electron capture)

11. (a,b,c,d) $r = \lambda \cdot N$

    $$\frac{r}{N} = \lambda = \text{constant} = \frac{0.693}{t_{1/2}}$$

    Also $t_{1/2} \propto (N)^{\circ}$

    $D = N_0 - N$ and $N = N_0 \cdot e^{-\lambda t}$

    and $\alpha = 1 - e^{-\lambda t}$

12. (a,c,d) These are facts.
13. (a,b,d) Only K-electron capture leads to X-ray emission.
14. (a,b,c,d) Radioactive emission give rise to the formation of neutral atom.
15. (a, b) Equating mass no. and atomic no. of two sides of change.

    (a) ${}_{4}^{9}\text{Be} + \gamma \longrightarrow {}_{4}^{8}\text{Be} + {}_{0}n^{1}$

    (b) ${}_{4}^{9}\text{Be} + {}_{1}^{1}P \longrightarrow {}_{4}^{8}\text{Be} + {}_{1}^{2}\text{H}$

COMPREHENSION BASED PROBLEMS

Comprehension 1 : Radioactive decay obey I order kinetics and the rate of any radiospecies can be given by $r = K[N_0]$ where all letters represent their usual notations. A sample contains 10^{-2} kg of two substances A and B with half lives of 4 and 8 sec respectively (Given that atomic mass of B is twice of A).

[1] The mass of A and B left after 16 second is:
(a) 0.625 g, 2.50 g (b) 0.625 g, 0.252 g
(c) 0.8 g, 0.2 g (d) 0.8 g, 0.2 g

[2] The ratio of initial rate of decay of A and B is:
(a) 3:2 (b) 2:1
(c) 4:1 (d) 3:4

[3] The mass ratio of A and B that must be taken so that initial rate of decay remains same:
(a) 3:2 (b) 2:1
(c) 4:1 (d) 1:4

[4] The ratio of average life of A and B is:
(a) 1:2 (b) 2:1
(c) 1:4 (d) 4:1

Comprehension 2 : A radioactive nuclide having $n/p > 1.0$ undergoes α-decay, β-decay succesively. The parent element on α-decay looses its atomic no. by two unit and mass no. by four units. In β-decay the parent atom gains its atomic no. by one unit whereas mass number remains same. The γ-emission occurs only when daughter element possesses some higher energy than required for its stability.

[1] An element ${}_{90}^{234}\text{Th}$ looses an α-particle. If Th belongs to III gp, the daughter element belongs to:
(a) I gp (b) II gp
(c) III gp (d) zero gp

[2] If atomic mass of Th is 232.18 and its at no. is 90. If it looses $6-\alpha$ and $4-\beta$ particles, the mass no. of finally stable element is:
(a) 208.18 (b) 208
(c) 226 (d) 212

[3] In the nuclear decay of an element ($Z = 88$, electron $= 88$, neutron $= 145$) emitting out ${}_{2}^{4}\text{He}$ nuclei (an α-particle), the number of proton, electron and neutrons in daughter element is:
(a) 86, 88, 143 (b) 86, 86, 143
(c) 86, 88, 144 (d) 86, 86, 142

[4] In the nuclear reaction $\overset{60\,m}{\text{Co}} \longrightarrow \overset{60}{\text{Co}}$ the emission occurs as:
(a) X-rays (b) γ-rays
(c) α-particle (d) K-electron capture

Comprehension 3 : The emission of penetrating α, β-particles (${}_{2}^{4}\text{He}$ and ${}_{-1}^{0}e$ respectively) along with γ-radiation ($h\nu$) was noticed from unstable nucleus. All elements having $Z > 82$ show this phenomenon. The emission was explained in terms of low binding energy (giving α-decay), high n/p ratio (neutron decay). γ-emission from a radioactive nuclide is secondary emission. The emission of one kind of a particles occurs at one time, later on may be followed by other. In addition to these emission positron emission and X-ray emission is also noticed due to $n/p < 1$ and K-electron capture respectively.

[1] The neutron decay leads to emission of β-particles and :
(a) neutrino (b) antineutrino
(c) mesons (d) γ-rays

[2] The missing term in ${}_{+1}^{1}p + {}_{-1}^{0}e \rightarrow {}_{0}^{1}n + ?$ is:
(a) γ-rays (b) infra red
(c) X-rays (d) visible rays

[3] An element of group III with atomic no. 90 and mass number 238 undergoes decay of one α-particle. The newly formed element belongs to:
(a) I group (b) II group
(c) III group (d) IV group

[4] An element ${}_{92}^{238}\text{U}$ of III gp undergoes radioactive decay to finally produce a stable element. The finally formed stable element belongs to:
(a) I gp (b) 13th gp
(c) II gp (d) 14th gp

[5] The emission of penetrating rays from a radioactive species can be shielded by:
(a) Bi blocks (b) Pb blocks
(c) C blocks (d) Mg blocks

[6] The value of 'n' for the parent and finally stable element obtained from the decay of $(4n+1)$ series respectively is:
(a) 60, 52 (b) 58, 54
(c) 58, 51 (d) 60, 54

Comprehension 4 : In the upper atmosphere, neutrons present in cosmic rays causes the following nuclear reaction.

$${}_{7}^{14}\text{N} + {}_{0}^{1}n \rightarrow {}_{6}^{14}\text{C} + {}_{1}^{1}\text{H}$$

The isotope ${}_{6}^{14}\text{C}$ gets circulated in the atmosphere as well as in living species. In a place where nuclear explosion takes place, the concentration of ${}^{14}\text{C}$ increases both in the atmosphere as well as in living species. The isotope ${}_{6}^{14}\text{C}$ disintegrates according to the reaction.

${}_{6}^{14}\text{C} \rightarrow {}_{7}^{14}\text{N} + {}_{-1}^{0}e + \bar{\nu}$ with a half life of 5760 years. When a species dies, the concentration of ${}^{14}\text{C}$ in it decreases due to the above disintegration reaction. the time at which species has died can be estimated from the knowledge of its ${}^{14}\text{C}$ content compared to that existing in atmosphere, Beyond 30,000 year, the activity of disintegration is too low to be used for the estimation of time period. **[IIT 2006]**

[1] In radiocarbon dating for finding the age of fossils, the correct statement is:

(a) During the life time ^{14}C assimilated by the human being is in equilibrium with the ^{14}C that decomposes by β emission resulting in the constant ratio of $^{14}C/^{12}C$ at a particular instant

(b) ^{14}C dating method is inappropriate for finding the life of a given sample because ^{14}C undergoes β emission and the ratio $^{14}C/^{12}C$ is not constant in human beings

(c) For a dead human being, the decay of ^{14}C depends in place to place

(d) None of the above

[2] Two organisms died on the same day. One died at a place where nuclear explosion had taken place while the other died at a place where no such explosion has occurred. The ratio of ^{14}C during life to that present in the fossil at an instant is r_1 for the former and r_2 for the latter. The age of the former was calculated at t_1 and for the latter as t_2. The correct choice for the timings t_1 and t_2 is:

(a) $t_1 > t_2$ (b) $t_1 < t_2$

(c) $t_1 = t_2$ (d) none of these

[3] In both the fossils are brought to a common place where no explosion has occurred then:

(a) $t_1 > t_2$ (b) $t_1 < t_2$

(c) $t_1 = t_2$ (d) none of these

SOLUTIONS

Comprehension 1

[1] (a) **For A :** $N_0 = 10^{-2} \times 10^3 = 10\,\text{g}$

$$t = \frac{2.303}{\lambda}\log\frac{N_0}{N}$$

$$16 = \frac{2.303 \times 4}{0.693}\log\frac{10}{w_A}$$

or $\log\frac{10}{w} = 1.2036 \quad \therefore w_A = \mathbf{0.625\ g}$

For B : $N_0 = 10^{-2} \times 10^3;\ N = 10\text{g}$

$$16 = \frac{2.303 \times 8}{0.693}\log\frac{10}{w_B}$$

$\therefore \quad w_B = \mathbf{2.50\ g}$

[2] (c) $r_A = \frac{0.693}{4} \times \frac{10}{a} \times N_A$

(Let a is atomic mass of A, then)

$$r_B = \frac{0.693}{8} \times \frac{10}{2a} \times N_A$$

$\therefore \quad \frac{r_A}{r_B} = 4$

[3] (d) $r'_A = \frac{0.693}{4} \times \frac{w_1}{a}$

$$r'_B = \frac{0.693}{8} \times \frac{w_2}{2a}$$

if $r'_A = r'_B$ then $\frac{0.693}{4} \times \frac{w_1}{a} = \frac{0.693}{8} \times \frac{w_2}{2a}$

$\therefore \quad \frac{w_1}{w_2} = \frac{1}{4}$

[4] (a) $T_A = \frac{1}{\lambda_A} = \frac{4}{0.693}$

$$T_B = \frac{1}{\lambda_B} = \frac{8}{0.693}$$

$$\frac{T_A}{T_B} = \frac{1}{2}$$

Comprehension 2

[1] (b) $^{230}_{88}\text{Ra}$ belongs to alkaline earth family.

[2] (b) $^{232}_{90}\text{Th} \longrightarrow {}^{208}_{82}\text{Pb} + \sigma\,{}^{4}_{2}\text{He} + 4e^{0}_{-1}$

[3] (b) Excess electrons are lost due to exchange of electron with atmosphere. Radioactive decay leads to neutral atom.

[4] (b) γ-rays are given by unstable nuclide left after α, β-emissions and are known as secondary emission.

Comprehension 3

[1] (b) ${}^{1}_{0}n \rightarrow {}^{1}_{1}P + {}^{0}_{-1}e + \underset{\text{(antineutrino)}}{\overline{\nu}}$

[2] (c) K-electron capture always leads to emission of X-rays.

[3] (b) $\underset{\text{III gp}}{{}^{238}_{90}\text{Th}} \rightarrow \underset{\text{II gp}}{{}^{234}_{88}\text{Ra}} + {}^{4}_{2}\text{He}$; Ra is alkaline earth metal.

[4] (d) The finally formed stable element for all three natural radioactive series is Pb belonging to gp 14.

[5] (b) Radioactive rays do not penetrate lead blocks.

[6] (a) $(4n+1)$ series has parent element ^{241}Pu and ^{209}Bi is finally formed stable element.

Comprehension 4

[1] (a) Follow text

[2] (a) $r_1 = \frac{[^{14}\text{C}]_{\text{living explosion}}}{[^{14}\text{C}]_{\text{dead}}}$ and $r_2 = \frac{[^{14}\text{C}]_{\text{living explosion}}}{[^{14}\text{C}]_{\text{dead}}}$

$$\therefore \quad \frac{r_1}{r_2} = \frac{[^{14}\text{C}]_{\text{living explosion}}}{[^{14}\text{C}]_{\text{living no explosion}}} \because r_1 > r_2 \therefore \quad t_1 > t_2$$

[3] (c) Here $r_1 = r_2 \qquad \therefore \quad t_1 > t_2$

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement **(S)** and explanation **(E)** is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) S is correct but E is wrong

(b) S is wrong but E is correct

(c) Both S and E are corect and E is correct explanation of S

(d) Both S and E are correct but E is not correct explanation of S

1. S: One will need a very powerful crane to lift a nuclear mass of even microscopic size.

E: The density of nucleus is very high.

2. S: Proton, electron and neutron each has its antiparticle.

E: Antiproton and antielectron has opposite charge to proton and electron are called antiproton and positron respectively. Antineutron possess only opposite spin.

3. S: Mesons have mass more than electron whereas hyperons have mass more than protons.

E: Mesons (short lived) on decomposition gives mesons, electrons, positrons, neutrinos, antineutrinos and γ-rays. Hyperons too are short lived on decay gives hyperons, mesons, neutrons and protons.

4. S: The density of nucleus is about 1.8×10^{17} kg m^{-3} and all nucleus have approximately same density.

E: The density of nucleus is independent of mass present in it.

5. S: The density of $^{12}_{6}C$ nuclide is about 1.8×10^{17} kg m^{3}.

E: The ratio of density of $^{12}_{6}C$ nuclide and water is about 1.8×10^{14} kg m^{-3}.

6. S: Packing fraction

$$= \frac{\text{isotopic mass} - \text{mass number}}{\text{mass number}} \times 10^4$$

E: Positive value of packing fraction implies for the unstability of nucleus.

7. S: The exchange of energy during nuclear reaction takes place in form of kinetic energy in nuclear fission.

E: The evolution of kinetic energy leads to other forms of energy during fission.

8. S: The half-life of a radioactive species is independent of temperature and mass of active species.

E: Radioactive decay takes infinite time to complete decay a given sample.

9. S: An atom on losing an α-particle forms its isodiapher.

E: Isodiaphers are the elements having same difference in their neutrons and protons.

10. S: The O_2 given out during photosynthesis in plants involves O-atoms of H_2O and not of CO_2.

E: $CO_2^{18} + H_2O \longrightarrow \text{Starch} + O_2^{18}$.

11. S: Nuclear fission is a chain reaction.

E: Extra neutrons generated during fission further attacks nuclide of fissionable material.

12. S: β-particles are deflected less than α-particles in electrical field.

E: β-particles have very low mass.

13. S: Nuclear fusion are made at very high temperature, *i.e.*, 10^7 K.

E: Nuclear fusion reactions are exoergic.

14. S: Radiolysis of water yields H_2.

E: The reaction during radiolysis of water is disproportionation reaction.

15. S : $^{56}_{26}Fe$ is most stable nucleus.

E : Binding energy per nucleon is maximum for $^{56}_{26}Fe$.

16. S : Neutron decay results in β-emission and emission of neutrino.

E : Higher values of n/p ratio give rise to neutron decay.

17. S : K-electron capture leads to emission of neutron and X-rays.

E : The vacancy created in K-shell is filled by electrons from higher levels and thus, X-rays are given out.

18. S : Binding energy/nucleons becomes almost constant at 7.6 for elements beyond Pb and onwards.

E : The lower value of binding energy/nucleons is responsible for decay of transuranic elements.

19. S : Yukawa predicted the existance of π-mesons.

E : π-mesons have their mass about 237 times more than electrons.

20. S : Parent element of $(4n+1)$ series is plutonium-241.

E : It decays to give 8α and 5β-particles.

21. S : Rutherford studied the first nuclear reaction:

$$^{14}_{7}N + ^{4}_{2}He \rightarrow ^{17}_{8}O + ^{1}_{1}H + 1.193 \text{ MeV}$$

E : α-particles lesser than energy 7.6 MeV were found ineffective.

22. S : The first man made atom produced by artificial transmutation was T_c.

E : The phenomenon of converting a stable nuclei into radioactive one is called artificial radioactivity.

23. S : $t_{1/2}$ of C^{14} is same whether it is in CO_2 or in cellulose or in coal.

E : The rate of decay of an element is independent of all external factors.

24. S : The neutrons are better initiator of nuclear reactions than protons, deutrons or α-particles.

E : Neutrons being uncharged particles, not exert repulsion forces from nucleus.

25. S : Nuclide $^{30}_{13}Al$ is less stable than $^{40}_{20}Ca$.

E : Nuclides having odd number of protons and neutrons are generally unstable.

26. S : Elements having high *n*/*p* ratio are less stable and emit β-particles.

E : They tend to lower their energy level by β-emission.

27. S : Neutrons are better projectile than protons to bring in nuclear reaction.

E : The neutrons being neutral do not experience repulsion from positively charged nucleus.

28. S : The reaction : ${}_6C^{11} \rightarrow {}_5B^{11}$ takes place with positron decay.

E : *n*/*p* ratio decreases in this change.

29. S : During nuclear fission, the products formed are radioactive.

E : Nuclear fusion requires high temperature.

30. S : ${}_6C^{11}$ lies below the belt of stability and thus decays to emit β-particle.

E : An element lying below the belt of stability try to make it stable by losing positron.

31. S : The binding energy per nucleon is in the order $^{9}_{4}Be > ^{7}_{3}Li > ^{4}_{2}He$

E : The binding energy per nucleon increases linearly upto ${}_{26}Fe$.

32. S : The position of an element in periodic table after emission of 1α + 2β particles remains the same.

E : The product formed in above case is isotope.

33. S: An example of *K*-electron capture is :

$$^{133}_{56}Ba + e^- \longrightarrow {}^{133}_{55}Cs + X\text{ - ray}$$

E: The atomic number decreases by one unit as a result of *K*-electron capture.

34. S: The plot of atomic number (*y*-axis) *vs.* number of neutrons (*x*-axis) for stable nuclei shows a curvature towards *x*-axis from the line of 45° slope as the atomic number is increased. **(IIT 2008)**

E: Proton-proton electrostatic repulsion begins to overcome attractive forces involving proton and neutrons in heavier nuclides.

ANSWERS (Statement Explanation Problems)

1. (c) Suppose we have to life a nuclear mass of microscopic size say $V = 10^{-5}\ \text{cm}^3$. The mass of this particle in nucleus = volume of particle × density of nucleus

$$\text{Density of nucleus} = \frac{\text{Mass of nucleus}}{\text{Volume of nucleus}}$$

$$= \frac{A \times 1.66 \times 10^{-24}}{\frac{4}{3}\pi r^3}$$

$$= \frac{A \times 1.66 \times 10^{-24}}{4/3 \times 3.14 \times (1.33 \times 10^{-13} \times A^{1/3})^3}$$

$$= \frac{1.66 \times 10^{-24} \times 3}{4 \times 3.14 \times 2.35 \times 10^{-39}}$$

$$= 1.68 \times 10^{14}$$

$$\text{mass of particle} = 10^{-5} \times 1.68 \times 10^{14}\ \text{g}$$

$$= 1.68 \times 10^{9}\ \text{g}$$

$$= \mathbf{1.68 \times 10^{6}\ kg}$$

2. (d) Proton ${}^{1}_{+1}p$, electron ${}^{0}_{-1}e$, neutron ${}^{1}_{0}n$
antiproton ${}^{1}_{-1}p$, positron ${}^{0}_{+1}e$, antineutron ${}^{1}_{0}n$

3. (d) Both are facts.

4. (d) —do—

5. (d) Density of each nucleus $= 1.8 \times 10^{17}\ \text{kg/m}^3$; density of water $= 1 \times 1000\ \text{kg/m}^3$.

6. (d) Both are facts. A negative value of packing fraction means mass number > isotopic mass, *i.e.*, some mass has been converted into binding energy to stabilize nucleus. This concept was primarily given to discuss the stability of nucleus.

7. (d) Both are facts.

8. (d) —do—

9. (c) $${}^{m}_{Z}A \longrightarrow {}^{m-4}_{Z-2}B + {}^{4}_{2}\text{He}$$
$$n - p = (m - 2Z) \qquad (m - 2Z)$$

10. (a) $CO_2 + H_2{}^{18}O \longrightarrow (C_6H_{10}O_5)_n + {}^{18}O_2$. This is obtained from tracer technique.

11. (c) Explanation is correct reason for statement.

12. (b) β-particles are deflected more towards anode.

13. (d) Both are facts.

14. (c) $2H_2O \longrightarrow H_2O_2 + H_2$

15. (c) The binding energy per nucleons increases upto ${}_{26}\text{Fe}$ and becomes maximum at 8.7 MeV. It then decreases. More is binding energy, lesser is energy level of nucleus more is its stability.

16. (b) Neutron decay occurs due to high n/p ratio as

$${}^{1}_{0}n \rightarrow {}^{1}_{1}p + {}_{-1}e^{0} + \overline{\nu}\ \text{(antineutrino)}$$

17. (b) Assertion represents K-electron capture.

18. (c) Follow answer 15.

19. (d) These are facts about π-mesons.

20. (c) Parent element of $(4n+1)$ series is ${}^{241}\text{Pu}$. The series gives 8α and 5β particles to give finally stable element ${}^{290}\text{Bi}$.

21. (d) α-particles with energy lesser than 7.6 MeV were not capable to penetrate nucleus and over power the repulsive forces.

22. (d) Both are facts.

23. (c) Explanation is correct reason for statement.

24. (c) Explanation is correct reason for statement.

25. (c) Al has 13 protons and 17 neutron. the stable atoms have even p-even n system and unstable atoms usually have odd p-odd neutron system.

26. (a) Elements having high n/p ratio tends to decrease it and thus neutron decay takes place to eject out β-particles.

27. (c) Positively charged particles are less suitable projectiles because they use a part of their kinetic energy to overpower the forces of repulsion from nucleus.

28. (a) A decay of ${}_{6}C^{11}$ takes place with positron emission but $\frac{n}{p}$ increases.

29. (b) Nuclear fusion requires as high as 10^7 K temperature.

30. (b) ${}_{6}C^{11} \rightarrow {}_{5}B^{11} + {}_{+1}e^{0}$. The given explanation is correct.

31. (c) Explanation is correct reason for statement.

32. (c) —do—

33. (d) Both are correct.

34. (c) Explanation is correct reason for statement.

MATCHING TYPE PROBLEMS

Type I : More Than One Match Are Possible

1. List-A	**List-B**
(A) Nuclear fission	1. Conservation of mass and energy
(B) Nuclear fusion	2. Heavier atoms
(C) β-decay	3. Lighter atoms
(D) Pair production	4. Exoergic
(E) α-decay	5. Self sustaining reaction
	6. Thermonuclear reactions

2. List-A	**List-B**
(A) $^{60\,m}_{27}$Co	1. γ-emitter
(B) $^{233}_{90}$Th	2. Cancer therapy
(C) $^{14}_{6}$C	3. β-emitter
(D) $^{232}_{90}$Th series	4. α-emitter
	5. Branching decay in series
	6. Emenation

3. List-A	**List-B**
(A) Proton rich nuclides	1. K-electron capture
(B) Artificially prepared elements	2. Proton emission
(C) $^{11}_{6}$C	3. Positron emission
(D) C—N cycle	4. $^{97}_{43}$Tc
(E) $^{43}_{21}$Sc	5. Transuranic elements

4. List A	**List B**
(A) Only β-emitter	1. $^{14}_{6}$C
(B) Maximum *n*/*p* ratio	2. $^{3}_{1}$H
(C) Positron emitter	3. $^{11}_{6}$C
(D) α, β-emitter	4. $^{235}_{92}$U
(E) $(4n+3)$ series	5. $^{81}_{37}$Rb
(F) electron capture	6. $^{223}_{87}$Fr

Type II : Only One Match From Each List

5. List-A	**List-B**	**List-C**
(A) α-emission	1. Isobar	a. proton rich nucleide lying below the belt of stability
(B) β^--emission	2. $^{32}_{15}$P	b. excited nucleus
(C) γ-emission	3. $^{60\,m}$Co	c. higher n/p ratio
(D) K-electron	4. β^+-emission	d. high binding energy
(E) Positron emission	5. Isodiapher	e. *X*-rays

ANSWERS

1. A–1, 2, 4, 5; B–1, 3, 4, 6; C–1, 4; D–1; E–1, 4
2. A–1, 2; B–3; C–3; D–3, 4, 5, 6
3. A–1, 2, 3; B–4, 5; C–3; D–3; E–2
4. A–1, 2, 6; B–2; C–3; D–4; E–4,6; F–5
5. A–5–d; B–1–c; C–3–b; D–2–e; E–4–a

5

Periodic Properties, Chemical Bonding and Complexes

• NUMERICAL PROBLEMS •

1. Specific heats of Li(s), Na(s), K(s), Rb(s) and Cs(s) at 398 K are 3.57, 1.23, 0.756, 0.363 and 0.242 $\text{J g}^{-1}\text{K}^{-1}$ respectively. Compute the molar heat capacities of these elements and identify any periodic trend. If there is trend, use it to predict molar heat capacity of Fr.

2. Calculate the energy required tc convert 5 mole of sodium atom in the gaseous state to form sodium ion. Ionisation enthalpy of Na $= 5.1$ eV / atom.

3. Calculate the energy required to convert 7.974 g of cesium atom in the gaseous state to form Cs^+ ions. Ionisation enthalpy of Cs $= 374 \text{ kJ mol}^{-1}$ and atomic mass of Cs is 132.9 amu.

4. Calculate the effective nuclear charge at the periphery of nitrogen atom when an extra electron is added in the formation of anion. Also calculate the effective nuclear charge of N-atom and O-atom.

5. Shielding constant for Ne is 4.15. Calculate the effective nuclear charge on Na^+ and F^- using only this value.

6. The ionization energy of Li is 5.39 eV. If ionization energy of H is 13.6 eV, then calculate the effective charge acting upon outermost electron of Li.

7. How much energy is given out when 1.0 g of chlorine atoms are converted into $Cl^-(g)$? Electron affinity of $Cl = -349$ kJ /mol and atomic mass of Cl is 35.5 amu.

8. For the gaseous phase reaction,

$$K + F \longrightarrow K^+ + F^-,$$

ΔH was calculated under conditions where the cations and anions by electrostatic separation from combining with each other. The ionisation energy of K is 4.3 eV. What is electron affinity of fluorine?

9. The first IP of lithium is 5.41 eV and electron affinity of Cl is −3.61 eV. Calculate ΔH in kJ mol^{-1} for the reaction:

$$Li(g) + Cl(g) \longrightarrow Li^+(g) + Cl^-(g)$$

10. You are given Avogadro's no. of 'X' atoms. If half of the atoms of X transfer one electron to the other half of 'X' atoms, 409 kJ must be added. If these X^- ions are subsequently converted to X^+, an additional 733 kJ must be added. Calculate IP and EA of X in eV. Use ($1 \text{ eV} = 1.602 \times 10^{-19}$ J and $N = 6.023 \times 10^{23}$).

11. Helium can be excited to the $1s^1 2p^1$ configuration by light of 58.44 nm. The lowest excited singlet state, with the configuration $1s^1, 2s^1$ lies 4857 cm^{-1} below the $1s^1 2p^1$ state. What would the average He—H bond energy have to be in order that HeH_2 could form non-endothermically from He and H_2? Assume that the compound would form from the lowest excited singlet state of helium. Neglect any differences between ΔE and ΔH. Take $\Delta H_f\,(H) = 218.0$ kJ / mol.

12. 1 g of Mg atoms in the vapour phase absorbs 50.0 kJ of energy. Find the composition of Mg^+ and Mg^{2+} formed as a result of absorption of energy. IE_1 and IE_2 for Mg are 740 and 1450 kJ mol^{-1} respectively.

13. Anhydrous $AlCl_3$ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution. (Ionisation energy for $AlCl_3 = 5137 \text{ kJ mol}^{-1}$; $\Delta_{\text{Hydration}}$ for $Al^{3+} = -4665 \text{ kJ mol}^{-1}$; $\Delta_{\text{Hydration}}$ for $Cl^- = -381 \text{ kJ mol}^{-1}$). **(IIT July 1997)**

14. A mixture contains atoms of fluorine and chlorine. The removal of an electron from each atom of sample absorbs 284 kJ while the addition of an electron to each atom of mixture releases 68.8 kJ. Determine the percentage composition of mixture. Given IE_1 for F and Cl are 27.91×10^{-22} and 20.77×10^{-22} kJ / atom respectively and EA_1 for F and Cl are -5.53×10^{-22} and -5.78×10^{-22} kJ / atom respectively.

15. The first ionisation energy of H and He are 13.6 eV and 24.6 eV respectively. How much energy would be given out during the formation of ground state of He atom from He^{2+} nucleus if it combines with two electrons?

16. The ionisation energy of lithium is 5.40 eV. If ionisation energy of H is 13.6 eV, then calculate the effective charge acting upon outermost electron of Li.

17. Calculate the electronegativity of fluorine from the following data:

$$E_{H-H} = 104.2 \text{ kcal mol}^{-1}$$

$$E_{F-F} = 36.6 \text{ kcal mol}^{-1}$$

$$E_{H-F} = 134.6 \text{ kcal mol}^{-1}$$ **(UPSEAT 1996)**

18. Ionisation potential and electron affinity of fluorine are 17.42 and 3.45 eV respectively. Calculate electronegativity of fluorine.

19. Calculate the electronegativity X of silicon using Allred-Rochow equation : $X = \dfrac{0.359Z'}{r^2\ (Å)} + 0.744$ where Z' is $Z_{\text{effective}}$ calculated on the basis of Slater's rule taking all the electrons. Covalent radius of Si = 1.175 Å.

20. The boiling point of krypton (Kr) and radon (Rn) are $-152°C$ and $-62°C$ respectively. Calculate the approximate boiling point of xenon.

21. Calculate the % ionic character in HCl molecule. Given bond length of HCl is 1.275 Å and $\mu_{HCl} = 1.03$ debye.

22. The dipole moment of LiH is 1.964×10^{-29} cm and the intermolecular distance between Li and H in this molecule is 1.596 Å. What is per cent ionic character in molecule?

23. The dipole moment of KCl is 3.336×10^{-29} coulomb metre which indicates that it is a highly polar molecule. The interatomic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. Calculate the dipole moment of KCl molecule, if there were opposite charges of one fundamental unit located at each nucleus. Calculate percentage ionic character of KCl. **(IIT 1993)**

24. A diatomic molecule has a dipole moment equal to 1.2 D. If bond length is 1.0 Å, what fraction of electronic charge '*e*' exists on each atom?

25. The experimental dipole moment of water molecule is 1.84 D. Calculate the bond angle H—O—H in water molecule, if dipole moment of OH bond is 1.5 D.

26. The H—O—H bond angle in the water molecule is 105°, the H—O bond distance being 0.94 Å. The dipole moment for the molecule is 1.85 D. Calculate the charge on the oxygen atom.

27. Assuming that all the four valency of carbon atom in propane pointing towards the corners of a regular tetrahedron, calculate the distance between the terminal carbon atoms in propane. Given, C—C single bond length is 1.54 Å.

28. In BI_3 molecule, distance between two I atoms is found to be 3.54 Å. Also BI_3 has sp^2-hybridised boron atom. If radius of covalently bonded I atom is 1.33, what will be covalent radius of boron?

29. Calculate the molar mass of HF if density of HF gas is 3.17 g / L at 300 K and 1.0 atm. Comment on the result.

30. Atomic radius of $F_{(g)}$ and $F^-_{(g)}$ are 72 and 136 pm respectively. Calculate the ratio and percentage increase in terms of volume during the formation of $F^-_{(g)}$ from $F_{(g)}$.

31. The multiple double bond radii of C is 0.67 Å. Calculate the multiple double bond radii of O if oxygen to oxygen bond length in CO_2 is 2.323 Å.

32. The atomic radius of Li and Li^+ are 1.23 Å and 0.76 Å respectively. Assuming that the difference in ionic radii relates to the space occupied by 2*s*-electron, calculate the % volume of Li-atom occupied by single valence electron.

33. In solid ammonia, each NH_3 molecule has six other NH_3 molecules as nearest neighbours. ΔH of sublimation of NH_3 at the melting point is 30.8 kJ/mol and the estimated ΔH of sublimation in the absence of hydrogen bonding is 14.4 kJ / mol. What is the strength of hydrogen bond in solid ammonia?

34. Assuming covalent radii to be additive property; calculate the iodine-iodine distances in o^-, m^-, *p*-di-iodobenzene. The benzene ring is regular hexagon and each C—I bond lies on a line passing through the centre of hexagon. The C—C bond length in C_6H_6 are 1.40 Å and covalent radius of iodine and carbon atom are 1.33 Å and 0.77 Å. Also neglect different overlapping effect.

35. Calculate the I—I distance in the given compound $H_2C = CI_2$ if C — I bond length is 2.10 Å.

36. What type of hybridisation are expected on central atom of each of the following molecule:

(a) BeH_2 (b) CH_2Br_2 (c) PF_6^- (d) BF_3 (e) CH_2^{2+} (f) CH_3^+ (g) CH_3^- (h) SF_6 (i) ICl_3 (j) AlH_3 (k) NH_3 (l) SbF_6^- (m) BH_4^- (n) ClO_4^- (o) I_3^- (p) ClO_3^- (q) ClO_3^+.

37. Point out the nature of hybridisation on underlined atoms:

(a) $F_2\underline{C}=\underline{C}=\underline{C}F_2$ (b) $F_2\underline{B}—\underline{C}\equiv\underline{C}—\underline{B}F_2$

(c) $\underline{C}(\underline{C}N)_4$

38. Draw the molecular structures of XeF_2, XeF_4 and XeO_2F_2 indicating the location of lone pair(s) of electrons.

39. Using VSEPR theory, identify the type of hybridisation and draw the structure of OF_2. What are oxidation states of O and F? **(IIT 1994)**

40. Write the MO configuration of O_2. Specify its bond order and magnetic properties. **(IIT 2000)**

41. Predict the type of hybridisation of each carbon atom in the following:

(a) CH_3CN,

(b) $CH_3CH=CH_2$,

(c) $H_3C—C\equiv C—CH_3$,

(d) $HC\equiv C—CH=CH_2$ **(IIT 1998)**

42. Draw the geometry of OSF_4 using VSEPR theory. **(IIT 2004)**

43. Arrange the following compounds/species in the order of O—O bond lengths. $O_2, O_2\,[AsF_4], [KO_2]$ **(IIT 2004)**

44. A solution containing 2.665 g of $CrCl_3 \cdot 6H_2O$ is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 2.87 g of AgCl. Deduce the structure of compound.

45. 1 g of the complex $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ was passed through a cation exchanger to produce HCl. The acid liberated was diluted to 1 litre. What is normality of this acid solution?

46. A solution containing 0.319 g of complex $CrCl_3 \cdot 6H_2O$ was passed through cation exchanger and the solution given out was neutralised by 28.5 mL of 0.125 M NaOH. What is the correct formula of complex?

47. Metal carbonyls having formula $M\,(CO)_x$, where x is the number of carbonyl units co-ordinated to metal M are formed by Fe, Cr and Ni. If effective atomic number of each metal is 36, what are the formula of metal carbonyls?

48. A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms (A) and (B). The form (A) reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia, whereas (B) gives a pale yellow precipitate soluble in concentrated ammonia. Write the formulae of (A) and (B) and state the hybridisation of chromium in each. Calculate their magnetic moments (Spin-only value). **(IIT 2009)**

49. Predict the number of water molecules (s) directly bonded to metal centre in $CuSO_4 \cdot 5H_2O$.

50. What is the co-ordination number of Al in the crystalline state of $AlCl_3$? **(IIT 2009)**

51. What type of hybridisation exists in BeF_2 in solid state?

52. Nitrogen forms oxides as N_2O, NO, NO_2, N_2O_3, N_2O_4 and N_2O_5. Which oxides contain N–N bonds? **(IIT 2009)**

SOLUTIONS (Numerical Problems)

1. Molar heat capacity $(\text{J mol}^{-1}\ \text{K}^{-1})$ = Atomic mass × specific heat $(\text{Jg}^{-1}\ \text{K}^{-1})$

Li(*s*) = $6.94 \times 3.57 = 24.78$
Na(*s*) = $22.99 \times 1.23 = 28.28$
K(*s*) = $39.10 \times 0.756 = 29.56$
Rb(*s*) = $85.47 \times 0.363 = 31.03$
Cs(*s*) = $132.91 \times 0.242 = 32.16$

There is a trend on plotting these values with atomic number, the extra polation of graph gives the value of $\text{Fr}(s) = 33.5\ \text{JK}^{-1}\ \text{mol}^{-1}$.

2. IE of Na $= 5.1\,\text{eV/atom} = 5.1 \times 6.023 \times 10^{23}\ \text{eV/mol}$

$= 5.1 \times 6.023 \times 10^{23} \times 1.602 \times 10^{-19}\ \text{J/mol}$

$= 492.091 \times 10^{3}\ \text{J/mol}$

∴ Energy required to convert 5 mole Na(*s*) to Na^+

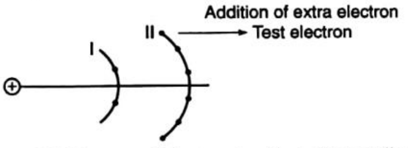
$= 5 \times 492.091 \times 10^{3}\ \text{J} = \mathbf{2.46 \times 10^{6}\ J}$

3. Mole of Cs atom $= \dfrac{7.974}{132.9} = 0.06$

∴ Energy required for 7.974 g Cs atom to form $\text{Cs}^+(g)$

$= 374 \times 0.06 = \mathbf{22.44\ kJ}$

4. **In N^--ion**

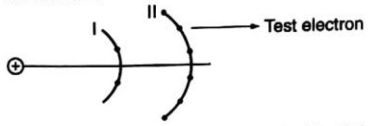


$\sigma = [(0.35 \times$ no. of electron in *n*th shell excluding valence electron) + $(0.85 \times$ no. of electrons in $(n-1)$th shell) + $(1.0 \times$ no. of electrons in inner shells)]

$\sigma = [0.35 \times 5] + [0.85 \times 2] = \mathbf{3.45}$

Effective nuclear charge $Z^* = Z - \sigma = 7 - 3.45 = \mathbf{3.55}$

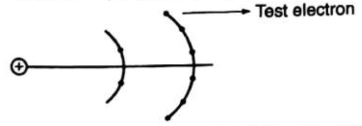
In N-atom



$\sigma = [0.35 \times 4] + [0.85 \times 2] = \mathbf{3.1}$

∴ Effective nuclear charge $= Z - \sigma = 7 - 3.1 = \mathbf{3.9}$

O-atom: $(1s^2)(2s^2 2p^4)$



$\sigma = [0.35 \times 5] + [0.85 \times 2] = \mathbf{3.45}$

∴ $Z^* = Z - \sigma = 8 - 3.45 = \mathbf{4.55}$

5. $_{10}\text{Ne} : (1s^2)(2s^2 2p^6)$
$_{11}\text{Na}^+ : (1s^2)(2s^2 2p^6)$
$_{9}\text{F}^- : (1s^2)(2s^2 2p^6)$

Thus, shielding constant σ is same for all these, *i.e.*, 4.15.

$Z^*_{\text{Ne}} = Z_{\text{Ne}} - \sigma = 10 - 4.15 = \mathbf{5.85}$
$Z^*_{\text{Na}^+} = Z_{\text{Na}^+} - \sigma = 11 - 4.15 = \mathbf{6.85}$
$Z^*_{\text{F}^-} = Z_{\text{F}^-} - \sigma = 9 - 4.15 = \mathbf{4.85}$

6. For Li, electronic configuration is $1s^2, 2s^1$, so given ionization energy value is for $(n = 2)$.

We know that: $E_n \dfrac{Z^2_{\text{eff}}}{n^2} \times E_1$

E_n = Energy of *n*th level, Z_{eff} = Effective nuclear charge, E_1 = Energy of first orbit of H-atom.

or $Z_{\text{eff}} = n \cdot \sqrt{\dfrac{E_n}{E_1}}$

Given $E_1 = -13.6\,\text{eV}$; $E_n = -5.39\,\text{eV}$ and $n = 2$

$Z = 2 \times \sqrt{\dfrac{5.39}{13.6}} = \mathbf{1.26}$

Thus, effective nuclear charge is 1.26 because 2*s*-electron is shielded by $1s^2$-electrons.

Also from Slater's rule $\sigma_{\text{Li}} = 0.85 \times 2 = 1.70$

$Z^*_{\text{Li}} = 3 - 1.70 = 1.30$

7. Mole of Cl atom $= \dfrac{1}{35.5}$

Thus energy released during

$\text{Cl} + e \longrightarrow \text{Cl}^-(g) = \dfrac{1}{35.5} \times 349 = \mathbf{9.83\ kJ}$

8. $\Delta H = 19 \times 10^{3}\ \text{cal/mol}$

$= 19 \times 10^{3} \times 4.18\ \text{J/mol} = \dfrac{19 \times 4.18 \times 10^{3}}{1.602 \times 10^{-19}}\ \text{eV/mol}$

$= \dfrac{19 \times 10^{3} \times 4.18}{1.602 \times 10^{-19} \times 6.023 \times 10^{23}}\ \text{eV/atom}$

$= 0.82\,\text{eV/atom}$

Also, $\Delta H = IE_1 + EA_1$

$0.82 = 4.3 + EA_1$

∴ $EA_1 = \mathbf{3.48\ eV/atom}$

9. ΔH/molecule of Li^+ and Cl^- $= \underset{\text{Li}}{IP_1} + \underset{\text{Cl}}{EA}$

$= 5.41 - 3.61 = 1.80\,\text{eV}$

∵ $\text{Li} \longrightarrow \text{Li}^+ + e \quad IP_1 = +\text{ve}$

and $\text{Cl} + e \longrightarrow \text{Cl}^- \quad EA = -\text{ve}$

∴ $\Delta H/\text{mol} = 1.8 \times 6.023 \times 10^{23}\ \text{eV}$

$= 1.8 \times 6.023 \times 10^{23} \times 1.602 \times 10^{-19}\ \text{J}$

$= 1.8 \times 6.023 \times 10^{23} \times 1.602 \times 10^{-19} \times 10^{-3}\ \text{kJ}$

$= \mathbf{173.7\ kJ}$

10.

$$X \longrightarrow X^+ + e; \qquad \Delta H = IP_1 = a\,\text{eV}$$

$$X + e \longrightarrow X^-; \qquad \Delta H = -EA_1 = -b\,\text{eV}$$

if $N/2$ atoms of X lose electrons which are taken up by remaining $N/2$ of X to give X^-, then

$$a \times \frac{N}{2} - b \times \frac{N}{2} = \frac{409 \times 10^3}{1.602 \times 10^{-19}}\,\text{eV}$$

or $$a - b = \frac{409 \times 10^3 \times 2}{1.602 \times 10^{-19} \times 6.023 \times 10^{23}}$$

$\therefore$ $$a - b = 8.477$$

Now, $N/2$ of X^- lose two electrons to give X^+

$$X^- \longrightarrow X + e; \qquad \Delta H = +EA_1 = +b$$

$$X \longrightarrow X^+ + e; \qquad \Delta H = +IP_1 = +a$$

$\therefore$ $$a \times \frac{N}{2} + b \times \frac{N}{2} = \frac{733 \times 10^3}{1.602 \times 10^{-19}}\,\text{eV}$$

or $$a + b = \frac{733 \times 10^3 \times 2}{1.602 \times 10^{-19} \times 6.023 \times 10^{23}}$$

$$a + b = 15.194$$

$\therefore$ $$a = \mathbf{11.835\ eV}$$

and $$b = \mathbf{3.358\ eV}$$

11. Formation of HeH_2 requires energy equal to sum of (i) energy for excitation from $1s^2$ to $1s^1 2s^1$ to form He singlet is equal to : [Energy needed for excitation from $1s^2$ to $1s^2 2p^1$–energy level difference in between $1s^1 2s^1$ and $1s^1 2p^1$]

Thus, E_{He} single $t = \frac{hc}{\lambda_1} - \frac{hc}{\lambda_2} = 3.40 \times 10^{-18} - 9.66 \times 10^{-20}\,\text{J}$

$$= \mathbf{3.30 \times 10^{-18}\ J / molecule}$$

where $\lambda_1 = 58.44 \times 10^{-9}$ m and $\frac{1}{\lambda_2} = 4857\,\text{cm}^{-1}$

(ii) energy to produce two mole of H, *i.e.*, $2 \times 218.0 = 436\,\text{kJ/mol}$

Thus, E for 2 mole bonds of He—H

$$= [3.30 \times 10^{-18} \times 6.023 \times 10^{23} + 436 \times 10^3]\,\text{J/mol}$$

$$= 2423.5\,\text{kJ mol}^{-1}$$

$\therefore E_{\text{He—H}} = \mathbf{1211.8\ kJ\ mol^{-1}}$

12. $$\text{Mole of Mg} = \frac{1}{24}$$

These mole of Mg will be converted to Mg^+ and Mg^{2+}. Let a mole of Mg^+ are formed, then

$$a \times 740 + \left(\frac{1}{24} - a\right) \times 2190 = 50$$

$\therefore$ $$a = 0.02845$$

$\therefore$ $$\% \text{ of } Mg^+ = \frac{0.02845}{1/24} \times 100 = \mathbf{68.28}$$

$$\% \text{ of } Mg^{2+} = \mathbf{31.72}$$

13. $$AlCl_3 + aq. \longrightarrow AlCl_3\,(aq.); \quad \Delta H = ?$$

ΔH = Energy released during hydration + Energy used during ionisation

$$= -4665 - 3 \times 381 + 5137 = -671$$

Thus, formation of ions will take place because $\Delta H_h > \Delta H_{\text{ionisation}}$.

14. Let the mixture contains a, b atoms of F and Cl respectively. Thus, total energy absorbed is:

$$284 = a \times 27.91 \times 10^{-22} + b \times 20.77 \times 10^{-22} \quad ...(1)$$

Also total energy released is:

$$-68.8 = a \times (-5.53 \times 10^{-22}) + b \times (-5.78 \times 10^{-22})$$

or $$68.8 = 5.53 \times 10^{-22} \times a + 5.78 \times 10^{-22} \times b \quad ...(2)$$

By Eqs. (1) and (2),

$\therefore$ $$a = 4.57 \times 10^{22}$$

$$b = 7.53 \times 10^{22}$$

$\therefore$ $$\% \text{ of F} = \left[\frac{4.57 \times 10^{22}}{4.57 \times 10^{22} + 7.53 \times 10^{22}}\right] \times 100 = \mathbf{37.76}$$

$$\% \text{ of Cl} = \mathbf{62.24}$$

15. Given $H \longrightarrow H^+ + e; \quad IE_1 = 13.6\,\text{eV}$

$$He \longrightarrow He^+ + e; \quad IE_1 = 24.6\,\text{eV}$$

We have to determine the values of

$$He^{2+} + e \longrightarrow He^+; \quad \Delta H = a$$

$$\underline{He^+ + e \longrightarrow He; \quad \Delta H = b}$$

$$He^{2+} + 2e \longrightarrow He; \quad \Delta H = (a + b)$$

The IE_1 of $He^+ = IE_{1H} \times 2^2 = 13.6 \times 4 = 54.4\,\text{eV}$

$\therefore$ $$a = -54.4\,\text{eV}$$

Also for $He^+ + e \longrightarrow He; \quad IE_1 = 24.6\,\text{eV}$

$\therefore$ $$b = -24.6\,\text{eV}$$

Thus, Total energy given out $= a + b = -54.4 + (-24.6)$

$$= \mathbf{-79\ eV}$$

16. Li : $1s^2, 2s^1 \therefore n = 2$

Also $$E_{\text{Li}} = \frac{Z^2}{n^2} \times E_{\text{H}}$$

where Z is effective charge

$\therefore$ $$Z = n\sqrt{\frac{E_{\text{Li}}}{E_{\text{H}}}} = 2 \times \sqrt{\frac{5.40}{13.6}} = \mathbf{1.26}$$

Thus effective charge is 1.26 because $2s$ electron is shielded by $1s^2$ electrons.

17. Let X_{H} and X_{F} be the electronegativity of H and F, then

$$X_{\text{H}} \sim X_{\text{F}} = 0.208\,[E_{\text{H—F}} - (E_{\text{H--H}} \times E_{\text{F—F}})^{1/2}]^{1/2}$$

$$X_{\text{H}} \sim X_{\text{F}} = 0.208\,[134.6 - (104.2 \times 36.6)^{1/2}]^{1/2}$$

$$X_{\text{H}} \sim X_{\text{F}} = 1.78 \text{ and } X_{\text{H}} < X_{\text{F}}$$

Since, $X_{\text{H}} = 2.1$ (although this value is not given in problem)

$$X_{\text{F}} = 2.1 + 1.78 = \mathbf{3.88}$$

18. The various equations to calculate electronegativity (X) are as:

$$\text{Mulliken scale } X_M = \frac{IE + EA}{2} \qquad ...(1)$$

where IE and EA are in eV

Pauling values are $\frac{1}{2.8}$ times lesser than Mulliken value

$$X_P = 0.336[X_M - 0.615] \qquad ...(2)$$

$$\text{By eq. (1)} \therefore \quad X_P = \frac{IE + EA}{2 \times 2.8} = \frac{IE + EA}{5.6} \qquad ...(3)$$

Also if IE and EA are in kJ mol^{-1} then by Eq. (1)

$$X_M = \frac{IE + EA}{2 \times 96.48} = \frac{IE + EA}{192.96} \qquad ...(4)$$

$$\text{and} \qquad X_P = \frac{IE + EA}{2 \times 2.8 \times 96.48} = \frac{IE + EA}{540.28} \qquad ...(5)$$

Thus, electronegativity of F on Pauling scale

$$= \frac{17.42 + 3.45}{5.6} = \mathbf{3.73}$$

Electronegativity of F on Mulliken scale

$$= \frac{17.42 + 3.45}{2} = \mathbf{10.435}$$

19. Electronic configuration of Si : $1s^2, 2s^2 2p^6, 3s^2 3p^2$

$Z_{\text{effective}} = Z - \sigma$ (where σ is screening constant) and

$\sigma = [ns$ and np electrons excluding test electron $\times 0.35]$
$+ [(n-1)$ electrons $\times 0.85] + [(n-2)$ electrons $\times 1.0]$

$Z = 14 - [3 \times 0.35 + 8 \times 0.85 + 2 \times 1.0] = 4.15$

$$\therefore \qquad X = \frac{0.359 \times 4.15}{(1.175)^2} + 0.744 = \mathbf{1.82}$$

(**Note :** if $n = 1$ then for $1s$ electron the value = $1s$ electrons $\times 3.0$)

20. The zero gp. members are He, Ne, Ar, Kr, Xe, Rn. Law of triad suggests that property of a middle element in a group of three is average of its two adjacent elements.

$$\therefore \text{ b. pt. of Xe} = \frac{\text{b. pt. of Kr} + \text{b. pt. of Rn}}{2}$$

$$= \frac{-152 + (-62)}{2} = -\frac{214}{2} = \mathbf{-107°C}$$

21.

$$\underset{\text{(Dipole moment)}}{\mu_{\text{HCl}}} = \delta \times d$$

$\because \qquad \mu = 1.03\text{ D} = 1.03 \times 10^{-18}$ esu cm

and $\qquad d = 1.275\text{ Å} = 1.275 \times 10^{-8}$ cm

$\therefore \qquad 1.03 \times 10^{-18} = \delta \times 1.275 \times 10^{-8}$

$\therefore \qquad \delta = 0.808 \times 10^{-10}$ esu

$\because \; 4.803 \times 10^{-10}$ esu charge, % ionic nature of HCl = 100

$\therefore \; 0.808 \times 10^{-10}$ esu charge, % ionic nature of HCl

$$= \frac{100 \times 0.808 \times 10^{-10}}{4.803 \times 10^{-10}} = \mathbf{16.82\%}$$

22.

$$\mu_{\text{molecule}} = \delta \times d$$

$\therefore \qquad 1.964 \times 10^{-29} = \delta \times 1.596 \times 10^{-10}$

$\therefore \qquad \delta = 1.2306 \times 10^{-19}$ coulomb

$\therefore \qquad$ % of ionic nature

$$= \frac{1.2306 \times 10^{-19}}{1.602 \times 10^{-19}} \times 100 = \mathbf{76.82\%}$$

23. Dipole moment $\mu = \delta \times d$

$\therefore \quad 3.336 \times 10^{-29} = \delta \times 2.6 \times 10^{-10}$

$$\therefore \qquad \delta = \frac{3.336 \times 10^{-29}}{2.6 \times 10^{-10}} = 1.283 \times 10^{-19} \text{ coulomb}$$

$\because \; 1.602 \times 10^{-19}$ charge on each, % character = 100

$\therefore \; 1.283 \times 10^{-19}$ charge on each, % character

$$= \frac{1.283 \times 10^{-19}}{1.602 \times 10^{-19}} \times 100 = 80.09\%$$

If one unit charge, then $\delta = 1.602 \times 10^{-19}$ C

$$\therefore \qquad \mu = 1.602 \times 10^{-19} \times 2.6 \times 10^{-10}$$

$$= \mathbf{4.1652 \times 10^{-29}} \textbf{ coulomb metre.}$$

24. $$\delta = \frac{\text{Dipole moment}}{d} = \frac{1.2 \times 10^{-18} \text{ esu cm}}{1.0 \times 10^{-8} \text{ cm}} = 1.2 \times 10^{-10} \text{ esu}$$

Thus, fraction of electronic charge on each end

$$= \frac{1.2 \times 10^{-10}}{4.8 \times 10^{-10}} = 0.25 = \mathbf{25\% \text{ of '}e\text{'}}$$

25.

$$\mu = \sqrt{\mu_1^2 + \mu_1^2 + 2\mu_1\mu_1 \cos\alpha}$$

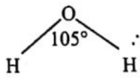
In H_2O only two dipoles equal to μ_1 are operating due to two O—H bonds.

Thus, $\qquad 1.84 = \sqrt{(1.5)^2 + (1.5)^2 + 2 \times (1.5) \times (1.5) \cos\alpha}$

$\therefore \qquad \cos\alpha = -0.2476$

$\therefore \qquad \alpha = \mathbf{104°20'}$

26.



$$\therefore \mu_{H_2O} = \sqrt{\mu_{\text{OH}}^2 + \mu_{\text{OH}}^2 + 2\mu^2 \cos(105°)}$$

Since, H_2O has two vectors of O—H bond acting at 105°. Let dipole moment of O—H bond be 'a'

$$\therefore \qquad 1.85 = \sqrt{2a^2(1 + \cos 105°)}$$

or $\quad a$, *i.e.*, $\mu_{\text{O—H}} = 1.52$ debye $= 1.52 \times 10^{-18}$ esu cm

Now $\qquad M_{\text{O—H}} = \delta \times d \quad$ where, δ is charge on either end

$\therefore \qquad 1.52 \times 10^{-18} = \delta \times 0.94 \times 10^{-8}$

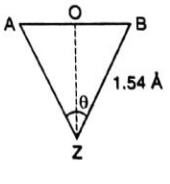
$\therefore \qquad \delta = 1.617 \times 10^{-10}$ esu

Since, O acquires 2δ charge, one δ charge from each bond and thus,

Charge on O atom $= 2\delta = 2 \times 1.617 \times 10^{-10}$

$$= \mathbf{3.23 \times 10^{-10}} \textbf{ esu cm}$$

27. The angle $\theta = 109°28'$ and $ZB = AZ = 1.54$ Å



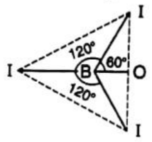
Now, $\frac{AO}{AZ} = \sin\left(\frac{\theta}{2}\right) = \sin\left(\frac{109^\circ 28'}{2}\right)$

$= \sin 54^\circ 44' = \sin 54.73^\circ$

or $AO = 0.816 \times AZ = 0.816 \times 1.54 = 1.257$ Å

$\therefore$ $AB = 2 \times AO = 1.257\text{Å} \times 2 = \mathbf{2.514}$ **Å**

28. The BI_3 molecule is coplaner in nature as shown in figure.



$\frac{IO}{BI} = \sin 60^\circ$

or $IO = BI \sin 60^\circ$

$\frac{3.54}{2} = BI \times 0.867$

$\therefore$ $BI = 2.04$ Å

$\therefore$ Covalent radius of boron = BI − covalent radius of I

$= 2.04 - 1.33 = \mathbf{0.71}$ **Å**

29. $\because$ $PV = \frac{w}{M}RT$

or $P = \frac{w}{V \cdot M}RT$

or $M = \frac{dRT}{P} = \frac{3.17 \times 0.0821 \times 300}{1} = \mathbf{78.08\ g\ mol^{-1}}$

molar mass of HF in gaseous state is 78.08, whereas its normal molar mass is $1 + 18 = 19\,\text{g mol}^{-1}$.

Thus, HF in gaseous state forms a tetramer due to strong H-bonding.

30. Volume of $F_{(g)} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times \pi \times (72)^3 = 1.56 \times 10^6$

Volume of $F^-_{(g)} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times \pi \times (136)^3 = 10.53 \times 10^6$

$\therefore$ $\frac{V_{F^-}}{V_F} = \frac{(136)^3}{(72)^3} = 6.74$

Also increase in volume $= (10.53 - 1.56) \times 10^6 = 8.97 \times 10^6$

$\therefore$ % increase $= \frac{8.97 \times 10^6}{1.56 \times 10^6} \times 100 = \mathbf{5.75 \times 10^2}$

31. CO_2 is $O{=}C{=}O$

Thus, O to O bond length in CO_2 can be given as

$2.323 = 2 \times$ radius of $(O{=}) + 2 \times$ radii of $(C{=})$

$2.323 = 2 \times$ radius of $(O{=}) + 2 \times 0.67$

$\therefore$ radius of $(O{=}) = \mathbf{0.49}$ **Å**

32. Volume of $Li^+ = \frac{4}{3}\pi \times (0.76 \times 10^{-8})^3$

Volume of $Li = \frac{4}{3}\pi \times (1.23 \times 10^{-8})^3$

$\therefore$ Volume occupied by 2*s* '*e*'

$= \frac{4}{3}\pi \times [(1.23 \times 10^{-8})^3 - (0.76 \times 10^{-8})^3]$

$= \frac{4}{3}\pi \times 1.422 \times 10^{-24}$

$\therefore$ % Volume occupied by 2*s* '*e*'

$$= \frac{\frac{4}{3}\pi \times 1.422 \times 10^{-24} \times 100}{\frac{4}{3}\pi \times (1.23 \times 10^{-8})^3}$$

$= 76.45$

33. Total strength of all hydrogen bonds

$= 30.8 - 14.4 = 16.4$ kJ / mol

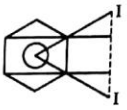
There are 6 nearest neighbours, but each hydrogen bond involves 2 ammonia molecules.

$\therefore$ Strength of each H-bond in solid NH_3

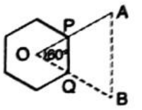
$= \frac{16.4}{3} = \mathbf{5.5}$ **kJ / mol**

34. (a) ***o*-di-iodobenzene:**

The distance between two I atoms $AB = AO = OB$, because ΔAOB is equilateral triangle.



or



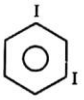
$\therefore$ $AB = OP + PA$

$\therefore$ $AB = OP +$ covalent radius of C + covalent radius of I

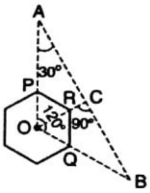
$= OP + 1.33 + 0.77 = 1.40 + 1.33 + 0.77$

$AB = \mathbf{3.50}$ **Å** ($OP = OQ = PQ$, because ΔOPQ is also equilateral triangle and $PQ = C{-}C$ bond length)

(b) ***m*-di-iodobenzene:**



or



The distance between two I atoms is

$AB = AC + BC = 2AC$ $(\because AC = BC)$

$= 2AO \cos 30^\circ = 2(AP + OP)\cos 30^\circ$

$= 2(AP + PR)\cos 30^\circ$

$(OP = PR$ $\because \Delta POR$ is equilateral)

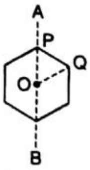
$= 2(2.10 + 1.40) \times 0.866$

$= \mathbf{6.06}$ **Å**

[$\because$ AP = covalent radius of C + covalent radius of I = 0.77 + 1.33 = 2.10 Å and PR = covalent bond length of C—C = 1.40]

(c) ***p*-di-iodobenzene:**

or



$\therefore$ $AB = OA + OB = 2OA$

$= 2(OP + PA)$

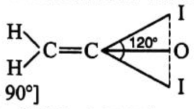
$= 2 \times (PQ + PA)$

$(\because OP = PQ;\ \Delta OPQ$ is equilateral)

$= 2\,(PQ + \text{covalent radius of C} + \text{covalent radius of I})$

$= 2 \times (1.40 + 0.77 + 1.33) = \mathbf{7.0\ Å}$

35. $CH_2 = CI_2$ has sp^2-hybridised carbon and thus ICI bond angle is 120°.



$\therefore \quad \frac{IO}{CI} = \sin 60°$

[In Δ $ICO \angle ICO = 60°$ and $\angle IOC = 90°$]

or $\quad IO = CI \sin 60° = 2.10 \times 0.866 = 1.8186\ Å$

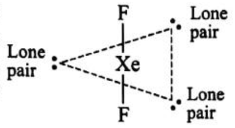
$\therefore \quad$ I—I distance $= 2 \times 1.8186 = \mathbf{3.64\ Å}$

36. (a) sp (b) sp^2 (c) sp^3d^2 (d) sp^2 (e) sp (f) sp^2 (g) sp^3 (h) sp^3d^2 (i) sp^3d (j) sp^2 (k) sp^3 (l) sp^3d^2 (m) sp^3 (n) sp^3 (o) sp^3d (p) sp^3 (q) sp^2.

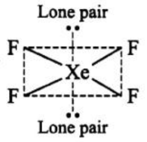
37. (a) sp^2, sp, sp^2 (b) sp^2, sp, sp, sp^2

(c) sp^3; sp^2 on all four carbon of CN.

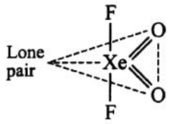
38. **XeF_2 :** Xe is in sp^3d-hybridised state having three lone pair of electrons located equationally and thus, shape is linear.



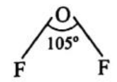
XeF_4 : Xe is in sp^3d^2-hybridised state having two lone pair of electrons located axially and thus, shape is square planar.



XeO_2F_2 : Xe is in sp^3d^3-hybridised state having one lone pair of electron at equatorial position and thus, shape is distorted trigonal pyramidal.



39. The structure of OF_2 is V-shape due to sp^3-hybridisation of oxygen with two lone pair of electrons on it.
Oxidation number of O and F are +2 and −1 respectively.



40. MO configuration of $O_2 : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \pi 2p_y^2, \pi 2p_z^2, \pi^* 2p_y^1, \pi^* 2p_z^1$.

Bond order $= \frac{1}{2}$ [No. of bonding electron − No. of antibonding electron]

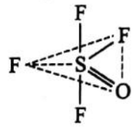
$= \frac{1}{2}[10 - 6] = 2$

Also O_2 is paramagnetic as it has two unpaired electrons.

41. (a) sp^3 and sp, (b) sp^3, sp^2 and sp^2

(c) sp^3, sp, sp and sp^3 (d) sp, sp, sp^2 and sp^2

42. S atom in OSF_4 shows sp^3d^2-hybridisation leading to trigonal bipyramidal geometry but distorted due to S $=$ O bond. The F atoms are at axial and equatorial positions whereas oxygen being less electronegative occupies one of the three equatorial positions.



43. The MO configuration of O_2, O_2^+ in $O_2[AsF_4]$ and O_2^- in $K^+O_2^-$ are:

$$O_2 : \ \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2 \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix} \begin{matrix} \pi^* \ 2p_y^1 \\ \pi^* \ 2p_z^1 \end{matrix}$$

$$O_2^+ : \ \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2 \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix} \pi^* \ 2p_y^1$$

$$O_2^- : \ \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2 \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix} \begin{matrix} \pi^* \ 2p_y^2 \\ \pi^* \ 2p_z^1 \end{matrix}$$

Thus, bond orders and bond length are:

Species	O_2	O_2^+	O_2^-
Bond order	2	2.5	1.5

Bond length $\quad O_2^+ < O_2 < O_2^-$

Higher is the bond order, lesser is bond length.

44. Mole of AgCl obtained

$=$ mole of Cl^- ions ionised from $\frac{2.665}{266.5}$ mole of $CrCl_3 \cdot 6H_2O$

$= 0.01$ (molar mass of $CrCl_3 \cdot 6H_2O = 266.5$)

$\therefore \quad$ Mole of Cl^- ionised $= \frac{2.87}{143.5} = 0.02$

Thus, 0.01 mole of complex $CrCl_3 \cdot 6H_2O$ gives 0.02 mole of Cl^- on ionisation.

Now, since co-ordination number of Cr is six and only one Cl ion is attached to Cr by co-ordinate bond or secondary valency and therefore, complex is $[CrCl \cdot (H_2O)_5]Cl_2 \cdot H_2O$.

$$[CrCl \cdot (H_2O)_5]Cl_2 \cdot H_2O \longrightarrow [CrCl(H_2O)_5]^{2+} + 2Cl^- + H_2O$$

$$2Cl^- + 2AgNO_3 \longrightarrow 2AgCl + 2NO_3^-$$

45. Molar mass of $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O = 266.5$

$\therefore \quad$ Mole of complex $= \frac{1}{266.5}$

Note : 1 mole of $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ will give 2 mole of Cl^- ions or 2 mole of HCl.

Thus, $\quad$ mole of HCl formed $= \frac{2 \times 1}{266.5}$

$\therefore \quad N_{HCl} = \frac{2 \times 1}{266.5 \times 1} = \mathbf{0.0075}$

46. The Cl atoms out side the co-ordination sphere will be ionised to produce acid HCl.

Thus, Meq. of Cl^- ions outside $=$ Meq. of HCl formed

$=$ Meq. of NaOH used

$= 28.5 \times 0.125 = 3.56$

$\frac{0.319}{266.5}$ mole or 1.197 *m* mole of complex produce 3.56 Meq. or millimole small of Cl^-.

Thus, 1 mole of complex will give 3 mole of Cl^-, *i.e.*, all the three Cl atoms are outside the co-ordination sphere.

Thus, complex is $\mathbf{[Cr(H_2O)_6]Cl_3}$.

47. $M(CO)_x$

In $Fe(CO)_x$: EAN = At. no. of Fe + 2 × No. of ligands, *i.e.*, CO

$\therefore \quad 36 = 26 + 2 \cdot x$

$\therefore \quad x = 5$

$\therefore$ Formula of iron carbonyl is $\mathbf{Fe(CO)_5}$

Similarly, $\mathbf{Cr(CO)_6}$ and $\mathbf{Ni(CO)_4}$.

48. Complex $Cr(NH_3)_4Cl_2Br$ has two isomers. Since, co-ordination number of Cr is six and thus, two forms may be :

$$\underset{(B)}{[Cr(NH_3)_4Cl_2]Br} \xrightarrow{AgNO_3} [Cr(NH_3)_2Cl_2]^+ + NO_3^- + AgBr\downarrow$$

yellow ppt. soluble partially in conc. NH_3, *i.e.*, $[Ag(NH_3)_2]Br$

and $$\underset{(A)}{[Cr(NH_3)_4Br \cdot Cl]Cl} \xrightarrow{AgNO_3} [Cr(NH_3)_4ClBr]^+ + NO_3^- + AgCl\downarrow$$

white ppt. soluble in dil. NH_3, *i.e.*, $[Ag(NH_3)_2]Cl$

Hybridisation of Cr in (*A*) and (*B*) is d^2sp^3 having 3 unpaired electrons ($3d^3$).

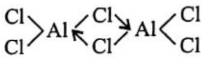
Magnetic moment = $\sqrt{n(n+2)}$ B. M.

$= \sqrt{3(3+2)} = \mathbf{3.87\ B.\ M.}$

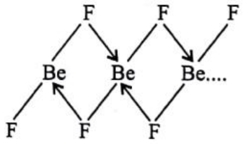
49. Cu^{2+} has coordination number four

$[Cu(H_2O)_4] \cdot SO_4 \cdot H_2O$.

50. In solid state $AlCl_3$ exists as Al_2Cl_6 and has co-ordination number four.

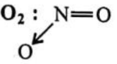


51. In solid state BeF_2 exists as $(BeF_2)_n$. The hybridisation in $(BeF_2)_n$ is sp^3.

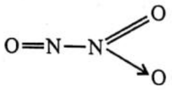


52. N_2O, N_2O_3, N_2O_4, $\mathbf{N_2O}$: $N \equiv N \rightarrow O$, **NO**: $N = O$,

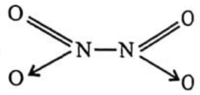
$\mathbf{NO_2}$:



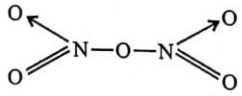
$\mathbf{N_2O_3}$:



$\mathbf{N_2O_4}$:

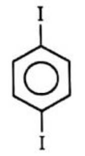


$\mathbf{N_2O_5}$:



• SINGLE INTEGER ANSWER PROBLEMS •

1. Number of σ bonds in $C(CN)_4$ are ......
2. Number of equitorial bonds in PCl_5 are ......
3. The ratio of *s*-character in *sp* and sp^3 hybridization is ......
4. Number of lone pair of electrons in $XeOF_4$ are ......
5. Number of shell in which valence electrons of iodine lies ......
6. Number of electron pairs in SF_6 at the corners of octahedron are ......
7. Number of electron pairs in XeF_4 at the corners of square are ......
8. Bond order of BN is ......
9. Maximum number of atoms which can be attached on N-atom is ......
10. Assuming C_6H_6 ring a regular hexagon and C—I bond lies on the line through the centre of hexagon. If the distance between adjacent carbon is 1.40 Å and covalent radius of iodine and carbon atoms are 1.33Å and 0.77Å. The I—I distance in Å is ......



11. The dipole moment of *AB* is 1.6×10^{-30} C-m. If intermolecular distance is 2.0×10^{-10} m, the % ionic character of *AB* is ......
12. Bond order for CO is ......
13. Ratio of bond pair-lone pair electrons in $XeOF_2$ is ......
14. Number of unpaired electrons in $O_2[AsF_4]$ is ......
15. Bond order of NO^+ is ......
16. Number of lone pairs of electrons on central iodine atom of I_3^- ion is ......
17. AX_n possess trigonal bipyramidal shape. If *A* has no lone pair, the value of *n* is ......
18. XeO_4 shows maximum oxidation state (+8). If Xe reacts with fluorine atom, the maximum oxidation state shown by Xe is + ...
19. Ratio of number of bond pair and lone pair in IF_4^- is ......
20. Number of hybridised orbitals populated with bonding electron pairs in ICl_2^- are ......
21. Ratio of σ and π bonds in OSF_4 is ......
22. Number of nearest neighbours of NH_3 molecules round each molecule in solid NH_3 are ......
23. Based on VSEPR theory, number of 90 degree F—Br—F bonds in BrF_5 is ...... **(IIT 2010)**
24. The ratio of shielding constant for Ne and Na^+ is.....
25. Bond order of CO is.....
26. The ratio of bond order in O_2^{2+} and O_2^- is.....
27. The number of anti bonding electrons in N_2^- is.....
28. The ratio of *p*-character and *s*-character in solid BeF_2 is.....
29. The number of σ -bonds in C $(CN)_4$.....
30. Number of lone pair of electrons on central atom of I_3^-.....
31. The ratio of σ and π-bonds in tetracyano methane is.....
32. Number of 90° F—Xe—F bond angles in XeF_4 is.....
33. Number of 90° F—I—F bond angles in IF_5 is.....
34. Number of covalent bonds in Al_2Cl_6 is ......
35. The number of three centre two electrons bonds in a molecule of diborane is ......
36. The ratio of σ -bond and π-bond in tetracyano methane is ......
37. Number of S–S bonds in cyclic trimer of SO_3 is ......
38. Ratio of number of σ -bonds and S–O–S bonds in trimer of SO_3 is ......
39. Number of π -bonds in trimer of SO_3 is ......
40. $H_2S_5O_6$ a polythionic acid on decomposition gives sulphur molecules equal to ......
41. The ratio of P—O and P = O bonds in P_4O_{10} is ......
42. Number of S—S bonds in $H_2S_5O_6$ is ......
43. Number of identical Cr – O bonds in $Cr_2O_7^{2-}$ ion is ......
44. The ratio of σ and π-bonds in benzene is ......

ANSWERS

1. Eight **2.** Three **3.** Two **4.** One **5.** Five **6.** Six **7.** Four **8.** Two **9.** Four **10.** Seven **11.** Five **12.** Three
13. Two **14.** One **15.** Three **16.** Three **17.** Five **18.** Six **19.** Two **20.** Two **21.** Five **22.** Six **23.** Zero **24.** One
25. Three **26.** Two **27.** Five **28.** Three **29.** Eight **30.** Three **31.** One **32.** Four **33.** Eight **34.** Six **35.** Two **36.** One
37. Zero **38.** Four **39.** Six **40.** Three **41.** Three **42.** Four **43.** Six **44.** Four

OBJECTIVE PROBLEMS (One Answer Correct)

1. Shielding constant σ for Ne is 4.15. The effective nuclear charge on Na^+ and F^- are respectively :

(a) 4.85, 6.85 (b) 5.85, 6.85

(c) 6.85, 4.85 (d) 4.85, 4.85

2. Electron gain enthalpy and ionisation energy of an atom are $-a$ and $+b$ eV respectively. The electronegativity of that atom on Mulliken scale is given by :

(a) $a - b$ (b) $\frac{b-a}{2}$

(c) $a + b$ (d) $\frac{a+b}{2}$

3. The atomic radii of Li is 1.23 Å and ionic radius of Li^+ is 0.76 Å. The fraction of the volume occupied by 2*s* electron in Li is :

(a) 0.764 (b) 0.184

(c) 0.595 (d) 0.236

4. Photons of monochromatic light having just sufficient energy to ionise Ar-atom are incidented over the mixture of inert gases He, Ne, Ar, Kr and Xe. The mixture will contain:

(a) He, Ne, gases; Ar^+, Kr^+, Xe^+ ions

(b) He^+, Ne^+ ions; Ar, Kr, Xe gases

(c) He^+, Ne^+, Ar^+, Kr^+ and Xe^+ ions

(d) He^+, Ne^+, Ar^+ ions and Kr, Xe gases

5. If EA_1 and EA_2 for oxygen atom are -142 kJ mol^{-1} and $+844$ kJ mol^{-1}. The energy released to form $2O + 2e \longrightarrow 2O^-$ will be : (in kJ mol^{-1})

(a) 986 (b) 702

(c) 284 (d) 1688

6. Dipole moment of K^+Cl^- is 3.336×10^{-29} cm and it is 80% ionic in nature. The inter ionic distance between K^+ and Cl^- is :

(a) 1.30 Å (b) 2.60 Å

(c) 3.9 Å (d) 1.20 Å

7. Bond order for CO^+ and NO^+ are respectively :

(a) 3.5, 3.0 (b) 2.5, 3.0

(c) 2.5, 2.5 (d) 3.0, 2.5

8. Bond order for N_2^+ and N_2^- are same. Which relation is correct for N_2^+ and N_2^-?

(a) Bond energy of N_2^+ = Bond energy of N_2^-

(b) Bond energy of N_2^+ > Bond energy of N_2^-

(c) Bond energy of N_2^+ < Bond energy of N_2^-

(d) Bond energy of $N_2^+ \gtrless$ Bond energy of N_2^-

9. The electron gain enthalpy of fluorine atom is 333 kJ mol^{-1} and dissociation energy of F_2 is 158.8 kJ mol^{-1}. Energy released during formation of 2 g F^- from 2 g F_2 (atomic mass 40) is :

(a) 33.3 kJ (b) 7.94 kJ

(c) 25.36 kJ (d) 41.24 kJ

10. The ionisation energy of lithium is 5.40 eV. If ionisation energy of H-atom is 13.6 eV, the effective charge acting upon outermost shell of Li is :

(a) 1.26 (b) 2.52

(c) 0.63 (d) 3.0

11. Which of the molecule is hypovalent but has complete octet?

(a) $AlCl_3$ (b) PH_3

(c) PCl_3 (d) SF_4

12. Which of the molecule does not possess hypervalent nature?

(a) IF_7 (b) SF_4

(c) BF_3 (d) SF_6

13. The species not having same bond order is :

(a) N_2^+ (b) O_2^+

(c) NO (d) NO^+

14. Least basic trihalide is :

(a) NF_3 (b) NCl_3

(c) NBr_3 (d) NI_3

15. Least acidic trihalide is :

(a) BF_3 (b) BCl_3

(c) BBr_3 (d) BI_3

16. During the reaction : $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$; the hybridised state of carbon changes from :

(a) sp^2 to sp (b) sp to sp^2

(c) sp^3 to sp (d) sp to sp^3

17. Which of the following is T-shaped?

(a) $XeOF_2$ (b) XeO_3

(c) $XeOF_4$ (d) XeF_4

18. Number of sigma bonds and double bonds in P_4O_{10} are respectively :

(a) 12, 4 (b) 6, 4

(c) 8, 2 (d) 10, 4

19. Which of the following is not correct for P_4O_{10} and P_4O_6?

(a) Both are acidic anhydride

(b) Both have sp^2-hybridised P-atoms

(c) Both have P — O — P bonds

(d) Both have six P — O — P bonds

20. A planar molecule has AB_X structure with six pairs of electrons around A and one lone pair. The value of X is :
(a) 2 (b) 4
(c) 6 (d) 7

21. Among the following species, identify the isostructural pairs:

$NF_3, NO_3^-, BF_3, H_3O^+, HN_3$

(a) $[NF_3, NO_3^-]$ and $[BF_3, H_3O^+]$
(b) $[NF_3, HN_3]$ and $[NO_3^-, BF_3]$
(c) $[NF_3, H_3O^+]$ and $[NO_3^-, BF_3]$
(d) $[NF_3, H_3O^+]$ and $[HN_3, BF_3]$

22. The two carbon atoms in calcium carbide are held by which of the following bonds :
(a) three sigma bonds
(b) ionic bonds
(c) two pi and one sigma bonds
(d) ionic and covalent bonds

23. Arrange the following compounds in order of increasing dipole moment : Toluene (I); *m*-dichlorobenzene (II); *o*-dichlorobenzene (III); *p*-dichlorobenzene (IV)
(a) I < IV < II < III (b) IV < I < II < III
(c) IV < I < III < II (d) IV < II < I < III

24. Among KO_2, AlO_2^-, BaO_2 and NO_2^+, unpaired electron is present in :
(a) NO_2^+ and BaO_2 (b) KO_2 and AlO_2^-
(c) KO_2 only (d) BaO_2 only

25. Which contains both polar and non-polar bonds :
(a) NH_4Cl (b) HCN
(c) H_2O_2 (d) CH_4

26. Which has sp^2-hybridization :
(a) CO_2 (b) SO_2
(c) N_2O (d) CO

27. The critical temperature of water is higher than that of O_2 because the H_2O molecule has :
(a) fewer electrons than O_2
(b) two covalent bonds
(c) V-shape
(d) dipole moment

28. The geometry and the type of hybrid orbitals present about the central atom in BF_3 is :
(a) linear, *sp* (b) trigonal planar, sp^2
(c) tetrahedral sp^3 (d) pyramidal, sp^3

29. The geometry of H_2S and its dipole moment are :
(a) angular and non-zero (b) angular and zero
(c) linear and non-zero (d) linear and zero

30. In compounds of type ECl_3, where E = B, P, As and Bi the angles Cl — E — Cl for different E are in the order :
(a) B > P = As = Bi (b) B > P > As > Bi
(c) B < P = As = Bi (d) B < P < As > Bi

31. In the compound $CH_2 = CH - CH_2 - CH_2 - C \equiv CH$, the $C_2 - C_3$ bond is of the type :
(a) sp-sp^2 (b) sp^3-sp^3
(c) sp-sp^3 (d) sp^2-sp^3

32. Which of the following shows biggest jump in II and III ionisation energy:
(a) $1s^2, 2s^2 2p^6, 3s^2$
(b) $1s^2, 2s^2 2p^6, 3s^2 3p^2$
(c) $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 4p^2$
(d) $1s^2, 2s^2$

33. Which of the following possesses highest second ionisation energy:
(a) $1s^2, 2s^2 2p^6, 3s^2$ (b) $1s^2, 2s^2 2p^6, 3s^1$
(c) $1s^2, 2s^2 2p^3$ (d) $1s^2, 2s^2 2p^4$

34. EA_1 of element is:
(a) always exothermic
(b) always endothermic
(c) may be exothermic or endothermic
(d) always zero

35. Element having highest I.E. but zero electron gain enthalpy:
(a) H (b) F
(c) He (d) B

36. The second electron gain enthalpy of O and S (in $kJ\ mol^{-1}$) respectively are :
(a) −844, +590 (b) +590, +844
(c) +844, +590 (d) −590, +844

37. Which factor is responsible to make Li as a powerful reducing agent:
(a) Electronegativity (b) Ionisation energy
(c) Electron gain enthalpy (d) Hydration energy

38. The first electron gain enthalpy of which pair is not correctly represented by:
(a) O > S (b) Cl > F
(c) N > P (d) B > C

39. Which of the following factors does not influence the covalent character in molecule:
(a) size of cation
(b) size of anion
(c) pseudo inert gas configuration of cation
(d) bond energy

40. If the formation of O^{2-} from O^- atom is shown below

$$O(g) + e \rightarrow O^-(g)\ ; \Delta H = -142\ k\ J\ mol^{-1}$$

$$O^-(g) + e \rightarrow O^{2-}(g)\ ; \Delta H = +844\ k\ J\ mol^{-1}$$

then which of the following statements are correct:

(a) $O(g) \rightarrow O^{2-}(g)$; $\Delta H = 702 \text{ k J mol}^{-1}$
(b) O^- ion opposes further addition of electron
(c) EA_2 of O > EA_1 of O
(d) All of these

41. The correct order of II ionisation energy shown in correct order is:
(a) $F > O > N > C$
(b) $C > N > O > F$
(c) $O > N > F > C$
(d) $O > F > N > C$

42. The correct order of increasing electron affinity of the following is:
(a) $O < S < F < Cl$
(b) $O < S < Cl < F$
(c) $S < O < F < Cl$
(d) $S < O < Cl < F$

43. Shielding constant of Ne is 4.15, the shielding constant of Na^+ would be:
(a) 4.15
(b) 3.70
(c) 5.20
(d) 6.20

44. First ionisation energy of Li and K are 5.4 and 4.3 eV respectively, approximate ionisation energy of Na will be:
(a) 8.7 eV
(b) 1.1 eV
(c) 4.9 eV
(d) 2.2 eV

45. Which of the following has the highest electron releasing tendency:
(a) F^-
(b) OH^-
(c) NH_2^-
(d) CH_3^-

46. The compound which contains both ionic and covalent bonds is:
(a) CH_4
(b) H_2
(c) KCN
(d) KCl

47. The octet rule is not valid for the molecule:
(a) CO_2
(b) H_2O
(c) O_2
(d) CO

48. Element X is strongly electropositive and element Y is strongly electronegative. Both are univalent. The compound formed would be:
(a) X^+Y^-
(b) X^-Y^+
(c) $X - Y$
(d) $X \rightarrow Y$

49. Which of the following compounds are covalent?
(a) H_2
(b) CaO
(c) KCl
(d) Na_2S

50. The total number of electrons that take part in forming the bond in N_2 is:
(a) 2
(b) 4
(c) 6
(d) 10

51. Which of the following is soluble in water:
(a) CS_2
(b) C_2H_5OH
(c) CCl_4
(d) $CHCl_3$

52. If a molecule MX_2, has zero dipole moment, the sigma bonding orbitals used by M (atomic number < 21) are:
(a) pure p
(b) sp hybrid
(c) sp^2 hybrid
(d) sp^3 hybrid

53. The ion that is isoelectronic with CO is:
(a) CN^-
(b) O_2^+
(c) O_2^-
(d) N_2^+

54. Among the following, the molecule that is linear is:
(a) CO_2
(b) NO_2
(c) SO_2
(d) ClO_2

55. Carbon tetrachloride has no net dipole moment because of:
(a) its planar structure
(b) its regular tetrahedral structure
(c) similar sizes of carbon and chlorine
(d) similar electron affinities of carbon and chlorine

56. Which one among the following does not have the hydrogen bond?
(a) phenol
(b) liquid NH_3
(c) water
(d) liquid HCl

57. The types of bonds present in $CuSO_4 \cdot 5H_2O$ are only:
(a) electrovalent and covalent
(b) electrovalent and coordinate covalent
(c) electrovalent, covalent and coordinate covalent
(d) covalent and coordinate covalent

58. On hybridization of one *s* and one *p* orbitals we get:
(a) two mutually perpendicular orbitals
(b) two orbitals at 180°
(c) four orbitals directed tetrahedrally
(d) three orbitals in a plane

59. The molecule having one unpaired electron is:
(a) NO
(b) CO
(c) CN^-
(d) O_2

60. The hydration energy of Mg^{2+} is greater than that of:
(a) Al^{3+}
(b) Na^+
(c) Be^{2+}
(d) Mg^{2+}

61. The bonds present in N_2O_5 are:
(a) only ionic
(b) covalent and coordinate
(c) only covalent
(d) covalent and ionic

62. The bond between two identical non-metal atoms has a pair of electrons:
(a) unequally shared between the two
(b) transferred fully from one atom to another
(c) with identical spins
(d) equally shared between them

63. The hydrogen bond is strongest in:
(a) O – H...... S
(b) S – H...... O
(c) F – H...... F
(d) F – H...... O

64. The hybridisation of sulphur in sulphur dioxide is:
(a) sp
(b) sp^3
(c) sp^2
(d) dsp^2

65. Hydrogen bonding is maximum in:
(a) Ethanol
(b) Diethyether
(c) Ethyl chloride
(d) Triethylamine

66. The first ionisation potential (in electron volt) of nitrogen and oxygen atoms are respectively:
(a) 14.6, 13.6 (b) 13.6, 14.6
(c) 13.6, 13.6 (d) 14.6, 14.6

67. Atomic radii of fluorine and neon (in Å) are respectively:
(a) 0.72, 1.60 (b) 1.60, 1.60
(c) 0.72, 0.72 (d) 1.60, 0.72

68. The correct increasing order of electronegativity is:
(a) $C < N < Si < P$ (b) $N < Si < C < P$
(c) $Si < P < C < N$ (d) $P < Si < N < C$

69. Which of the following has zero dipole moment?
(a) 1, 1-dichloro ethane
(b) *cis*-1, 2-dichloro ethene
(c) *trans*-1, 2-dichloro ethene
(d) none of the above

70. The bond between carbon atom (1) and carbon atom (2) in $N \equiv C - CH = CH_2$ involves hybridisation:
(a) sp^2, sp^2 (b) sp^3, sp
(c) sp, sp^2 (d) sp, sp

71. The correct order for IE_1 is:
(a) $Na < Mg > Al < Si$ (b) $Na > Mg > Al > Si$
(c) $Na < Mg < Al > Si$ (d) $Na > Mg > Al < Si$

72. The species in which the central atom uses sp^2 hybrid orbitals in its bonding is:
(a) PH_3 (b) NH_3
(c) CH_3^+ (d) SbH_3

73. The molecule that has linear structure is:
(a) CO_2 (b) NO_2
(c) SO_2 (d) SiO_2

74. The molecule which has zero dipole moment is:
(a) CH_2Cl_2 (b) BF_3
(c) NF_3 (d) ClO_2

75. The molecule which has pyramidal shape is:
(a) PCl_3 (b) SO_3
(c) CO_3^{2-} (d) NO_3^-

76. The compound in which carbon use its sp^3 hybrid orbitals for bond formation is:
(a) $H\overset{\bullet}{C}OOH$ (b) $(H_2N)_2\overset{\bullet}{C}O$
(c) $(CH_3)_3\overset{\bullet}{C}OH$ (d) $CH_3\overset{\bullet}{C}HO$

77. Which of the following is paramagnetic:
(a) O_2 (b) CN
(c) CO (d) NO^+

78. Which has highest ionisation energy:
(a) $[Ne]\,3s^2 3p^1$ (b) $[Ne]\,3s^2 3p^3$
(c) $[Ne]\,3s^2 3p^2$ (d) $[Ar]\,3d^{10}, 4s^2 4p^3$

79. The hybridisation of carbon atom in C–C single bond of $HC \equiv C - CH = CH_2$ is:
(a) $sp^3 - sp^3$ (b) $sp^2 - sp^2$
(c) $sp - sp^2$ (d) $sp^3 - sp$

80. The type of hybrid orbitals used by the chlorine atom in ClO_3^- is:
(a) sp^3 (b) sp^2
(c) sp (d) none of these

81. The maximum possible number of hydrogen bonds a water molecule can form is:
(a) 2 (b) 4
(c) 3 (d) 1

82. The cyanide ion, CN^- and N_2 are isoelectronic. But in contrast to CN^-, N_2 is chemically inert, because of:
(a) low bond energy
(b) absence of bond polarity
(c) unsymmetrical electron distribution
(d) presence of more number of electrons in bonding orbitals

83. Allyl isocyanide has:
(a) 9σ and 4π bonds
(b) 8σ and 5π bonds
(c) 9σ, 3π bonds and 2 non bonding electrons
(d) 8σ, 3π bonds and 4 non bonding electrons

84. Which one is most ionic:
(a) P_2O_5 (b) CrO_3
(c) MnO (d) Mn_2O_7

85. Number of paired electrons in O_2 molecule is:
(a) 7 (b) 8
(c) 16 (d) 14

86. Which of the following statement is true about $CsBr_3$:
(a) It is a covalent compound
(b) It contains Cs^{3+} and Br^- ions
(c) It contains Cs^+ and Br_3^- ions
(d) It contains Cs, Br^- and lattice Br_2 molecule

87. KF combines with HF to form KHF_2. The compound contains:
(a) K^+, F^- and H^+ (b) K^+, F^- and HF
(c) K^+ and $[HF_2]^-$ (d) $[KHF]^+$ and F^-

88. Among the following compounds the one that is polar and has the central atom with sp^2 hybridisation is:
(a) H_2CO_3 (b) SiF_4
(c) BF_3 (d) $HClO_2$

89. Which one of the following compounds has sp^2 hybridisation?
(a) CO_2 (b) SO_2
(c) N_2O (d) CO

90. The incorrect statement is:
(a) IE_1 of Al < IE_1 of Mg (b) IE_2 of Mg > IE_2 of Na
(c) IE_1 of Na < IE_1 of Mg (d) IE_3 of Mg < IE_3 of Al

91. The geometry and type of hybridisation about central atom of BF_3 is:

(a) linear, *sp* (b) trigonal planar sp^2

(c) tetrahedral sp^3 (d) pyramidal, sp^3

92. The correct order of increasing C – O bond length of CO, CO_3^{2-}, CO_2 is:

(a) $CO_3^{2-} < CO_2 < CO$ (b) $CO_2 < CO_3^{2-} < CO$

(c) $CO < CO_3^{2-} < CO_2$ (d) $CO < CO_2 < CO_3^{2-}$

93. Ionic radii of:

(a) $Ti^{4+} < Mn^{7+}$ (b) $^{35}Cl^- < ^{37}Cl^-$

(c) $K^+ > Cl^-$ (d) $P^{3+} > P^{5+}$

94. In the compound $CH_2 = CH - CH_2 - CH_2 - C \equiv CH$, the $C_2 - C_3$ bond is of the type:

(a) $sp - sp^2$ (b) $sp^3 - sp^3$

(c) $sp - sp^3$ (d) $sp^2 - sp^3$

95. The correct order of radii is: **(IIT2000)**

(a) $N < Be < B$ (b) $F^- < O^{-2} < N^{3-}$

(c) $Na < Li < K$ (d) $Fe^{3+} < Fe^{2+} < Fe^{4+}$

96. Molecular shape of SF_4, CF_4 and XeF_4 are: **(IIT 2000)**

(a) the same with 2, 0 and 1 lone pair of electron respectively

(b) the same with 1, 1 and 1 lone pair of electron respectively

(c) different with 0, 1 and 2 lone pairs of electrons respectively

(d) different with 1, 0 and 2 lone pairs of electron respectively

97. The hybridisation of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ are: **(IIT 2000)**

(a) *sp*, sp^3 and sp^2 respectively

(b) *sp*, sp^2 and sp^3 respectively

(c) sp^2, *sp* and sp^3 respectively

(d) sp^2, sp^3 and *sp* respectively

98. Amongst H_2O, H_2S, H_2Se and H_2Te, the one with the highest boiling point is: **(IIT 2000)**

(a) H_2O because of H-bonding

(b) H_2Te because of higher molar mass

(c) H_2S because of H-bonding

(d) H_2Se because of lower molar mass

99. The correct order of hybridization of the central atom in the following species NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 is: **(IIT 2001)**

(a) dsp^2, dsp^3, sp^2, sp^3 (b) sp^3, dsp^2, sp^3d, sp^2

(c) dsp^2, sp^2, sp^3, dsp^3 (d) dsp^2, sp^3, sp^2, dsp^3

100. The common features among the species CN^-, CO and NO^+ are: **(IIT 2001)**

(a) bond order 3 and isoelectronics

(b) bond order 3 and weak field ligands

(c) bond order 2 and π-acceptor

(d) isoelectric and weak field ligands

101. The set representing the correct order for first ionisation potential **(IIT 2001)**

(a) $K > Na > Li$ (b) $Be > Mg > Ca$

(c) $B > C > N$ (d) $Ge > Si > C$

102. Specify the coordination geometry around and hybridization of N and B complex of NH_3 and BF_3: **(IIT 2002)**

(a) N : tetrahedral, sp^3; B : tetrahedral, sp^3

(b) N : pyramidal, sp^3; B : pyramidal, sp^3

(c) N : pyramidal, sp^3; B : planar, sp^3

(d) N : pyramidal, sp^3; B : tetrahedral, sp^3

103. The least stable amongst the following is: **(IIT 2002)**

(a) Li^- (b) Be^-

(c) B^- (d) C^-

104. Which of the following molecular species has unpaired electrons: **(IIT 2002)**

(a) N_2 (b) F_2

(c) O_2^- (d) O_2^{2-}

105. The nodal plane is the π-bond of ethene is located in:

(a) the molecular plane

(b) a plane parallel to molecular plane

(c) a plane perpendicular to the molecular plane which bisects the carbon-carbon sigma and at right angles

(d) a plane perpendicular to the molecular plane which contains the carbon-carbon sigma bond

106. Among the following the molecule with the highest dipole moment is: **(IIT 2003)**

(a) CH_3Cl (b) CH_2Cl_2

(c) $CHCl_3$ (d) CCl_4

107. Which of the following are isoelectronics and isostructural:

$$NO_3^-, CO_3^{2-}, ClO_3^-, SO_3$$

(IIT 2003)

(a) NO_3^-, CO_3^{2-} (b) SO_3, NO_3^-

(c) ClO_3^-, CO_3^{2-} (d) CO_3^{2-}, SO_3

108. Which of the following represents the given mode of hybridization sp^2-sp^2-*sp*-*sp* from left to right: **(IIT 2003)**

(a) $CH_2 = CH - C \equiv CH$

(b) $CH \equiv C - C \equiv CH$

(c) $CH_2 = C = C = CH_2$

(d) $CH_2 = CH - CH = CH_2$

109. Total number of lone pair of electrons in $XeOF_4$ is : **(IIT 2004)**

(a) 0 (b) 1

(c) 2 (d) 3

110. Which statement is correct about O_2^+ : **(IIT 2004)**

(a) Paramagnetic and bond order $< O_2$

(b) Paramagnetic and bond order $> O_2$

(c) Diamagnetic and bond order $< O_2$

(d) Diamagnetic and bond order $> O_2$

111. Which species has the maximum number of lone pair of electrons on the central atom : **(IIT 2005)**

(a) $[ClO_3]^-$ (b) XeF_4

(c) SF_4 (d) $[I_3]^-$

112. If the bond length of C—O bond in carbon monoxide is 1.128 Å, then what is the value of C—O bond length in $Fe(CO)_5$: **(IIT 2006)**

(a) 1.15 Å (b) 1.128 Å

(c) 1.72 Å (d) 1.118 Å

113. The species having different bond order that of CO is : **(IIT 2007)**

(a) NO (b) NO^+

(c) CN^- (d) N_2

114. Among the following the paramagnetic compound is : **(IIT 2007)**

(a) Na_2O_2 (b) O_3

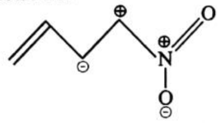
(c) N_2O (d) KO_2

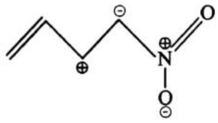
115. The percentage of *p*-character in the orbitals of P_4 forming P—P bond is : **(IIT 2007)**

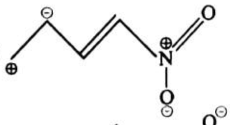
(a) 25 (b) 33

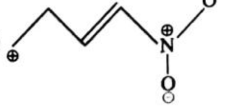
(c) 50 (d) 75

116. Among the following, the least stable resonance structure is: **(IIT 2007)**

(a) 

(b) 

(c) 

(d) 

117. Among the following statement, the correct statement about PH_3 and NH_3 is : **(IIT 2008)**

(a) NH_3 is a better electron donor because the lone pair of electron occupies spherical *s*-orbital and is less directional.

(b) PH_3 is a better electron donor because the lone pair of electron occupies sp^3-orbital and is more directional

(c) NH_3 is a better electron donor because the lone pair of electron occupies sp^3-orbital and more directional.

(d) PH_3 is a better electron donor because the lone pair of electron occupies spherical *s*-orbital and is less directional.

118. The correct stability order of the following resonating structures is : **(IIT 2009)**

(i) $H_2C=\overset{+}{N}=\overset{-}{N}$ (ii) $H_2\overset{+}{C}—N=\overset{-}{N}$

(iii) $H_2\overset{-}{C}—\overset{+}{N}\equiv N$ (iv) $H_2\overset{-}{C}—N=\overset{+}{N}$

(a) (i) > (ii) > (iv) > (iii) (b) (i) > (iii) > (ii) > (iv)

(c) (ii) > (i) > (iii) > (iv) (d) (iii) > (i) > (iv) > (ii)

119. The species having pyramidal shape is : **(IIT 2010)**

(a) SO_3 (b) BrF_5

(c) SiO_3^{2-} (d) OSF_2

120. Assuming that Hund's rule is violeted, the bond order and magnetic nature of diatomic molecule of B_2 is : **(IIT 2010)**

(a) 1 and diamagnetic (b) zero and diamagnetic

(c) 1 and paramagnetic (d) zero and paramagnetic

121. In allene (C_3H_4), the type(s) of hybridization of the carbon atoms is/are : **(IIT 2012)**

(a) *sp* and sp^3 (b) *sp* and sp^2

(c) only sp^2 (d) sp^2 and sp^3

122. The shape of XeO_2F_2 molecule is : **(IIT 2012)**

(a) trigonal bipyramidal (b) square planar

(c) tetrahedral (d) see-saw

123. Which one of the following molecules is expected to exhibit diamagnetic behaviour ? **[JEE (Main) 2013]**

(a) O_2 (b) S_2

(c) C_2 (d) N_2

124. In which of the following pairs of molecules/ions, both the species are not likely to exist ? **[JEE (Main) 2013]**

(a) H_2^{2+}, He_2 (b) H_2^-, He_2^{2+}

(c) H_2^+, He_2^{2-} (d) H_2^-, He_2^{2-}

125. Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar? **[JEE (Main) 2013]**

(a) Ba < Ca < Se < S < Ar (b) Ca < Ba < S < Se < Ar

(c) Ca < S < Ba < Se < Ar (d) S < Se < Ca < Ba < Ar

126. Stability of the species Li_2, Li_2^- and Li_2^+ increases in the order of: **[JEE (Main) 2013]**

(a) $Li_2 < Li_2^- < Li_2^+$ (b) $Li_2^- < Li_2 < Li_2^+$
(c) $Li_2 < Li_2^+ < Li_2^-$ (d) $Li_2^- < Li_2^+ < Li_2$

127. The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^+ will be : **[JEE (Main) 2013]**

(a) –10.2 eV (b) +2.55 eV
(c) –2.55 eV (d) –5.1 eV

SOLUTIONS (One Answer Correct)

1. (c) $_{10}Ne: 1s^2, 2s^2 2p^6$ $_{11}Na^+: 1s^2 2s^2 2p^6$
$_{12}F^-: 1s^2, 2s^2 2p^6$
All have same shielding constant.
Also, $Z_{eff} = Z - \sigma$ $\therefore Z_{eff\,Na} = 11 - 4.15 = 6.85$
and $Z_{eff\,F^-} = 9 - 4.15 = 4.85$

2. (d) $EN = \frac{IE + EA}{2}$ and $EA = -E_{ga}$

3. (a) $V_{Li} = \frac{4}{3} \times 3.14 \times (1.23)^3 = 7.79\,(Å)^3$
$V_{Li^+} = \frac{4}{3} \times 3.14 \times (0.76)^3 = 1.84\,(Å)^3$
Volume occupied by 2s-electron
$= 7.79 - 1.84 = 5.95\,(Å)^3$
∴ Fraction of volume occupied by 2s-electron
$= \frac{5.95}{7.79} = 0.764$

4. (a) IE_1 decreases down the gp. Thus Ar, Kr and Xe will show ionisation.

5. (c) $O + e \longrightarrow O^-; \Delta H = -144$ kJ
$\therefore 2O + 2e \longrightarrow 2O^-; \Delta H = 2 \times (-142) = -284$ kJ

6. (b) $\mu = \delta \times d$

$$3.336 \times 10^{-29} = \frac{1.602 \times 10^{-19} \times 80}{100} \times d$$

$$\therefore \quad d = \frac{3.336 \times 10^{-29} \times 100}{1.602 \times 10^{-19} \times 80} = 2.60 \times 10^{-10}\ \text{m} = 2.60\ Å$$

7. (a) $NO^+ : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \pi 2p_y^2, \pi 2p_z^2$
$\therefore \ BO = \frac{1}{2}[10 - 4] = 3$
$CO^+ : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma 2p_x^2, \pi 2p_y^2; \pi 2p_z^2, \sigma^* 2s^1$
$\therefore \ BO = \frac{1}{2}[10 - 3] = 3.5$

8. (b) $N_2 : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \pi 2p_y^2, \pi 2p_z^2$
In N_2^+ : one bonding electron is less but in N_2^- one antibonding electron is more.
∴ N_2^+ is more stable than N_2^-.

9. (c) $F_2 \longrightarrow 2F; \quad \Delta H = 158.8\ \text{kJ mol}^{-1}$
$F + e \longrightarrow F^-; \quad E_{ga} = -333\ \text{kJ mol}^{-1}$
$2\text{g}\ F_2 = \frac{2}{40}\ \text{mol}\ F_2$
$\therefore \Delta H = \frac{158.8 \times 2}{40} = 7.94\ \text{kJ mol}^{-1}$
Also, $\frac{2}{40}\ \text{mol}\ F_2 = 2 \times \frac{2}{40}$ g-atom of F
$= \frac{1}{10}$ g-atom of F
$\therefore \ E_{A(T)} = 333 \times \frac{1}{10} = 33.3$
$\therefore \ \Delta H$ for 2 g ($F_2 \longrightarrow 2F^-$) $= -33.3 + 7.94$
$= -25.36$ kJ

10. (a) $Li: 1s^2, 2s^1 \quad n = 2$
$E_{Li} = \frac{Z^2}{n^2} \times E_H$, where Z is effective charge.
$\therefore \ Z = n\sqrt{\frac{E_{Li}}{E_H}} = 2 \times \sqrt{\frac{5.40}{13.6}} = 1.26$

11. (a) $AlCl_3$ is hypovalent but $AlCl_3$ completes its octet by coordinate bond forming Al_2Cl_6.

12. (c) Except BF_3 all have expanded octet.

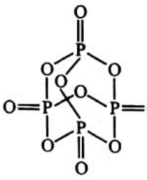
13. (d) Bond order for N_2^+, O_2^+ and NO is 2.5. For NO^+ it is 3.

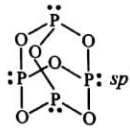
14. (a) Due to more +ve charge on N on account of more electronegativity of F.

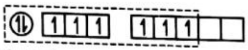
15. (a) Due to back bonding.

16. (a) C_2H_4 has sp^2-hybridised carbon and CO_2 has sp-hybridization.

17. (a) $XeOF_2$ has sp^3d-hybridization with two lone pairs of electrons leading trigonal by pyramid shape in T-shaped molecule.

18. (a) P_4O_{10} is  sp^2-hybridised P

19. (b) P_4O_6 is  sp^3-hybridised P

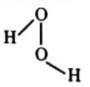
20. (c) A :  sp^3d^3 six B are attached on A

21. (c) NF_3 and H_3O^+ have sp^3-hybridization; NO_3^- and BF_3 have sp^2-hybridization.

22. (c) $\overline{C} \equiv \overline{C}$ bonding in CaC_2.

23. (b) p-dichlorobenzene is non-polar ($\mu = 0$), o-isomer has maximum dipole moment $\cos \alpha = 60°$.

24. (c) KO_2 has $K^+O_2^-$ structure having one unpaired electron.

25. (c)  non-planar.

Polar

26. (b) S in SO_2 has sp^2-hybridization.

27. (d) More is dipole moment, more is attraction among molecules, more will be T_C.

28. (b) B in BF_3 has sp^2-hybridization and trigonal planar.

29. (a) S in H_2S shows sp^3-hybridization with angular V-shape due to the presence of two lone pairs on S-atom. Also, $\mu \neq 0$.

30. (b) BCl_3 is s^2-hybridised (120°); Rest all are sp^3-hybridised. Also angle decreases from P to Bi.

31. (d) $\underset{sp^2}{\overset{1}{CH_2}} = \underset{sp^2}{\overset{2}{CH}} - \underset{sp^3}{\overset{3}{CH_2}} - \underset{sp^3}{\overset{4}{CH_2}} - \underset{sp}{\overset{5}{CH}} \equiv \underset{sp}{\overset{6}{CH}}$

32. (d) In all biggest jump will be in ${}_4Be$ as 1s is closest to nucleus.

33. (b) After removal of I electron, next electron will be removed from $2p^6$.

34. (c) First EA are exothermic however in alkaline earth metals these are endothermic.

35. (c) He has completely filled 1s orbital.

36. (c) In O^- and S^-, EA_2 will be +ve because addition of electron is opposed by anionic sphere in each. Also repulsion will be more predominant in O^-.

37. (d) $Li_{(g)} \rightarrow Li^+_{(g)} + e$; IE = less +ve

$$\begin{array}{l} Li^+_{(g)} + Aq. \rightarrow Li^+_{aq} \;;\; \Delta H_h = \text{more} -ve \\ \hline Li_{(g)} + Aq. \rightarrow Li^+_{aq} \;;\; \Delta H = -ve \end{array}$$

due to small size of cation

38. (a) EA_1 of S > O; EA_1 of Cl > F ; EA_1 of N > F and EA_1 of B > EA_1 of C

39. (d) Rest all influence polarisation of anion.

40. (d) Addition of electron in anion is opposed by ionic sphere.

41. (d) After the removal of one electron in oxygen, it acquires half filled configuration, *i.e.*, O^+ $1s^2, 2s^2sp^3$

42. (a) Follow text.

43. (a) Ne : $1s^2, 2s^2 2p^6$

Na^+ : $1s^2, 2s^2 2p^6$ Shielding effect will be same.

44. (c) $IE\ Na = \dfrac{IE\ K + IE\ Li}{2}$

45. (d) The basic nature is $CH_3^- > NH_2^- > OH^- > F^-$

46. (c) K^+ and $[C \equiv N]^-$

47. (b) H–O–H; H has duplet of electron.

48. (a) X^+Y^- as X loses electron

49. (a) H — H

50. (c) $:N \equiv N:$

51. (b) Due to H-bonding

52. (b) *eg.* CO_2 or BeF_2

53. (a) CN^- and CO both have 14 electrons.

54. (a) *sp*-hybridisation $O = C = O$

55. (b) Net $\mu = 0$ due to regular tetrahedron geometry.

56. (d) H-bonding is observed if H is attached on N, O or F atoms.

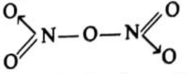
57. (c) $[Cu(H_2O)_4]^{2+} \cdot SO_4 \cdot H_2O$

58. (b) *sp*-hybridisation has 180° angle.

59. (a) NO has 15 electrons

60. (b) Mg^{2+} is smaller than Na^+ and has more charge

61. (b)



62. (d) Non polar bond *e.g.*, H–H

63. (c) F–H > O–H > N–H

64. (c) $O = \underset{sp^2}{S} = O$

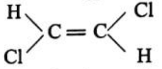
65. (a) Diethyl ether, ethyl chloride and triethyl amine do not show H-bonding.

66. (a) IE_1 of N > IE_1 of O due to half filled nature of orbitals in N.

67. (a) F has covalent radius whereas Ne has van der Waals' radius. Covalent radius is smaller.

68. (c) Electronegativity increases along the period, decreases down the gp.

69. (c)



$\mu = 0$

70. (c) $N \equiv \underset{sp}{\overset{1}{C}} - \underset{sp^2}{\overset{2}{CH}} = \underset{sp^2}{\overset{3}{CH_2}}$

71. (a) Ionisation energy order ; IE of Al < IE of Mg due to ellipticity.

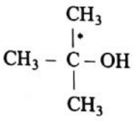
72. (c) CH_3^+ has sp^2-hybridisation.

73. (a) Due to *sp*-hybridisation

74. (b) $\mu_{Total} = 0$ due to coplanar (sp^2) geometry.

75. (a) Due to sp^3-hybridisation with one lone pair on P atom.

76. (c)



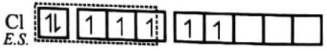
$CH_3 - \overset{\overset{CH_3}{|^{\bullet}}}{\underset{\underset{CH_3}{|}}{C}} - OH$, $C^{\bullet}$ has 4σ-bonds.

77. (a) O_2 is paramagnetic has two unpaired electrons.

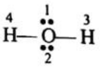
78. (b) Half filled nature. Also IE decreases down the gp

79. (c) $\overset{4}{HC} \equiv \underset{sp}{\overset{3}{C}} - \underset{sp^2}{\overset{2}{CH}} = \overset{1}{CH_2}$

80. (a) Cl in ClO_3^- has sp^3-hybridisation.



81. (b)



$\overset{4}{H} - \underset{\underset{2}{\bullet\bullet}}{\overset{\overset{1}{\bullet\bullet}}{O}} - \overset{3}{H}$

82. (b) CN^- is polar; N_2 is non polar.

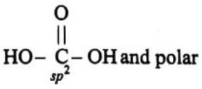
83. (c) $CH_2 = CH - CH_2 - C \equiv N$; 9σ, 3π and 2 non bonding electrons on N.

84. (c) Lowest oxidation states of metals are more ionic.

85. (d) O_2 has 16 electrons out of which two are unpaired.

86. (c) $CsBr_3$ has Cs^+ and Br_3^- ions

87. (c) KHF_2 has K^+ and $[HF_2]^-$ ions

88. (a) 
$HO-\underset{sp^2}{\overset{\overset{O}{||}}{C}}-OH$ and polar

89. (b) $O=S=O$

90. (b) Removal of 2nd electron from 3*s* in Mg and 2*p* in Na (more closer)
$\therefore$ IE_2 of Na > IE_2 of Mg

91. (b) sp^2 leads to coplanar trigonal geometry of BF_3

92. (d) Follow resonance

93. (d) Due to more effective nuclear charge on P^{5+}, the radii decreases.

94. (d) $\underset{sp^2}{\overset{1}{CH_2}}=\underset{sp^2}{\overset{2}{CH}}-\underset{sp^3}{\overset{3}{CH_2}}-\underset{sp^3}{\overset{4}{CH_2}}-\underset{sp}{\overset{5}{C}}\equiv\underset{sp}{\overset{6}{CH}}$

95. (b) Each has 10 electrons. The size of isoelectronic decreases along the period

96. (d) SF_4 has sp^3d-hybridization with one lone pair, CF_4 has sp^3-hybridization with no lone pair and XeF_4 has sp^3d^2-hybridization with two lone pairs.

97. (b) The hybridised states of N in NO_2^+, NO_3^- and NH_4^+ are *sp*, sp^2 and sp^3 respectively.

98. (a) It is a reason for given fact.

99. (b) N in NH_3 (sp^3), Pt in $[PtCl_4]^{2-}$ (dsp^2), P in PCl_5 (sp^3d) and B in BCl_3 (sp^2).

100. (a) Each possesses 14 electrons with bond order 3.

101. (b) The IE_1 decreases down the gp

102. (a) $\underset{sp^3}{NH_3}+\underset{sp^2}{BF_3}\longrightarrow[\underset{sp^3}{H_3N}\longrightarrow\underset{sp^3}{BF_3}]$

103. (b) $Li^-: 1s^2, 2s^2$ $(EA_1 = -ve)$
$Be^-: 1s^2, 2s^2 2p^1$ $(EA_2 = +ve)$

104. (c) O_2^- has one unpaired electron.

105. (a) A π-bond nodel plane passing through the two bonded nuclei, *i.e.*, molecular plane.

106. (a) $\mu_{CCl_4} = 0, \mu_{CHCl_3} = 1.0\ D, \mu_{CH_2Cl_2} = 1.6\ D,$
$\mu_{CH_3Cl} = 1.8\ D$

107. (a) Both NO_3^- and CO_3^{2-} have 32 electrons and central atom in each is sp^2-hybridized.

108. (a) $\underset{sp^2}{CH_2}=\underset{sp^2}{CH}-\underset{sp}{C}\equiv\underset{sp}{CH}$

109. (b) Xe in $XeOF_4$ shows sp^3d^2-hybridization with one lone pair on Xe-atom.

110. (b) Both O_2^+ and O_2 are paramagnetic : Bond order of $O_2 = 2$, Bond order $O_2^+ = 2.5$.

111. (d) I_3^-, XeF_4, SF_4 and ClO_3^- have 3, 2, 1, 1 lone pair of electrons respectively.

112. (a) Due to synergic bond formation between CO and metal, C—O bond length increases.

113. (b) Bond order of CO is 3 and of NO^+ is 2.5.

114. (d) It has O_2^{-1} in having one unpaired electron.

115. (d) P_4 has sp^3-hybridization: *s*-character 25%, *p*-character 75%

116. (a) Follow text

117. (c) Basic character of hydrides $NH_3 > PH_3$.

118. (b) Follow characteristics of resonance

119. (d) Due to sp^3-hybridisation of *S* and one lone pair.

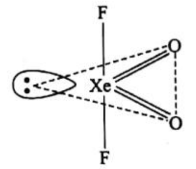
120. (a) In absence of Hund's rule, molecular orbital diagram of B_2 will be :

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2$$

121. (b) The different hybridization in C_3H_4 ($H_2C{=}C{=}CH_2$) are :

$$\overset{sp^2}{H_2C}=\overset{sp}{C}=\overset{sp^2}{CH_2}$$

122. (d) Xenon in XeO_2F_2 shows sp^3d-hybridization having one lone pair of electron



sp^3d-hybridization (see-saw)

123. (c,d) Both (C_2 and N_2) are diamagnetic as both have no unpaired electron

M.O. configuration of

$$C_2: \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2 \begin{bmatrix}\pi 2p_y^2\\ \pi 2p_z^2\end{bmatrix}$$

M.O. configuration of

$$N_2: \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2 \begin{bmatrix}\pi 2p_y^2\\ \pi 2p_z^2\end{bmatrix} \sigma 2p_x^2$$

O_2 and S_2 both have two unpaired electrons.

124. (a) Both H_2^{2+} and He_2 ($\sigma 1s^2 \sigma^* 1s^2$) have bond order zero.

125. (a) Ionisation enthalpy increases along the period but decreases down the group.

126. (d) Bond order for Li_2, Li_2^+ and Li_2^- are 1, 0.5, 0.5 respectively. However Li_2^+ (one antibonding electron) is more stable than Li_2^- because Li_2^- has three antibonding electrons.

127. (d) $Na(g)\longrightarrow Na^+(g)+e; IE = 5.1 eV$
$Na^+(g)+e\longrightarrow Na(g); EA = -IE = -5.1 eV$

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Select the correct statements :
   (a) Ionisation energy increases for each successive electron removal.
   (b) The greatest increase in ionisation enthalpy is experienced on removal of electron from the case of noble gas.
   (c) End of valence electrons is marked by a big jump in ionisation enthalpy.
   (d) Removal of electron from orbitals bearing lower *n* values is easier than from orbital having higher *n* value.

2. Which of the following compounds have electrovalent, covalent and coordinate bonds but do not have hydrogen bond?
   (a) $CaCl_2 \cdot 2H_2O$ (b) $CuSO_4 \cdot 5H_2O$
   (c) $FeSO_4 \cdot 7H_2O$ (d) $Na_2SO_4 \cdot 10H_2O$

3. Which are correct about the structure of trimer of SO_3, *i.e.*, S_3O_9?
   (a) It has cyclic structure
   (b) It has two S—S bonds
   (c) It has three S—O—S bonds
   (d) It has sp^2-hybridization of S and 12σ and 6π-bonds

4. Which are correct for white phosphorus molecule?
   (a) It exists as P_4
   (b) P—P bond length equal to 2.21 Å
   (c) P—P bond angle is 109°28′
   (d) It has sp^3-hybridization and tetrahedron structure

5. Which of the following are correct about bond angles?
   (a) $OSF_2 < OSCl_2 < OSBr_2$
   (b) $SbI_3 < AsI_3 < PI_3$
   (c) $PF_3 > PCl_3 < PBr_3 < PI_3$
   (d) $NO_2^- < NO_2 < NO_2^+$

6. Which of the following are correct for CO^+, N_2^+ ?
   (a) Both have 13 electrons
   (b) N_2^+ has bond order 2.5 whereas CO^+ has bond order 3.5
   (c) Both have same M.O. configuration
   (d) Bond length of N—N in N_2^+ is greater than N_2 but bond length of CO^+ is shorter than CO

7. Which facts are correctly represented?
   (a) Bond length : $NO^+ < NO^{2+} < NO < NO^-$
   (b) Bond order : $NO^+ > NO^{2+} = NO > NO^-$
   (c) Bond length : $NO^+ < NO^{2+} = NO < NO^-$
   (d) Bond order : $NO^+ > NO^{2+} > NO > NO^-$

8. In which of the following H-atom attached on carbon atom shows H-bonding?
   (a) $CCl_3 \cdot CH(OH)_2$
   (b) $CHCl_3$ in acetone
   (c) $CH_3 \cdot CO \cdot CH_3$
   (d) $CH_3 \cdot CO \cdot CH_2COOC_2H_5$

9. Which of the following are correct?
   (a) PH_5 and $BiCl_5$ does not exist
   (b) SeF_4 and CH_4 have same geometry
   (c) $p\pi - d\pi$ bonds are present in SO_2
   (d) Nodal plane in the π-bonds of ethane are located in molecular plane

10. Select the correct statements :
    (a) IE_1 of deuterium is more than IE_1 of H
    (b) maximum electron affinity exists for F
    (c) maximum *IE* stands for He
    (d) *trans*-pent-2-ene is polar

11. Select the correct statements :
    (a) There are two π-bonds in N_2 molecule
    (b) Delocalisation involving sigma bonds orbitals is called hyperconjugation
    (c) Dipole moment of CH_3F is greater than CH_3Cl
    (d) $C_2H_2, CO_2, SnCl_2$ all are linear molecules

12. Resonance molecule should have:
    (a) identical arrangement of atoms
    (b) nearly same energy content
    (c) the same number of paired electrons
    (d) identical bonding

13. Dipole moment is shown by:
    (a) 1, 4-dichloro ethane
    (b) *cis*-1,2-dichloro ethane
    (c) *trans*-1 2-dichloro ethane
    (d) 1, 2-dichloro-2-pentene

14. CO_2 is isostructural with:
    (a) $HgCl_2$ (b) $SnCl_2$
    (c) C_2H_2 (d) NO_2

15. Which of the following are correct:
    (a) The ionisation potential of oxygen is less than that of nitrogen
    (b) The ionisation potential of nitrogen is greater than that of oxygen
    (c) The two ionisation potential values are comparable
    (d) The differences between the two ionisation potential values is too large

16. Sodium sulphate is soluble in water whereas barium sulphate is sparingly soluble because:

(a) The hydration energy of Na_2SO_4 is more than its lattice energy
(b) The lattice energy of $BaSO_4$ is more than its hydration energy
(c) The lattice energy has no role is solubility
(d) The hydration energy of Na_2SO_4 is less than its lattice energy

17. The linear structure is assumed by:
(a) $SnCl_2$
(b) NCO^-
(c) CS_2
(d) NO_2^+
(e) SO_2

18. Which of the following have identical bond order?
(a) CN^-
(b) O_2^-
(c) NO^+
(d) CN^+

19. The molecules that will have dipole moment are:
(a) 2, 2-dimethylpropane
(b) *trans*-2-pentene
(c) *cis*-3-hexene
(d) 2,2,3,3-tetramethylbutane

20. Pick out the isoelectronic structrues from the following:
I CH_3^+
II H_3O^+
III NH_3
IV CH_3^-
(a) I and II
(b) III and IV
(c) I and III
(d) II, III and IV

21. *A*, *B* and *C* are hydroxy compounds of the elements *X*, *Y* and *Z* respectively. *X*, *Y* and *Z* are in the same period of periodic table. A gives an aqueous solution of pH less than 7. *B* reacts with both strong acid and strong base. *C* gives an aqueous solution which is strongly basic. Which of the following statements is/are true?
(a) The three elements are non-metal
(b) The electronegativities decrease from *X* to *Z*
(c) The atomic radius decreases in the order $Z > Y > X$
(d) *X*, *Y* and *Z* may be phosphorous, aluminium and potassium respectively

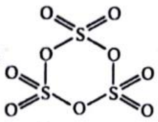
22. Which of the following statement is incorrect?
(a) O_2 is paramagnetic, O_3 is also paramagnetic
(b) O_2 is paramagnetic N_2^{2+} is also paramagnetic
(c) B_2 is paramagnetic, C_2 is also paramagnetic
(d) Different observation is found in their bond length when $NO \longrightarrow NO^+$ and $CO \longrightarrow CO^+$

23. Which of the following statement(s) is/are correct?
(a) The removal of one electron from $Na^+(g)$ ion requires more energy than that from $Mg^+(g)$
(b) The hydration energy of Na^+ ion is more than that of K^+ ion
(c) Ionic radii follows the order for three elements (*X*, *Y*, *Z*) of same period belonging to group 1, 2 and 3 (*i.e.*, IA, IIA and IIIA) in the periodic table is $X^+ > Y^{2+} > Z^{3+}$.
(d) With the increasing electronegativity (which increases with increasing positive charge), the basic strength of any elemental oxide decreases

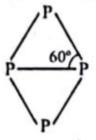
24. Which of the following shows same hybridized state :
(a) central N atom of azide ion (N_3^-)
(b) N atom in NO_2F
(c) central O atom of ozone
(d) N atoms in N_2F_2

SOLUTIONS (More Than One Answer Correct)

1. (a,b,c) Lower is the value of n higher is the energy.
2. (a,c,d) $CuSO_4 \cdot 5H_2O$ has $[CuSO_4 \cdot H_2O]4H_2O$.
3. (a,c,d) S_3O_9 has



4. (a,b,d) P_4 is



The molecule is under strain and active in nature due to bond angle 60°

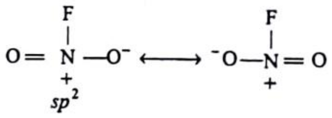
5. (a,b,c,d) Follow concepts of bonding (in concepts of physical chemistry by P. Bahadur, Prakash Publications, Muzaffarnagar).
6. (a,b,d) $N_2^+ : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix}, \sigma 2p_x^2$

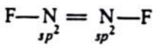
   $CO^+ : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma 2p_x^2 \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix}, \sigma^* 2s^1$

   2s-orbital of O-atom has lower energy than 2s-orbital of C-atom. When they mix to form $\sigma 2s$ an $\sigma^* 2s$-orbitals, the latter has so high energy that it goes above $\sigma 2p_x$ as well as $\pi 2p_y$ and $\pi 2p_z$.
7. (a,b) NO^{2+} has one antibonding electron less than NO and thus bond length in NO is more

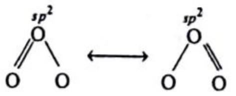
   $NO : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2 \sigma 2p_x^2, \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix}, \pi^* 2p_y^1$
8. (a,b) Due to increasing charge density of carbon on account of higher electronegativity of Cl.
9. (a,c,d) SeF_4 (sp^3d), CH_4 (sp^3)
10. (a,b,c,d) Follow concepts.
11. (a,b,c) $SnCl_2$ is angular due to sp^2-hybridization.
12. (a,b,c) These are characteristics of resonance.
13. (b,d) μ for $(a) = 0$ and μ for $(c) = 0$
14. (a.c) Both has sp-hybridization
15. (a,b,c) These are facts.
16. (a,b) These are facts.
17. (b,c) Both are linear.
18. (a,c) Bond order for both is 3.
19. (b,c) μ for $(a) = 0$, μ for $(d) = 0$ due to symmetry.
20. (b,d) These have sp^3-hybridization.
21. (b,c) X is non metal. (*e.g.*, O_3Cl—OH—acidic)
    Y is amphoteric (*e.g.*, $Al(OH)_3$ —amphoteric)
    Z is metal (*e.g.*, KOH—basic)
22. (b,d) Follow text.
23. (a,b,c,d) —do—
24. (b,c,d) The central atom of azide ion has sp-hybridisation.

$^{-}\text{N}=\overset{sp}{\text{N}}\overset{\rightarrow}{=}\text{N};$





$\text{F}—\underset{sp^2}{\text{N}} = \underset{sp^2}{\text{N}}—\text{F}$



COMPREHENSION BASED PROBLEMS

Comprehension 1 : Dipole moment of a bond is a vector and physical quantity to calculate the percentage ionic character in a covalent bond. It is expressed as :

$$\text{Dipole moment } (\mu) = \overrightarrow{\partial \times d}$$

where, δ is dipole moment and *d* is the bond length

It is usually expressed in terms of CGS unit known as Debye (D) $1\,D = 10^{-18}$ esu cm. In SI unit it is expressed in Coulomb meter. Resultant dipole moment (μ_R) of two bond moments (μ_1 and μ_2) acting at an angle θ, is given by :

$$\mu_R = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$$

If $\mu_1 = \mu_2$, Also if $\cos\theta = -1$, *i.e.*, $\theta = 180°$ then $\mu = 0$. (molecule is non polar)

If $\mu \neq 0$ molecule is polar.

Dipole moment plays an important role in deciding the stability order of alkanes, *i.e.*, a more stable alkane has less dipole moment. The dipole moment of a molecule can predict the geometrical and position isomers as well as orientations in benzene nucleus and polarity of molecule.

[1] Dipole moment of HCl molecule is found to be 0.816 D. Assuming HCl bond length to be equal to 1 Å, the % ionic character of HCl molecule is:
(a) 10% (b) 17%
(c) 27% (d) 37%

[2] The correct increasing order of dipole moment of the following compounds is,
I Toluene; II *o*-dichlorobenzene;
III *m*-dichlorobenzene; IV *p*-dichlorobenzene
(a) I<II<III<IV (b) IV<I<III<II
(c) I<IV<III<II (d) IV<I<II<III

[3] Dipole moment of
(1) *p*-dinitrobenzene (2) *p*-dichlorobenzene and
(3) *p*-dimethoxybenzene are in the order:
(a) 3>2>1 (b) 3=2>1
(c) 3=2=1 (d) 3>(2=1)

[4] Match the compounds in list-I with their correct values of dipole moment in list-II :

List-I Compound	List-II Dipole moment (D)	
1. *o*-nitrophenol	(A)	0.05
2. *o*-dichlorobenzene	(B)	1.00
3. *o*-xylene	(C)	1.20

(a) 1–A, 2–B, 3–C (b) 1–B, 2–A, 3–C
(c) 1–C, 2–A, 3–B (d) 1–C, 2–B, 3–A

[5] Identify the correct increasing order of the stability of the following alkenes, I *cis*-2-butene; II *trans*-2-butene; III isobutene:
(a) II<III<I (b) I<III<II
(c) I<II<III (d) III<II<I

[6] Which of the following species is non polar?
(a) Ammonia (b) Sulphur dioxide
(c) Water (d) Sulphur trioxide

[7] The increasing order of dipole moment of bond in halogen acids is:
(a) HF > HCl > HBr > HI (b) HI > HCl > HBr > HF
(c) HCl > HBr > HI > HF (d) HI > HBr > HF > HCl

[8] Which molecule is non polar?
(a) *trans*-Pent-2-ene (b) *cis*-Pent-2-ene
(c) *cis*-1-chloropropene (d) SF_6

[9] Which species is polar?
(a) *trans*-Hex-3-ene (b) *trans*-But-2-ene
(c) PCl_5 (d) XeF_6

SOLUTIONS

Comprehension 1

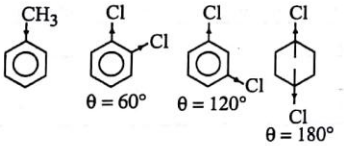
[1]. (b) $\mu_m = \overrightarrow{\delta \times d}$

$0.816 \times 10^{-18} = \delta \times 10^{-8}$

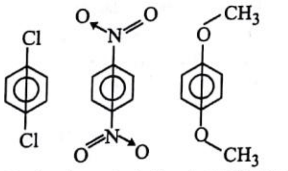
$\therefore\ \delta = 0.816 \times 10^{-10}$ esu

$\therefore$ % ionic character $= \dfrac{0.816 \times 10^{-10}}{4.803 \times 10^{-10}} \times 100 = 16.9\%$

[2]. (b)

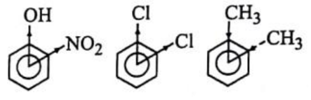


[3]. (d)

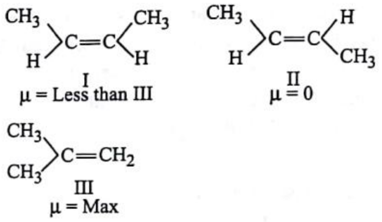


Notice the orientation in methoxy group.

[4]. (c)



[5]. (d)



The stability order is
cis-2-butene > *trans*-2-butene > isobutene

[6]. (d) SO_3 has sp^2-hybridization and three equal vectors acts at 120°.

[7]. (a) The electronegativity order is F > Cl > Br > I.

[8]. (d) SF_6 has octahedral geometry having $\mu = 0$.

[9]. (d) XeF_6 has sp^3d^3-hybridization and pentagonal pyramidal nature.

STATEMENT-EXPLANATION PROBLEMS

In each sub question given below a statement **(S)** and explanation **(E)** is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) S is correct but **E** is wrong

(b) S is wrong but **E** is correct

(c) Both S and E are corect and E is correct explanation of S

(d) Both S and E are correct but E is not correct explanation of S

1. S : Cs and F_2 reacts violently.

E : Cs is most electropositive and F_2 is most electronegative.

2. S : Transition elements exhibit horizontal and vertical relationship.

E : The shielding effect as well as same outermost shell configuration in transition metals are responsible for their behaviour.

3. S : $BiCl_5$ does not exist.

E : In Bi inert pair effect is predominant.

4. S : Bond order for CO^+ is more than bond order in CO whereas bond order in N_2^+ is less than N_2 whereas both are isoelectronics.

E : Both have same bond order.

5. S : Bond order for N_2^+ and N_2^- are same but N_2^+ is more stable than N_2^-.

E : Antibonding electrons are more in N_2^-.

6. S : The bond angles in NO_2^+, NO_2 and NO_2^- are 180°, 134° and 115° respectively.

E : Bond angles in a molecule also depends upon the presence of lone electron as well as lone pair of electron.

7. S : Bond angle of $PF_3 > PCl_3$ but bond angle of $PCl_3 < PBr_3$.

E : The bond angles show an increase on decreasing electronegativity of attached other atom on central atom but in PF_3 $p\pi - d\pi$ bonding results in an increase in bond angle.

8. S : Although carbon in HCHO is sp^2-hybridized and all the three bond angles are 120° C.

E : In HCHO, presence of multiple bond gives rise two bond angle. $<$ HCO is 122° and $<$ HCH is 116°.

9. S : N_2O is represented by (i) $N=N=O$ and (ii) $N \equiv N \rightarrow O$ but later is more stable.

E : The form (ii) shows resonance.

10. S : CS_2 is linear whereas H_2S is non-linear.

E : C in CS_2 is *sp*-hybridized whereas S in H_2S is sp^3-hybridized.

11. S : Nitric oxide, though an odd electron molecule is diamagnetic in liquid state.

E : There occurs only partial dimerisation of NO to N_2O_2.

12. S : All the Al—Cl bonds in Al_2Cl_6 are equivalent.

E : The terminal Al—Cl bonds are different from bridge Al—Cl bonds.

13. S : Bond dissociation energy of F_2 is lesser than Cl_2.

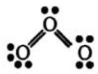
E : An additional π-bond formation is created by donor-acceptor mechanism in Cl_2 in which an unshared electron of one Cl-atom overlaps with a free 3*d*-orbital electron of another Cl-atom.

14. S : LiCl is predominantly a covalent compound.

E : Electronegativity difference between Li and Cl is too small.

15. S : The electronic structure of O_3 is:

E :



structure of O_3 is not allowed.

16. S : Sulphate is estimated as $BaSO_4$ and not as $MgSO_4$.

E : Ionic radius of Mg^{2+} is smaller than that of Ba^{2+}

17. S : Helium and Beryllium have similar outer electronic configuration.

E : Both are chemically inert.

18. S : The size decreases as $Pb > Pb^{2+} > Pb^{4+}$.

E : The nuclear charge/electron increases, *i.e.*, the force of attraction towards nucleus increases.

19. S : The S—S—S bond angle in S_8 molecule is 105°.

E : S_8 has V-shape.

20. S : O—O bond length in H_2O_2 is shorter than that of O_2F_2.

E : H_2O_2 is a covalent compound.

21. S : Fluorine molecule has bond order one.

E : The number of electrons in antibonding molecular orbitals is two less than in bonding molecular orbitals.

22. S : The dipole moment helps to predict whether molecule is polar or non-polar.

E : The dipole moment helps to predict the geometry of molecules.

23. S : All F—S—F bond angles in SF_4 are greater than 90° but lesser than 180°.

E : The lone pair-bond pair repulsion is weaker than bond pair-bond pair repulsion.

24. S : N_2 and NO^+ both are diamagnetic substances.
E : NO^+ is isoelectronic to N_2.

25. S : The bond angle of PBr_3 is greater than PH_3 but the bond angle of NBr_3 is lesser than NH_3.
E : Electronegativity of P-atom is less than that of N-atom.

26. S : CaF_2 is soluble in water but CaI_2 not.
E : CaF_2 is more ionic than CaI_2.

27. S : O_3 and NO_2^- are isoelectronic.
E : Bond angles of O_3 and NO_2^- are 116.8° and 115° respectively.

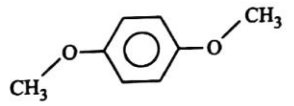
28. S : NO_2 is readily dimerised to N_2O_4.
E : NO_2 has one unpaired electron and two such electrons with opposite spin in two NO_2 molecules forms bond between two N-atoms readily.

29. S : Both Cu^+ and Na^+ have almost same radii.
E : Cu^+ possesses more power to polarise an anion.

30. S : IE_1 for He is maximum and EA_1 for Cl is more than EA_1 of F.
E : He possesses paired electrons in 1*s* sub-shell, closest to nucleus, whereas electron density in F is maximum which exerts more electron-electron repulsion.

31. S : If difference of electronegativity between two atoms is zero the resultant molecule will be non-polar covalent.
E : The shared pair of electron lies just in the middle of two atoms.

32. S : *p*-dimethoxy benzene is polar molecule.
E : The two methoxy groups at para positions are located as



33. S : The lattice energy of silver halides is
$AgF > AgCl > AgBr > AgI$.
E : AgF is water soluble

34. S : The molecule *cis*-1-chloropropene is more polar than *trans*- 1-chloropropene.
E : The magnitude of resultant vector in *trans*-1-chloro- propene is non-zero.

35. S : IF_7 is super octet molecule.
E : Central atom of I in IF_7 has 14 electrons.

36. S : $FeCl_2$ is more covalent than $FeCl_3$ because electronegativity of $Fe^{3+} > Fe^{2+}$.
E : Higher is the charge on cation, more is deformation of anion, more is covalent character.

37. S : MO configuration of CO is
$\sigma 1s^2, \sigma^* 1s^2 \sigma 2s^2, \sigma 2p_x^2, \pi 2p_y^2, \pi 2p_z^2, \sigma^* 2s^2$.
E : The bond energy level $\sigma * 2s^2$ possesses higher energy because then only bond length order for CO (more) and CO^+ (less) can be explained.

38. S : The dipole moment of NH_3 is less than NF_3.
E : The lone pair present on N shows additive nature to N—H vector whereas it is subtractive to N—F vector.

39. S : The bond energy of P—Cl bond in PCl_3 and PCl_5 are different.
E : In $PCl_3, sp^3 - p$ overlapping whereas in $PCl_5, sp^3d - p$ overlapping is noticed.

40. S : SF_4 has lone pair of electron at equatorial position in preference to apical position in the overall trigonal bipyramidal geometry
E : If lone pair is at equatorial position then only repulsion is minimum.

41. S : BF_3 molecule is planar with an angle of 120°C.
E : BF_3 has bond pair-lone pair electron ratio 1 : 3.

42. S : N and P show a maximum covalency of five.
E : P can expand the outer shell of electrons beyond an octet by involving *d*-orbitals present in its valence shell.

43. S : All molecules with polar bond have dipole moment.
E : Dipole moment is a vector quantity.

44. S : PCl_5 conducts current in solid state.
E : PCl_5 exists as $[PCl_4]^+$ and $[PCl_6]^-$ ions.

45. S : EA_2 for halogens is endothermic.
E : Halogens have ns^2np^5 configuration and can accommodate only one electron.

46. S : F atom has less electron affinity than Cl atom.
E : Additional electrons are repelled more effectively by 3*p*-electrons in Cl atom than by 2*p*-electrons in F atom.

47. S : The ionisation energy of ${}_1H^2$ is more than ionisation energy of ${}_1H^1$.
E : This is due to isotopic effect.

48. S : Solubility of NaOH in water increases with rise in temperature, although it is exothermic dissolution.
E : Changes showing exothermic nature occurs in backward direction if temperature is raised.

49. S : Solubility of NaCl in D_2O is less than, H_2O.
E : Higher viscosity of D_2O is responsible for low solubility of NaCl.

50. S : NH_3 and CH_3^- both have pyramidal shape.
E : N in NH_3 and C in CH_3^- both have sp^3-hybridisation with one lone pair of electron on each.

51. S : The bond angle in H_2O is greater than H_2S.
E : H-bonding does not occur in H_2S due to low electronegativity of S.

52. S : The bond angle in BF_3 is smaller than that in BF_4.
E : BF_3 has sp^2-hybridisation, whereas BF_4^- has sp^3-hybridisation.

53. S : The first ionisation energy of N is greater than O.
E : N atom has half filled *p*-orbitals.

54. S : The first ionisation energy of Be is greater than that of B. **[IIT 2000]**
E : 2*p*-orbital is lower in energy than 2*s*-orbital.

ANSWERS (Statement Explanation Problems)

1. (c) Explanation is correct reason for statement.

2. (c) —do—

3. (c) —do—

4. (a) Both N_2 and CO have different MO configuration but bond order is same which results a change in N_2^+ and CO^+ configuration and thus, bond order of N_2^+ and CO^+ are different.

5. (c) Explanation is correct reason for statement.

6. (c) —do—

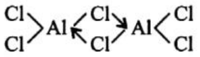
7. (c) —do—

8. (b) It is a fact.

9. (a) Form II is more stable due to lesser formal charge on N-atom.

10. (c) Explanation is correct reason for statement.

11. (b) It is an experimental fact.

12. (b) Al_2Cl_6 has the structure. 

13. (c) Explanation is correct reason for statement.

14. (a) LiCl is covalent due to high polarising power of Li^+.

15. (d) Both are correct.

16. (d) $BaSO_4$ is insoluble. $MgSO_4$ is soluble.

17. (a) Be is reactive metal.

18. (c) Explanation is correct reason for statement.

19. (a) S_8 has puckered ring structure.

20. (b) O—O bond is H_2O_2 and O_2F_2 are same.

21. (c) Explanation is correct reason for statement.

22. (c) Explanation is correct reason for statement.

23. (a) Bond angles in $SF_4(sp^3d^2)$ are 116°.

24. (d) Both statements are correct.

25. (d) —do—

26. (b) CaF_2 is insoluble in water but more ionic having high lattice energy due to small size of F^-.

27. (d) Both are correct. The difference in bond angle is due to lone pair-bond pair repulsion in O_3 and lone electron-bond pair repulsion in NO_2^-.

28. (c) Since the process does not require any rearrangement and thus energy of activation for dimerisation of NO_2 is low.

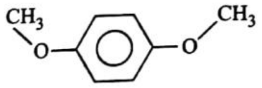
29. (d) The more power of Cu^+ to polarise an anion is due to its pseudo noble gas structure.

$$r_{Cu^+} = 0.96Å; r_{Na^+} = 0.95Å$$

30. (c) Explanation is correct reason for statement.

31. (c) Explanation is correct reason for statement.

32. (a) *p*-dimethoxy benzene is polar due to orientation of CH_3 group as, the resultant vector is not zero.



33. (d) Inspite of higher lattice energy AgF is soluble because F^- is extensively hydrated and heat of hydration predominates over lattice energy.

34. (b) Both *cis*-and *trans*-forms are polar. *Trans* is more polar due to higher value of dipole moment due to additive nature of CH_3 and Cl vectors.

35. (c) Explanation is correct reason for statement.

36. (b) This is Fajans' rule. $FeCl_3$ is more covalent.

37. (c) Explanation is correct reason for statement.

38. (b) That is why $\mu_{NH_3} > \mu_{NF_3}$.

39. (c) Explanation is correct reason for statement.

40. (c) Explanation is correct reason for statement.

41. (d) BF_3 is planar due to sp^2-hybridisation.Also in BF_3, three bond pair on boron atom and 9 lone pairs of electrons on F atoms.

42. (b) N shows maximum covalence of +3 along with one coordinate bond whereas P shows maximum covalence of +5 due to given explanation.

43. (b) Molecules having polar bonds may (*e.g.*, ClF_3 polar) or may not (*e.g.*, BF_3) have dipole moment. The resultant vector of bond moment decides the net dipole moment in molecule.

44. (b) Solid ionic compounds conduct current only in fused state. PCl_5 in solid state exists as $[PCl_6]^-[PCl_4]^+$.

45. (b) Halogens can have only EA_1 value because they can accommodate only one electron (ns^2np^5 to ns^2np^6): No scope for further addition, thus EA_2 for halogens is zero.

46. (a) Electron affinity of F < Electron affinity of Cl. Due to more 2*p*-test electron repulsion in F atom.

47. (c) Explanation is correct reason for statement.

48. (d) Assertion is an experimental fact observed against Le Chatelier principle.

49. (c) Explanation is correct reason for statement.

50. (c) Explanation is correct reason for statement.

51. (d) The bond angle in H_2S is smaller because S atom has bigger size than O.Also H_2S does not show H-bonding.

52. (b) In sp^2-hybridisation bond angle is 120°. In sp^3 it is 109°28′.

53. (c) Removal of electron from N atom requires more energy due to half filled *p*-orbital in N atom.

54. (a) Energy level of 2*s* is lesser than 2*p*-orbital.

MATCHING TYPE PROBLEMS

Type I : Only One Match Are Possible

1.

	List A		List B
(A)	Melting point	(i)	$O^{2-} < O^- < O < O^+$
(B)	Thermal stability	(ii)	$F^- < Cl^- < Br^- < I^-$
(C)	Polarisability	(iii)	$HI < HBr < HCl < HF$
(D)	Electron affinity	(iv)	$XeF_6 < XeF_4 < XeF_2$

2.

	List A		List B
(A)	SO_2Cl_2	(i)	Paramagnetic
(B)	Ice	(ii)	Refrigerant
(C)	$CuSO_4$ (anhy.)	(iii)	Testing NH_3
(D)	$K_2HgI_4 + NaOH$	(iv)	Testing H_2O
(E)	Fluorocarbons	(v)	H-bonding
(F)	NO	(vi)	Tetrahedral

Type II : More Than One Match Are Possible

3.

	List A		List B
(A)	B_2	(p)	Paramagnetic
(B)	N_2	(q)	Undergoes oxidation
(C)	O_2^-	(r)	Undergoes reduction
(D)	O_2	(s)	Bond order ≥ 2
		(t)	Mixing of s and p-orbitals

[IIT 2009]

4.

	List A		List B
(A)	sp^3-hybridisation	1.	NH_3
(B)	Lone pair effect	2.	Diethyl ether
(C)	Heteromolecular species	3.	H_2O
(D)	Paramagnetism	4.	N_2O
(E)	Dipole moment	5.	O_2
(F)	H-bonding	6.	N_2^-

Type III : Only One Match From Each List

5.

List A	List B	List C
A. See-saw	1. I_3^-	a. ClF_3
B. T-shaped	2. e^{-2}	b. CS_2
C. Linear	3. IF_4^+	c. 0.14
D. Ratio of probable density of electron at $r = a_0$ and $r = 0$	4. $XeOF_2$	d. 0.018
E. Ratio of probable density of electron at $r = 2a_0$ and $r = 0$	5. e^{-4}	e. SF_4

6.

List A	List B	List C
A. Electrovalent bonding	a. Kossel and Lewis	1. Ions
B. Covalent bonding	b. Lewis	2. Polarity
C. Singlet linkage	c. Sugden	3. One sided sharing of 'e'
D. Co-ordinate bonding	d. Menzies	4. One sided sharing of 'e' pair
E. Valence bond theory	e. Heitlor and London	5. Hybridization
F. Molecular orbital theory	f. Hund -Mulliken	6. Paramagnetism

7.

List A	List B	List C
A. PCl_5	a. sp^3d	1. Linear
B. $BeCl_2$	b. sp	2. Trigonal bipyramids
C. NH_3	c. sp^3	3. Pyramidal
D. XeF_4	d. sp^3d^2	4. Square planar
E. XeF_6	e. sp^3d^3	5. Pentagonal pyramid

8.

List A	List B	List C
A. XeF_4	1. sp^3d^2	a. V-shaped
B. $HgCl_2$	2. sp^3d	b. See-saw
C. I_3^-	3. sp	c. T-shaped
D. NO_2^-	4. sp^2	d. Tetrahedral
E. ClO_4^-	5. sp^3	e. Linear
F. $XeOF_3$		f. Square planar
G. ICl_4^-		
H. ICl_2^-		
I. $TeCl_4$		

ANSWERS

1. A – iv; B – iii; C – ii; D – i
2. A – (vi); B – (v); C – (iv); D – (iii); E – (ii); F – (i)
3. A–p, q, r, t; B–q, r, s, t; C–p, q, r, t; D–p, q, r, s, t
4. A – 1, 2, 3; B – 1, 2, 3; C – 1, 2, 3, 4; D – 4, 5, 6; E – 1, 2, 3, 4; F – 1, 3
5. A – 3 – e; B – 4 – a; C – 1 – b; D – 2 – c; E – 5 – d
6. A – a – 1; B – b – 2; C – c – 3; D – d – 4; E – e – 5; F – f – 6
7. A – a – 2; B – b – 1; C – c – 3; D – d – 4; E – e – 5
8. A – 1 – f; B – 3 – e; C – 2 – e; D – 4 – a; E – 5 – d; F – 2 – c; G – 1 – f; H – 2 – e; I – 2 – b

6

Oxidation-Reduction

[A] Oxidation-reduction

(1) Oxidation is a process which liberates electrons, *i.e.*, de-electronation.

(2) Reduction is a process which gains electrons, *i.e.*, electronation.

Oxidation	**Reduction**
$M \longrightarrow M^{+n} + ne$	$M^{+n} + ne \longrightarrow M$
$A^{-n} \longrightarrow A + ne$	$A + ne \longrightarrow A^{-n}$
$n_2 > n_1\ M^{+n_1} \longrightarrow M^{+n_2} + (n_2 - n_1)e$	$M^{+n_2} + (n_2 - n_1)e \longrightarrow M^{+n_1}$
$n_1 > n_2\ A^{-n_1} \longrightarrow A^{-n_2} + (n_1 - n_2)e$	$A^{-n_2} + (n_1 - n_2)e \longrightarrow A^{-n_1}$

(3) Oxidants are substances which:

(a) oxidize other.

(b) reduced themselves.

(c) show electronation.

(d) show a decrease in oxidation no. during a redox change.

(e) has higher oxidation no. in a conjugate pair of redox.

(4) Reductants are substances which:

(a) reduce other.

(b) oxidized themselves.

(c) show de-electronation.

(d) show an increase in oxidation no. during a redox change.

(e) has lower oxidation no. in a conjugate pair of redox.

(5) A redox change is one in which a reductant is oxidized to liberate electrons, which are then used up by an oxidant to get itself reduced.

$$M_1 \longrightarrow M_1^{+n} + ne \quad \text{Oxidation}$$

$$\underline{M_2^{+n} + ne \longrightarrow M_2} \quad \text{Reduction}$$

$$M_1 + M_2^{+n} \longrightarrow M_1^{+n} + M_2 \quad \text{Redox reaction}$$

(6) A redox change occurs simultaneously.

[B] Types of Redox changes

(1) **Intermolecular redox reactions :** Two substances reacts; one of them is oxidant and other is reductant, *e.g.*,

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow$$

$$2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$

$$Mn^{7+} + 5e \longrightarrow Mn^{2+}$$

(2) **Auto redox reactions or disproportionation :** The same element is oxidized and reduced as well, *e.g.*,

$$2Cu^{2+} \longrightarrow Cu^{2+} + Cu^0$$

Cu^+ is oxidized to Cu^{2+} and Cu^+ is reduced to Cu.

(3) **Intramolecular redox reactions :** One element of a compound is oxidized and other element of the same compound is reduced, *e.g.*,

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

Cl is reduced ($Cl^{5+} + 6e \longrightarrow Cl^-$) and O is oxidized

$$[2(O^{2-})_3 \longrightarrow 3O_2^0 + 12e]$$

$$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$$

N is oxidized ($2N^{3-} \longrightarrow N_2^0 + 6e$) and Cr is reduced

$$[(Cr^{6+})_2 + 6e \longrightarrow (Cr^{3+})_2]$$

[C] Oxidation Number

(1) Oxidation no. of an element in a particular compound represents the no. of electrons lost or gained by an element during its change from free state into that compound.

or Oxidation no. of an element in a particular compound represents the extent of oxidation or reduction of an element during its change from free state into that compound.

(2) Oxidation no. is given positive sign if electrons are lost. Oxidation no. is given negative sign if electrons are gained.

(3) Oxidation no. represents real charge in case of ionic compounds. However, in covalent compounds it represents imaginary charge.

[D] Rules for Deriving Oxidation Number

Following rules have been arbitrarily adopted to decide oxidation no. of elements on the basis of their periodic properties.

(1) In uncombined state or free state, oxidation no. of an element is zero.

(2) In combined state oxidation no. of......

(a) ......F is always −1.

(b) ......O is −2. In peroxides it is −1. However in F_2O it is +2.

(c) ......H is +1. In ionic hydrides it is −1. (*i.e.*, IA, IIA and IIIA metals)

(d) ......halogens as halide is always −1.

(e) ......sulphur as sulphide is always −2.

(f) ......metals is always +ve.

(g) ......alkali metals (*i.e.*, IA group–Li, Na, K, Rb, Cs, Fr) is always +1.

(h) ......alkaline earth metals (*i.e.*, IIA group—Be, Mg, Ca, Sr, Ba, Ra) is always +2.

(3) The algebraic sum of all the oxidation no. of elements in a compound is equal to zero, *e.g.*, $KMnO_4$.

Ox. no. of K + Ox. no. of Mn + (Ox. no. of O) × 4 = 0

(4) The algebraic sum of all the oxidation no. of elements in a radical is equal to the net charge on the radical, *e.g.*, CO_3^{2-}.

Oxidation no. of C + 3 × (Oxidation no. of O) = −2

(5) Oxidation number can be zero, +ve, −ve (integer or fraction).

(6) Maximum oxidation no. of an element is = Group no. (Except O and F)

Minimum oxidation no. of an element is = Group no.–8 (Except metals)

[E] Oxidation State

It is defined as oxidation no. per atom, *e.g.*, in $KMnO_4$

Oxidation no. of Mn is = +7

Oxidation state of Mn is = Mn^{7+}

[F] Balancing a half reaction

Consider for example : $Fe_2O_3 \longrightarrow Fe_3O_4$

Step I : Write down the symbol of element with its oxidation number on two sides of reaction.

$$Fe^{3+} \longrightarrow Fe^{8/3+}$$

Step II : Write the elemental form of element in which it exist in that compound as shown below.

$$(Fe^{3+})_2 \longrightarrow (Fe^{8/3+})_3$$

Step III : Make the number of atoms same on two sides as reported below :

$$3(Fe^{3+})_2 \longrightarrow 2(Fe^{8/3+})_3$$

Step IV : Multiply the all digits on right hand side $\left[i.e., 2 \times 3 \times \left(+\frac{8}{3}\right) = +16\right]$ and on left hand side [*i.e.*, 3 × 2 × (+3) = +18] than subtract the value of left hand side from right hand side [*i.e.*, +16 − (+18) = −2],

Put this number (−2) with electron on right hand side, with its sign.

$$3(Fe^{3+})_2 \longrightarrow 2(Fe^{8/3+})_3 - 2e$$

[G] Balancing of Redox Equations

Two methods are commonly used for this purpose.

1. Ion Electron Method

It involves three sets of rules depending upon the nature of medium (*i.e.*, neutral, acid or alkaline) in which reaction occurs.

(a) Neutral medium:

e.g., $H_2C_2O_4 + KMnO_4 \longrightarrow CO_2 + K_2O + MnO + H_2O$

Step 1. Select the oxidant, reductant atoms and write their half reactions, one representing oxidation and other reduction.

i.e., $(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$

$$5e + Mn^{7+} \longrightarrow Mn^{2+}$$

Step 2. Balance the no. of electrons and add the two equations.

$$5(C^{3+})_2 \longrightarrow 10C^{4+} + 10e$$

$$10e + 2Mn^{7+} \longrightarrow 2Mn^{2+}$$

$$\overline{5(C^{3+})_2 + 2Mn^{7+} \longrightarrow 10C^{4+} + 2Mn^{2+}}$$

Step 3. Write complete molecule of the reductant and oxidant from which respective redox atoms were obtained.

$$5H_2C_2O_4 + 2KMnO_4 \longrightarrow 10CO_2 + 2MnO$$

Step 4. Balance other atoms if any (except H and O).

In above example K is unbalanced, therefore,

$$5H_2C_2O_4 + 2KMnO_4 \longrightarrow 10CO_2 + 2MnO + K_2O$$

(mentioned as product)

Step 5. Balance O-atom using H_2O on desired side.

$$5H_2C_2O_4 + 2KMnO_4 \longrightarrow 10CO_2 + 2MnO + K_2O + 5H_2O$$

(b) Acidic medium:

e.g., $NO_3^- + H_2S \xrightarrow{H^+} HSO_4^- + NH_4^+$

proceed like neutral medium for step 1 to step 4.

Step 1. $8e + N^{5+} \longrightarrow N^{3-}$

$$S^{2-} \longrightarrow S^{6+} + 8e$$

Step 2. $N^{5+} + S^{2-} \longrightarrow N^{3-} + S^{6+}$

Step 3. $NO_3^- + H_2S \longrightarrow NH_4^+ + HSO_4^-$

Step 4. No other atom (except H and O) is unbalanced and thus, no need for this step.

Step 5. Balance O-atom: Balancing of O-atom is made by using H_2O and H^+ ions.

Add desired molecules of H_2O on the side deficient with O-atom and double H^+ on opposite side. Therefore,

$$H_2O + NO_3^- + H_2S \longrightarrow NH_4^+ + HSO_4^- + 2H^+$$

Step 6. Balance charge by H^+:

$$3H^+ + H_2O + NO_3^- + H_2S \longrightarrow NH_4^+ + HSO_4^- + 2H^+$$

∴ Finally balanced equation is,

$$H^+ + H_2O + NO_3^- + H_2S \longrightarrow NH_4^+ + HSO_4^-$$

(c) Alkaline medium:

e.g., $Fe + N_2H_4 \xrightarrow{OH^-} Fe(OH)_2 + NH_3$

Proceed like neutral medium for step 1 to step 4.

Step 1. $Fe \longrightarrow Fe^{2+} + 2e$

$2e + (N^{2-})_2 \longrightarrow 2N^{3-}$

Step 2. $Fe + (N^{2-})_2 \longrightarrow Fe^{2+} + 2N^{3-}$

Step 3. $Fe + N_2H_4 \longrightarrow Fe(OH)_2 + 2NH_3$

Step 4. No other atom (except H and O) is unbalanced and thus, no need for this step.

Step 5. Balance O-atom: Balancing of O-atom is made by using H_2O and OH^- ions.

Add desired molecules of H_2O on the side rich with O-atoms and double OH^- on opposite side. Therefore,

$$4OH^- + Fe + N_2H_4 \longrightarrow Fe(OH)_2 + 2NH_3 + 2H_2O$$

Step 6. Balance charge by H^+:

$$4OH^- + 4H^+ + Fe + N_2H_4 \longrightarrow Fe(OH)_2 + 2NH_3 + 2H_2O$$

∴ Finally balanced equation is,

$$2H_2O + Fe + N_2H_4 \longrightarrow Fe(OH)_2 + 2NH_3$$

2. Oxidation State Method

e.g., $KMnO_4 + H_2C_2O_4 \longrightarrow CO_2 + K_2O + MnO + H_2O$

The initial step 1 should be written as

Step 1. $Mn^{7+} \longrightarrow Mn^{2+}$ *i.e.*, change in oxidation no. of Mn $(+7 \longrightarrow +2) = 5$ units

$(C^{3+})_2 \longrightarrow 2C^{4+}$ *i.e.*, change in oxidation no. of C $(+6 \longrightarrow +8) = 2$ units

Step 2. Proceed from step 2 to last step for neutral, acidic or alkaline medium as in ion electron method.

[H] Balancing of Half Reactions

Example 1. $I_2 \longrightarrow IO_3^-$ (Acid medium)

Step 1. Balance atoms other than O and H if needed, *i.e.*,

$$I_2 \longrightarrow 2IO_3^-$$

Step 2. Balance O-atoms using H^+ and H_2O as reported earlier.

$$I_2 + 6H_2O \longrightarrow 2IO_3^- + 12H^+$$

Step 3. Balance charge by electrons.

$$I_2 + 6H_2O \longrightarrow 2IO_3^- + 12H^+ + 10e$$

This is balanced half reaction.

Example 2. $S_2O_3^{2-} \longrightarrow SO_2$ (Basic medium)

Step 1. As above $S_2O_3^{2-} \longrightarrow 2SO_2$

Step 2. Balance O-atom by H_2O and OH^- as reported earlier.

$$2OH^- + S_2O_3^{2-} \longrightarrow 2SO_2 + H_2O$$

Step 3. Balance charge by electrons.

$$2OH^- + S_2O_3^{2-} \longrightarrow 2SO_2 + H_2O + 4e$$

This is balanced half reaction.

• NUMERICAL PROBLEMS •

1. Determine the oxidation no. of following elements given in bold letters:
   (a) $K\mathbf{Mn}O_4$, (b) H_2SO_5, (c) $H_2\mathbf{S}_2O_8$, (d) NH_4NO_3, (e) $K_4\mathbf{Fe}(CN)_6$, (f) $\mathbf{Os}O_4$, (g) HCN, (h) HNC, (i) HNO_3, (j) $K\mathbf{O}_2$, (k) $\mathbf{Fe}_3O_4$, (l) $K\mathbf{I}_3$, (m) $^-\mathbf{O}CN$, (n) $\mathbf{Fe}(CO)_5$, (o) $\mathbf{Fe}_{0.94}O$, (p) $NH_2 \cdot NH_2$, (q) $\mathbf{Fe}SO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (r) NOCl, (s) $NOClO_4$, (t) $Na_2[\mathbf{Fe}(CN)_5NO]$, (u) $[\mathbf{Fe}(NO)(H_2O)_5]SO_4$, (v) $Na_2\mathbf{S}_4O_6$, (w) Dimethyl sulphoxide or $(CH_3)_2SO$, (x) $Na_2\mathbf{S}_2O_3$, (y) $\mathbf{Cr}O_5$ or $\mathbf{Cr}O(O_2)_2$, (z) $CaO\mathbf{Cl}_2$.
2. Determine the oxidation number of following elements given in bold letters :
   (a) $\mathbf{Cu}H$, (b) $Na_2\mathbf{S}_3O_6$, (c) $\mathbf{N}_2O$, (d) $Ba_2\mathbf{Xe}O_6$, (e) $\mathbf{C}_3O_2$, (f) $\mathbf{V}(BrO_2)_2$, (g) $Ca(\mathbf{ClO}_2)_2$, (h) $Cs_4Na(H\mathbf{V}_{10}O_{28})$, (i) $LiAlH_4$, (j) $K[\mathbf{Co}(C_2O_4)_2 \cdot (NH_3)_2]$, (k) $[\mathbf{Ni}(CN)_4]^{2-}$, (l) $Na_2\mathbf{S}_2$, (m) $[\mathbf{Xe}O_6]^{4-}$, (n) HOCN, (o) $(CN)_2$
3. Find the oxidation number of Fe in Fe_3O_4 and in $Fe(III)_4[Fe(II)(CN)_6]_3$.
4. Find out the value of *n* in:
$$MnO_4^- + 8H^+ + ne \longrightarrow Mn^{2+} + 4H_2O$$
5. Calculate the oxidation number of Mn in the product formed on strongly heating Mn_2O_7.
6. Calculate the oxidation number of Mn in the product of alkaline oxidative fusion of MnO_2. **(IIT 2009)**
7. One mole of N_2H_4 loses 10 mole electrons to form a new compound *Y*. Assuming that all the N_2 appears in new compound, what is oxidation state of N in *Y*?
8. In the reaction, $Al + Fe_3O_4 \longrightarrow Al_2O_3 + Fe$
   (a) Which element is oxidized and which is reduced?
   (b) Total no. of electrons transferred during the change.
9. The composition of a sample of wustite is $Fe_{0.93}O_{1.00}$. What percentage of iron is present in the form of Fe (III)? **(IIT 1994)**
10. Select the species acting as reductant and oxidant in the reaction given below:
$$PCl_3 + Cl_2 \longrightarrow PCl_5$$
11. Identify the substance acting as oxidant or reductant reduced if any in the following :
    (i) $AlCl_3 + 3K \longrightarrow Al + 3KCl$
    (ii) $SO_2 + 2H_2S \longrightarrow 3S + H_2O$
    (iii) $BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2NaCl$
    (iv) $3I_2 + 6NaOH \longrightarrow NaIO_3 + 5NaI + 3H_2O$
12. Arrange the following in order of:
    (a) Increasing oxidation no.of Mn: $MnCl_2, MnO_2, Mn(OH)_3, KMnO_4$
    (b) Decreasing oxidation no. of *X* : HXO_4, HXO_3, HXO_2, HXO
    (c) Increasing oxidation no. of I: I_2, HI, HIO_4, ICl **(IIT 1986)**
13. Which of the following are oxidants and which are reductants? Justify your answer with half equations?
$$Fe^{3+}, SO_3, NO_3^-, I^-, Na$$
14. HNO_3 acts only as oxidant whereas, HNO_2 acts as reductant and oxidant both.
15. Balance the following equations:
    (a) $BaCrO_4 + KI + HCl \longrightarrow BaCl_2 + I_2 + KCl + CrCl_3 + H_2O$
    (b) $SO_2 + Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2SO_4 + Cr_2(SO_4)_3 + H_2O$
    (c) $C_2H_5OH + I_2 + OH^- \longrightarrow CHI_3 + HCO_2^- + H_2O + I^-$ (Basic)
16. Write down the disproportionation of HNO_2 in cold water.
17. Eight mole of chlorine (Cl_2) undergoes a loss and gain of 14 mole of electrons to form two oxidation state of chlorine (Cl). Write down the two half reaction and equation for disproportionation of chlorine, Cl_2.

SOLUTIONS (Numerical Problems)

1. (a) **$KMnO_4$**: Ox. no. of K = +1 by rules

Ox. no. of Mn = a

Ox. no. of O = −2 by rules

$\therefore \quad 1 + a + 4 \times (-2) = 0$

$\therefore \quad a = +7$

(b) H_2SO_5: Ox. no. of H = +1

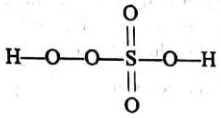
Ox. no. of O = −2

Ox. no. of S = a

$\therefore \quad 2 \times 1 + a + 5 \times (-2) = 0$

$a = +8$ **(wrong)**

But this cannot be true as maximum ox. no. for S (VI gp) stands + 6. The exceptional value is due to the fact that two O-atoms in H_2SO_5 show peroxide linkage, *i.e.*,



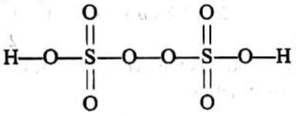
$$H{-}O{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}O{-}H$$

Thus, evaluation of ox. no. of S should be made as

$2 \times 1 + a + 3 \times (-2) + 2 \times (-1) = 0$

$\therefore \quad a = +6$

(c) $H_2S_2O_8$: Here too, two O-atoms form peroxide linkage, *i.e.*,



$$H{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}O{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}O{-}H$$

$\therefore \quad 2 \times 1 + 2a + 6 \times (-2) + 2 \times (-1) = 0$

$\therefore \quad a = +6$

(d) NH_4NO_3: $2 \times a + 4 \times 1 + 3 \times (-2) = 0$ by rules

$a = +1$ **(wrong)**

No doubt there are two N-atoms in NH_4NO_3, but one N-atom has negative ox. no. (attached to H) and the other has positive ox. no. (attached to O). Therefore, evaluation should be made separately as

Ox. no. of N in NH_4^+	and	Ox. no. of N in NO_3^-
$a + 4 \times (+1) = +1$		$a + 3 \times (-2) = -1$
$\therefore \quad a = -3$		$\therefore \quad a = +5$

(e) $K_4Fe(CN)_6$: By rules, Ox. no. of K = + 1 **(MLNR 1986)**

Ox. no. of CN^{-1} = − 1

Ox. no. of Fe = a

$\therefore \quad 4 \times 1 + a + 6 \times (-1) = 0$

$\therefore \quad a = +2$

(f) OsO_4: $a + 4 \times (-2) = 0$

$\therefore \quad a = +8$

Note : **1.** The element Os and Ru show highest oxidation state, *i.e.*, + 8.

2. Recently Ba_2XeO_6 has been reported in which ox. no. of Xe is + 8.

(g) HCN : The evaluation cannot be made directly in some cases, *e.g.*, HCN by using rules proposed earlier since we have no rule for ox. no. of both N and C.

In all such cases evaluation of ox. no. should be made using indirect concept or using fundamentals by which rules have been framed.

(1) Each covalent bond contributes one unit for ox. no.

(2) Covalently bonded atoms with less electronegativity acquires positive ox. no. whereas other with more electronegativity acquires negative ox. no.

(3) In case of co-ordinate bond, give + 2 value for ox. no. to atom from which co-ordinate bond is directed to a more electronegative atom and − 2 value to more electronegative atom.

If co-ordinate bond is directed from more electronegative to less electronegative atom, then neglect contribution of co-ordinate bond for both atoms in which co-ordinate bond exist.

Thus, $H{-}C{\equiv}N$

$1 + a + 3 \times (-1) = 0$

$a = +2$

$\because$ **Three bonds on N-atom and N is more electronegative**

$\therefore$ **Ox. no. of N $= 3 \times (-1) = -3$**

(h) HNC : $H{-}N\overset{\rightarrow}{\equiv}C$

Ox. no. of H = + 1

$$\text{Ox. no. of N} = [\underset{\substack{\text{for covalent}\\ \text{bond with C}}}{-2} + \underset{\substack{\text{[for covalent}\\ \text{bond with H]}}}{(-1)} + \underset{\substack{\text{No. contribution}\\ \text{for co-ordinate bond}}}{0}] = -3$$

(According to fundamental concept)

= −3

$\therefore \quad 1 + (-3) + a = 0$

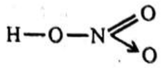
$\therefore \quad a = +2$

(i) HNO_3: By rules

$1 + a + 3 \times (-2) = 0$

$\therefore \quad a = +5$

By fundamental approach



Ox. no. of H = + 1

$$\text{Ox. no. of N} = \underset{\substack{\text{Covalent bond}\\ \text{with O}}}{+1} + \underset{\substack{\text{Two covalent}\\ \text{bond with O}}}{(+2)} + \underset{\substack{\text{Co-ordinate}\\ \text{bond}}}{(+2)} = +5$$

$\because$ N being less electronegative than O.

(j) **KO_2:** A super oxide of K; **(MLNR 1988)**

Ox. no. of $K = +1$

Ox. no. of $O = a$

$$1 + 2 \times a = 0$$

$$\therefore \quad a = -\frac{1}{2}$$

(k) **Fe_3O_4:** $3 \times a + 4 \times (-2) = 0$

$$\therefore \quad a = +\frac{8}{3}$$

or Fe_3O_4 is a mixed oxide of $FeO \cdot Fe_2O_3$

$\therefore$ Fe has two oxidation no. +2 and +3 separately. However, factually speaking ox. no. of Fe in Fe_3O_4 is an average of two values (*i.e.*, +2 and +3)

$$\text{Average ox. no.} = \frac{+2 + 2 \times (+3)}{3} = +\frac{8}{3}$$

(l) **KI_3:** $1 + 3 \times (a) = 0$

$$a = -\frac{1}{3}$$

or KI_3 is $KI + I_2$

$\therefore$ I has two oxidation no. −1 and 0 respectively. However, factually speaking ox. no. of I in KI_3 is an average of two values −1 and 0.

$$\text{Average Ox. no.} = \frac{-1 + 2 \times (0)}{3} = -\frac{1}{3}$$

(m) **^-OCN:** $^-O—C \equiv N$

$$a + 4 - 3 = -1 \quad \text{(Follow covalent rules)}$$

$$\therefore \quad a = -2$$

(n) **$Fe(CO)_5$:** Sum of ox. no. of $CO = 0$

$$\therefore \quad a + 5 \times (0) = 0$$

$$\therefore \quad a = 0$$

(o) **$Fe_{0.94}O$:** $0.94 \times a + (-2) = 0$

$$a = \frac{200}{94}$$

(p) $NH_2 \cdot NH_2$: Both N have same nature.

$$a + 2 + a + 2 = 0$$

$$\therefore \quad a = -2$$

(q) **$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$:** Ox. no. of $Fe = a$

Sum of ox. no. for $(NH_4)_2SO_4 = 0$

Sum of ox. no. for $H_2O = 0$

Sum of ox. no. for $SO_4^{2-} = -2$

$$\therefore \quad a + (-2) + 0 + 6 \times (0) = 0$$

$$\therefore \quad a = +2$$

(r) NOCl: $Cl—N{=}O$ or use NO^+Cl^-

Ox. no. of $N = +1$ (for covalent bond with Cl)

Ox. no. of $N = +2$ (for two covalent bonds with O)

$\therefore$ Total ox. no. of N in $NOCl = +3$

(s) **$NOClO_4$:** The compound may be written as $NO^+ClO_4^-$ for ClO_4^-.

For ClO_4^-, let Ox. no. of $Cl = a$

$$a + 4 \times (-2) = -1$$

$$a = +7$$

(t) **$Na_2[Fe(CN)_5NO]$:** NO in iron complex has NO^+ nature.

$$\therefore \quad 2 \times 1 + [a + 5 \times (-1) + (+1)] = 0$$

$$\therefore \quad a = +2$$

(u) **$[Fe(NO)(H_2O)_5]SO_4$:**

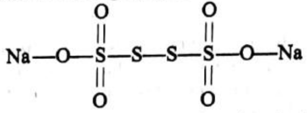
$$a + 1 + 5 \times 0 + (-2) = 0$$

$$a = +1$$

(v) **$Na_2S_4O_6$:** $2 \times (+1) + 4a + 6 \times (-2) = 0$

$$\therefore \quad a = +\frac{5}{2}$$

Here also this value is the average oxidation no. of S. The structure of $Na_2S_4O_6$ is



$$Na—O—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—S—S—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—O—Na$$

Thus, ox. no. of each S-atom forming double bond is +5 whereas, ox. no. of each S-atom involved in pure covalent bonding is zero.

$$\therefore \quad \text{Average ox. no.} = \frac{+5 + 5 + 0 + 0}{4} = +\frac{5}{2}$$

(w) Dimethyl sulphoxide or $(CH_3)_2SO$:

Ox. no. of $CH_3 = +1$; Ox. no. of $O = -2$

$$\therefore \quad 2 \times (+1) + a + (-2) = 0$$

$$a = 0$$

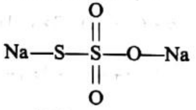
(x) $Na_2S_2O_3$:

$$2 \times 1 + 2 \times a + 3 \times (-2) = 0$$

$$\therefore \quad a = +2$$

Here too it is the average ox. no.

The structure of $Na_2S_2O_3$ is

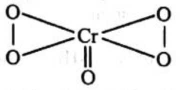


$$Na—S—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—O—Na$$

The ox. no. of S involved in double bond is +5.

The ox. no. of other S-atom is −1.

(y) **CrO_5** or **$CrO(O_2)_2$:** CrO_5 has butterfly structure as:



i.e., two peroxide bonds and thus four oxygen atoms have ox. no. = −1 and one oxygen atom has ox. no. −2

Thus, $a + 4 \times (-1) + 1 \times (-2) = 0 \quad \therefore a = +6$

(z) **$CaOCl_2$:** In bleaching powder two Cl-atoms are as $Ca(OCl) \cdot Cl$, *i.e.*, one as Cl^- having ox. no. **−1** and other as OCl^- having ox. no. **+1.**

2. (a) **CuH:** $a + 1 = 0$

$\therefore \quad a = -1$ ($\because$ H in CuH has +1 oxidation number)

(b) $Na_2S_3O_6$: $2 \times 1 + 3 \times a + 6 \times (-2) = 0$

$$\therefore \quad a = +\frac{10}{3}$$

(c) **N_2O:** $2\times a+(-2)=0$

$$a=+1$$

Although it is average of two oxidation numbers as shown below :

$$\underset{0}{N}\equiv\underset{+2}{N}\longrightarrow\underset{-2}{O}$$

(d) Ba_2XeO_6: $2\times 2+a+6\times(-2)=0$

$$a=+8$$

(e) C_3O_2: $3\times a+2\times(-2)=0$

$\therefore$ $a=+\frac{4}{3}$

(f) $V(BrO_2)_2$: The BrO_2 ion is monovalent and thus oxidation number of $V=+2$

(g) $Ca(ClO_2)_2$: The ClO_2 ion is monovalent and thus for ClO_2^- ion

$$a+2\times(-2)=-1 \quad \therefore \; a=+3$$

(h) $Cs_4Na(HV_{10}O_{28})$:

$4\times 1+1\times 1+[1+10\times a+28\times(-2)]=0 \;\therefore\; a=+5$

(i) $LiAlH_4$: $1+a+4\times(-1)=0$

$\therefore$ $a=+3$

(j) $K[Co(C_2O_4)_2\cdot(NH_3)_2]: 1+[a+2\times(-2)+2\times 0]=0$

$\therefore$ $a=+3$

(k) $[Ni(CN)_4]^{2-}$: $a+4\times(-1)=-2$

$$a=+2$$

(l) Na_2S_2: Like peroxide, ox. no. of S in S_2^{2-} is -1.

(m) $[XeO_6]^{4-}$: In per xenate Xe has $+8$ oxidation number

$$a+6\times(-2)=-4$$

$$a=+8$$

(**Note :** No per oxide bond).

(n) HOCN : Follow bonding rules to evaluate oxidation number.

$$\begin{array}{cccc} +1 & -1 & +1 & -3 \\ H\!-\!\!\!\! & O\!-\!\!\!\! & C\equiv & N \\ & -1 & +3 & \\ \hline +1 & -2 & +4 & -3 \end{array}$$

(o) $(CN)_2$: $(\overset{+3}{C}\equiv\overset{-3}{N})_2$

Follow bonding rules to evaluate oxidation number.

3. Let the oxidation number of Fe be a

Fe_3O_4 : $3\times a+4\times(-2)=0$

$$a=+\frac{8}{3}$$

Actually this is average oxidation number of Fe in Fe_3O_4. It exist in $FeO\cdot Fe_2O_3$ having oxidation number of Fe $+2$ in FeO and $+3$ in Fe_2O_3. Thus, average oxidation number

$$=\frac{2\times 1\text{atom of Fe (in FeO)}+3\times 2\text{atoms of Fe (in }Fe_2O_3)}{3\text{ (Total atoms of Fe)}}=+\frac{8}{3}$$

$Fe(III)_4[Fe(II)(CN)_6]_3$: Fe(III) has $+3$ oxidation number

Fe(II) has $+2$ oxidation number

Also, average oxidation number

$$=\frac{4\times(+3)+3\times(+2)}{7}=+\frac{18}{7}$$

4. Total charge on LHS = Total charge on RHS.

$$(-1)+8+(-n)=+2$$

$\therefore$ $n=5$

5. $2Mn_2O_7 \xrightarrow{\Delta} 4MnO_2+3O_2$, oxidation number of Mn in MnO_2 is $+4$.

6. $2MnO_2+4KOH+O_2 \longrightarrow 2K_2MnO_4+2H_2O$, oxidation number of Mn in K_2MnO_4 is $+6$.

7. $N_2H_4 \longrightarrow (Y)+10e$

$\because$ Y contains all N-atoms

$\therefore$ $(N^{2-})_2 \longrightarrow (2N)^a+10e$

Therefore, $2a-(-4)=10$

$$a=+3$$

8. $2Al^0 \longrightarrow (Al^{3+})_2+6e$ ...(1)

$8e+(Fe^{8/3+})_3 \longrightarrow 3Fe^0$ ...(2)

Multiplying Eq. (1) by 4 and Eq. (2) by 3, then adding

$$8Al^0 \longrightarrow 4(Al^{3+})_2+24e$$

$$24e+3(Fe^{8/3+})_3 \longrightarrow 9Fe^0$$

$$\underline{8Al^0+3(Fe^{8/3+})_3 \longrightarrow 4(Al^{3+})_2+9Fe^0}$$

or $8Al+3Fe_3O_4 \longrightarrow 4Al_2O_3+9Fe$

Therefore, it is clear that

(a) **Al is oxidized and $Fe^{8/3+}$ is reduced.**

(b) Total no. of electrons transferred during change = **24.**

9. Oxidation no. of Fe in wustite is $=\frac{200}{93}=2.15$

It is an intermediate value in between two oxidation state of Fe as, Fe (II) and (III),

Let percentage of Fe (III) be a, then

$$2\times(100-a)+3\times a=2.15\times 100$$

or $a=15.05$

$\therefore$ Percentage of Fe (III) = **15.05%**

10. $P^{3+} \longrightarrow P^{5+}+2e$

$$2e+Cl_2^0 \longrightarrow 2Cl^{1-}$$

$\therefore$ **PCl_3 is reductant**
and **Cl_2 is oxidant.**

$\because$ In a conjugate pair of redox the one having higher ox. no. is oxidant.

11. In a conjugate pair, oxidant has higher ox. no.

(i) **For $AlCl_3$:** $Al^{3+}+3e \longrightarrow Al^0$;

$\therefore$ **Oxidant is $AlCl_3$**

For K : $K^0 \longrightarrow K^{1+}+e$

$\therefore$ **Reductant is K.**

(ii) **For SO_2 :** $S^{4+}+4e \longrightarrow S^0$;

$\therefore$ **SO_2 is oxidant.**

For H_2S : $S^{2-} \longrightarrow S^0+2e$

$\therefore$ **H_2S is reductant.**

(iii) No change in ox. no. of either of the conjugate pair.

$\therefore$ **None is oxidant or reductant.**

(iv) **For I_2 :** $I_2^0 \longrightarrow 2I^{5+}+10e$ and $I_2^0+2e \longrightarrow 2I^{1-}$

$\therefore$ **I_2 acts as oxidant and reductant both.**

12. (a) $\mathrm{MnCl_2 < Mn(OH)_3 < MnO_2 < KMnO_4}$

Ox. no. $+2 \quad +3 \quad +4 \quad +7$

(b) $\mathrm{HXO_4 > HXO_3 > HXO_2 > HXO}$

Ox. no. $+7 \quad +5 \quad +3 \quad +1$

(c) $\mathrm{HI < I_2 < ICl < HIO_4}$

Ox. no. $-1 \quad 0 \quad +1 \quad +7$

13. Oxidants : $\mathrm{Fe^{3+}, NO_3^-, SO_3}$

$$\mathrm{Fe^{3+} + 3}e \longrightarrow \mathrm{Fe}$$
$$\mathrm{N^{5+} + 2}e \longrightarrow \mathrm{N^{3+}}$$
$$\mathrm{S^{6+} + 2}e \longrightarrow \mathrm{S^{4+}}$$

Reductants : $\mathrm{I^-, Na}$

$$\mathrm{Na} \longrightarrow \mathrm{Na^+} + e$$
$$\mathrm{2I^-} \longrightarrow \mathrm{I_2} + 2e$$

14. $\mathrm{HNO_3}$: Ox. no. of N is +5 in $\mathrm{HNO_3}$

Maximum ox. no. of N is +5

Minimum ox. no. of N is –3

Thus, ox. no. of N in $\mathrm{HNO_3}$ is maximum and it can decrease only. That is why $\mathrm{HNO_3}$ acts as oxidant only.

$\mathrm{HNO_2}$: Ox. no. of N is +3 in $\mathrm{HNO_2}$

Maximum ox. no. of N is +5

Minimum ox. no. of N is –3

Thus, ox. no. of N (in $\mathrm{HNO_2}$) can show an increase or decrease as the case may be. That is why $\mathrm{HNO_2}$ acts as oxidant and reductant both.

15. (a) $\mathrm{BaCrO_4 + KI + HCl \longrightarrow BaCl_2 + I_2 + KCl + CrCl_3 + H_2O}$

Step I. $3e + \mathrm{Cr^{6+}} \longrightarrow \mathrm{Cr^{3+}}$

$$\mathrm{2I^-} \longrightarrow \mathrm{I_2} + 2e$$

Step II.

$$\begin{array}{l} 6e + \mathrm{2Cr^{6+}} \longrightarrow \mathrm{2Cr^{3+}} \\ \mathrm{6I^-} \longrightarrow \mathrm{3I_2} + 6e \\ \hline \mathrm{2Cr^{6+} + 6I^- \longrightarrow 2Cr^{3+} + 3I_2} \end{array}$$

Step III. $\mathrm{2BaCrO_4 + 6KI \longrightarrow 2CrCl_3 + 3I_2}$

Step IV. Balancing of other atoms except (H and O), *i.e.*, Ba, K and Cl.

$$\mathrm{2BaCrO_4 + 6KI + 16HCl \longrightarrow 2CrCl_3 + 3I_2 + 6KCl + 2BaCl_2}$$

Step V. Balance H-atom

$$\mathrm{2BaCrO_4 + 6KI + 16HCl \longrightarrow 2CrCl_3 + 3I_2 + 6KCl + 2BaCl_2 + 8H_2O}$$

(b) $\mathrm{SO_2 + Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2SO_4 + Cr_2(SO_4)_3 + H_2O}$

Step I. $\mathrm{S^{4+}} \longrightarrow \mathrm{S^{6+}} + 2e$

$$6e + \mathrm{2Cr^{6+}} \longrightarrow \mathrm{(Cr^{3+})_2}$$

Step II.

$$\begin{array}{l} \mathrm{3S^{4+}} \longrightarrow \mathrm{3S^{6+}} + 6e \\ 6e + \mathrm{2Cr^{6+}} \longrightarrow \mathrm{(Cr^{3+})_2} \\ \hline \mathrm{3S^{4+} + 2Cr^{6+} \longrightarrow 3S^{6+} + (Cr^{3+})_2} \end{array}$$

Three $\mathrm{S^{6+}}$ atoms are distributed in $\mathrm{2Na_2SO_4}$ and $\mathrm{1Cr_2(SO_4)_3}$

Step III.

$$\mathrm{3SO_2 + 2Na_2CrO_4 \longrightarrow 2Na_2SO_4 + Cr_2(SO_4)_3}$$

Balancing of other atoms, *i.e.*, S in $\mathrm{SO_4}$.

Step IV. $\mathrm{3SO_2 + 2Na_2CrO_4 + 2H_2SO_4 \longrightarrow 2Na_2SO_4 + Cr_2(SO_4)_3}$

Step V. Balance H-atom

$$\mathrm{3SO_2 + 2Na_2CrO_4 + 2H_2SO_4 \longrightarrow 2Na_2SO_4 + Cr_2(SO_4)_3 + 2H_2O}$$

(c) $\mathrm{C_2H_5OH + I_2 + OH^- \longrightarrow CHI_3 + HCO_2^- + H_2O + I^-}$

Step I. $\mathrm{(C^{2-})_2} \longrightarrow \mathrm{2C^{2+}} + 8e$

$$2e + \mathrm{I_2^0} \longrightarrow \mathrm{2I^{1-}}$$

Step II.

$$\begin{array}{l} \mathrm{(C^{2-})_2} \longrightarrow \mathrm{2C^{2+}} + 8e \\ 8e + \mathrm{4I_2} \longrightarrow \mathrm{8I^-} \\ \hline \mathrm{(C^{2-})_2 + 4I_2 \longrightarrow 2C^{2+} + 8I^-} \end{array}$$

Step III. $\mathrm{2C^{2+}}$ are distributed one each in $\mathrm{CHI_3}$ and $\mathrm{HCO_2^-}$, $\mathrm{8I^-}$ are distributed three in $\mathrm{CHI_3}$ and 5 in $\mathrm{I^-}$

$\therefore$ $\mathrm{C_2H_5OH + 4I_2 \longrightarrow CHI_3 + HCO_2^- + 5I^-}$

Step IV. Balancing other atoms . . . . . . no need since no other (except H and O) atoms are unbalanced.

Step V. Balance O-atom by $\mathrm{OH^-}$ and $\mathrm{H_2O}$

$$\mathrm{C_2H_5OH + 4I_2 + 2OH^- \longrightarrow CHI_3 + HCO_2^- + 5I^- + H_2O}$$

Step VI. Balance charge by $\mathrm{H^+}$

$$\mathrm{C_2H_5OH + 4I_2 + 2OH^- \longrightarrow CHI_3 + HCO_2^- + 5I^- + H_2O + 4H^+}$$

Do not leave $\mathrm{OH^-}$ and $\mathrm{H^+}$ free in an equation and thus,

$$\mathrm{C_2H_5OH + 4I_2 + 2OH^- + 4OH^- \longrightarrow CHI_3 + HCO_2^- + 5I^- + H_2O + 4H^+ + 4OH^-}$$

$$\mathrm{C_2H_5OH + 4I_2 + 6OH^- \longrightarrow CHI_3 + HCO_2^- + 5I^- + 5H_2O}$$

16. $\mathrm{3H\overset{+3}{N}O_2 \longrightarrow 2\overset{+2}{N}O + H\overset{+5}{N}O_3 + H_2O}$

17. $\mathrm{Cl_2}$ can undergo only in $\mathrm{Cl^-}$ state to show loss of electron. Since loss and gain of 14 electrons occurs between $\mathrm{Cl_2}$ and thus 7 mole show oxidation.

$$\begin{array}{l} \mathrm{Cl_2} + 2e \longrightarrow \mathrm{2Cl^-}] \times 7 \\ \mathrm{Cl_2^0} \longrightarrow \mathrm{2Cl^{7+}} + 14e \\ \hline \mathrm{8Cl_2 \longrightarrow 2Cl^{7+} + 14Cl^-} \end{array}$$

● SINGLE INTEGER ANSWER PROBLEMS ●

1. The positive oxidation no. of Xe in perxenate ion is:

2. The value of *n* in the reaction :

$$Cr_2O_7^{2-} + ne + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

3. Total number of electrons involved in change:

$$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe.$$

4. If four mole of Br_2 undergo a loss and gain of six mole electrons to form two new oxidation state of Br. How much Br_2 mole acts as reductant?

5. The total number of electrons involved in redox change:

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2.$$

6. The stoichiometric coefficient *n* in the reaction is:

$$nH_2CO_2 + 2KMnO_4 \longrightarrow nCO_2 + K_2O + MnO + H_2O$$

7. Intramolecular redox

$$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$$

shows a loss and gain of how much electron?

8. The stoichiometric coefficient of blue perchromate in its reaction with H_2SO_4 is ....

9. The tailing of mercury on exposure to air shows a change in oxidation number by ....

10. Total number of electrons involved per molecule oxidation of FeC_2O_4 to Fe^{3+} and CO_2.

11. No. of peroxide bonds in blue perchromate is ....

12. In the reaction $P_4 + NaOH \longrightarrow PH_3 + NaH_2PO_2$, mole ratio of NaH_2PO_2 and PH_3 is ....

13. In the reaction : $Mn^{2+} + S_2O_8^{2-} \longrightarrow SO_4^{2-} + MnO_4^-$ (acid mid.) the number of mole of $S_2O_8^{2-}$ required to oxidise 2 mole Mn^{2+}.

14. The ratio of oxygen atom having −2 and −1 oxidation numbers in $S_2O_8^{2-}$ is ....

15. Five mole of Ferric oxalate are oxidised by how much mole of $KMnO_4$ in acid medium?

16. 1 mole of Cu_2S reduces how many mole of $KMnO_4$? If the redox reaction is

$$Cu_2S + KMnO_4 + H_2SO_4 \longrightarrow CuSO_4 + MnSO_4 + K_2SO_4 + H_2O$$

17. Number of electrons lost per molecule of Fe_3O_4 during its oxidation to Fe_2O_3 is ....

18. Number of H_2O_2 mole needed to convert two mole of $Cr(OH)_3$ in alkaline medium into sodium chromate are ....

19. Number of mole of KO_2 required to absorb one mole of CO are ....

20. Six mole of I_2 undergoes disproportionation involving 10 electrons, what is the oxidation number of oxidised iodine atom?

21. The ratio of oxidation numbers of carbon in hydrocyanic acid and isocyanic acid is :

22. Oxidation number of Xe in Barium perxenate is :

23. The number of electrons involved in the change :

$$Cu_2S \longrightarrow Cu^{2+} + SO_2 \text{ is :}$$

24. On heating $FeCr_2O_4$ with Na_2CO_3 in presence of $KClO_3$, the total number of electrons lost by one Cr atom are :

25. The oxidation number of Cr in the product formed on heating $K_2Cr_2O_7$ with KOH is :

26. On combustion of CH_4 to CO_2 and H_2O, the oxidation number of carbon changes by :

27. Oxidation no. of carbon in NaCNS is :

28. On passing NO to $FeSO_{4(aq)}$ brown ring formation takes place, the oxidation number of Fe changes by :

29. The most common oxidation state of an element is −2. The number of electrons present in its outer most shell is:

30. The difference in oxidation number of two nitrogen atoms in NH_4NO_3 is ....

31. The difference in oxidation number of Cl atoms in $CaOCl_2$ is ....

32. How much of the following have per oxide bonds ? Blue per chromate, Barium per xenate, Barium per oxide, H_2SO_5, PbO_2, $H_2S_2O_8$, Permanganic acid, Perchloric acid.

33. The sum of the oxidation numbers of two different oxidation states of Fe atoms in Fe_3O_4 is ....

34. Number of electrons involved in the redox change : $2Fe + O_2 + 4H^+ \longrightarrow 2Fe^{2+} + 2H_2O$, are ....

35. Oxidation number of Na in Na-Hg amalgam is ....

36. In the reaction, $VO + Fe_2O_3 \longrightarrow FeO + V_2O_5$, the number of electrons used in redox reaction are ....

37. Number of O—O bonds in K_3CrO_8 is ....

38. 4 mole of Cl_2 undergoes disproportionation involving six electrons in change. How much Cl_2 molecules are oxidised?

39. Number of pi bonds in Br_3O_8 are ....

40. Among the following, the number of elements showing only one non zero oxidation state is .... **(IIT 2010)**

O, Cl, F, N, P, Sn, Tl, Na, Ti

41. The value of *n* in the molecular formula $Be_nAl_2Si_6O_{18}$ is .... **(IIT 2010)**

42. The difference in the oxidation number of the two types of sulphur atoms in $Na_2S_4O_6$ is .... **(IIT 2011)**

ANSWERS

1. Eight	**2.** Six	**3.** Six	**4.** One	**5.** Eight	**6.** Five	**7.** Six	**8.** Four	**9.** One	**10.** Three	**11.** Two	**12.** Three
13. Five	**14.** Three	**15.** Six	**16.** Two	**17.** One	**18.** Three	**19.** Two	**20.** Five	**21.** One	**22.** Eight	**23.** Eight	**24.** Zero
25. Six	**26.** Eight	**27.** Four	**28.** One	**29.** Six	**30.** Eight	**31.** Two	**32.** Four	**33.** Five	**34.** Four	**35.** Zero	**36.** Six
37. Four	**38.** One	**39.** Eight	**40.** Two	**41.** Three	**42.** Five						

OBJECTIVE PROBLEMS (One Answer Correct)

1. In which of the following highest oxidation state is not possible:
(a) $[XeO_6]^{4-}$
(b) XeF_8
(c) OsO_4
(d) RuO_4

2. Number of per oxide bonds in per xenate ion $[XeO_6]^{4-}$ is:
(a) 0
(b) 2
(c) 3
(d) 1

3. Oxidation number of Pr in Pr_6O_{11} is:
(a) $\frac{22}{6}$
(b) $\frac{20}{6}$
(c) 3
(d) 4

4. Oxidation number of S in H_2SO_5 is:
(a) +8
(b) +6
(c) +4
(d) +2

5. Which one is not correct about the change given below?

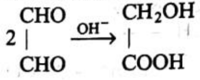
$$K_4Fe(CN)_6 \xrightarrow{\text{oxi}} Fe^{3+} + CO_2 + NO_3^-$$

(a) Fe is oxidised Fe^{2+} to Fe^{3+}
(b) Carbon is oxidised from C^{2+} to C^{4+}
(c) N is oxidised from N^{3-} to N^{5+}
(d) Carbon is not oxidised

6. Which of the following is not a intramolecular redox?
(a) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$
(b) $2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$
(c) $2KClO_3 \longrightarrow 2KCl + 3O_2$
(d) $2H_2O_2 \longrightarrow 2H_2O + O_2$

7. Which of the following is not disproportionation?
(a) $P_4 + 5OH^- \longrightarrow H_2PO_4^- + PH_3$
(b) $Cl_2 + OH^- \longrightarrow ClO + ClO^-$
(c) $2H_2O_2 \longrightarrow 2H_2O + O_2$
(d) $PbO_2 + H_2O \longrightarrow PbO + H_2O_2$

8. Which of the following is intermolecular redox reaction?

(a) 

$$2\begin{array}{c}CHO\\|\\CHO\end{array} \xrightarrow{OH^-} \begin{array}{c}CH_2OH\\|\\COOH\end{array}$$

(b) $2C_6H_5CHO \xrightarrow{Al(OC_2H_5)_3} C_6H_5COOH + C_6H_5CH_2OH$
(c) $4CrO_5 + 6H_2SO_4 \longrightarrow 2Cr_2(SO_4)_3 + 6H_2O + 7O_2$
(d) $As_2S_3 + HNO_3 \longrightarrow H_3AsO_4 + H_2SO_4 + NO$

9. The number of electrons lost in the change are:

$$Fe + H_2O \longrightarrow Fe_3O_4 + H_2$$

(a) 2
(b) 4
(c) 6
(d) 8

10. The oxidation state of A, B and C in a compound are +2, +5 and −2 respectively. The compound is:
(a) $A_2(BC)_2$
(b) $A_2(BC)_3$
(c) $A_3(BC_4)_2$
(d) $A_2(BC_4)_3$

11. In the equation : $NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + ne$; n stands for:
(a) 1
(b) 2
(c) 3
(d) 4

12. The oxidation number of sulphur in S_8, S_2F_2 and H_2S are:
(a) 0, +1 and −2
(b) +2, +1 and −2
(c) 0, +1 and +2
(d) −2, +1 and −2

13. In a reaction, 4 mole of electrons are transferred to 1 mole of HNO_3, the possible product obtained due to reduction is :
(a) 0.5 mole of N_2
(b) 0.5 mole of N_2O
(c) 1 mole of NO_2
(d) 1 mole of NH_3

14. The colour of $K_2Cr_2O_7$ changes from red-orange to lemon-yellow on treatment with KOH ($aq.$) because of:
(a) Reduction of Cr (VI) to Cr (III)
(b) Formation of chromium hydroxide
(c) Conversion of dichromate into chromate ion
(d) Oxidation of potassium hydroxide to potassium peroxide

15. During developing of an exposed camera film, one step involves in the following reaction,

(Hydroquinol)

$+ 2Ag + 2H_2O + 2Br^-$

which of the following best describes the role of hydroquinol :
(a) It acts as an acid
(b) It act as reducing agent
(c) It acts as oxidant
(d) It act as a base

16. Which of the following is not correct for the reaction,

$$(CN)_2 + 2OH^- \longrightarrow CNO^- + CN^- + H_2O$$

(a) It is a disproportionation reaction
(b) N atom disproportionates and oxidation number of N are −3 in $(CN)_2$, −2 in CN^- and −5 in CNO^-
(c) C atom disproportionate and oxidation number carbon are +3 in $(CN)_2$, +4 in CNO^- and +2 in CN^-
(d) $(CN)_2$ undergoes auto redox

17. One mole of N_2H_4 loses 10 mole of electrons to form a new compound y. Assuming that all the nitrogen appears in the new compound, what is the oxidation state of N in y. (There is no change in the oxidation state of H.)
(a) −1
(b) −3
(c) +3
(d) +5

18. The oxidation number of carbon in CH_2O is :
(a) −2
(b) +2
(c) 0
(d) +4

19. The brown ring complex is formulated as $[Fe(H_2O)_5NO]SO_4$. The oxidation number of Fe is :
(a) +1 (b) +2
(c) +3 (d) 0

20. The oxidation number of phosphorus in $Ba(H_2PO_2)_2$ is :
(a) +3 (b) +2
(c) +1 (d) −1

21. The oxidation state of the most electronegative element in the products of the reaction, BaO_2 with dil H_2SO_4 are :
(a) 0 and −1 (b) −1 and −2
(c) −2 and 0 (d) −2 and +1

22. For the redox reaction,

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

The correct coefficients of the reactants for the balanced reaction are :

	MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	2	5	16
(b)	16	5	2
(c)	5	16	2
(d)	2	16	5

23. Oxidation number of carbon in C_3O_2 and Mg_2C_3 are respectively:
(a) $+\frac{2}{3}, -\frac{2}{3}$ (b) $+\frac{4}{3}, -\frac{4}{3}$
(c) $-\frac{4}{3}, +\frac{4}{3}$ (d) $-\frac{2}{3}, +\frac{2}{3}$

24. In the reaction : $NaH + H_2O \longrightarrow NaOH + H_2$, which one is not correct :
(a) H-atom undergoes oxidation
(b) H-atom undergoes reduction
(c) It is a redox change
(d) It is disproportionation reaction

25. Ozone tails mercury due to :
(a) oxidation of Hg
(b) reduction of Hg
(c) adsorption of O_3 on Hg
(d) none of these

26. The tailing of mercury is removed by :
(a) O_2 (b) H_2O_2
(c) SO_2 (d) O_3

27. Iodine has +7 oxidation state in :
(a) HIO_4 (b) H_3IO_5
(c) H_5IO_6 (d) all of these

28. Which of the following compound is not possible for +7 oxidation state of iodine ?
(a) IF_7 (b) I_2O_7
(c) ICl_7 (d) None of these

29. Amongst the following identify the species with an atom in +6 oxidation state: **(IIT 2000)**
(a) MnO_4^- (b) $Cr(CN)_6^{3-}$
(c) NiF_6^{2-} (d) CrO_2Cl_2

30. In the standardisation of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent mass of $K_2Cr_2O_7$ is: **(IIT 2001)**
(a) $M/2$ (b) $M/6$
(c) $M/3$ (d) M

31. The reaction;

$$3ClO^-\,(aq.) \longrightarrow ClO_3^-\,(aq.) + 2Cl^-\,(aq.)$$

is an example of: **(IIT 2001)**
(a) oxidation reaction (b) reduction reaction
(c) disproportion (d) decomposition

32. Maximum oxidation state is present in: **(IIT 2004)**
(a) CrO_2Cl_2 and MnO_4^-
(b) MnO_2
(c) $[Fe(CN)_6]^{3-}$ and $[Co(CN)_6]^3$
(d) MnO

33. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type; the oxidation states of phosphorus in phosphine and the other product are respectively : **(IIT 2012)**
(a) redox reaction; −3 and − 5
(b) redox reaction; +3 and + 5
(c) disproportionation reaction; −3 and + 1
(d) disproportionation reaction; −3 and + 3

34. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen? **(IIT 2012)**
(a) HNO_3, NO, NH_4Cl, N_2
(b) HNO_3, NO, N_2, NH_4Cl
(c) HNO_3, NH_4Cl, NO, N_2
(d) NO, HNO_3, NH_4Cl, N_2

35. Consider the following reaction :

$$xMnO_4^- + y\,C_2O_4^{2-} + zH^+ \longrightarrow xMn^{2+} + 2y\,CO_2 + \frac{z}{2}H_2O$$

The values of x, y and z in the reaction are, respectively : **[JEE (Main) 2013]**
(a) 2, 5 and 16 (b) 5, 2 and 8
(c) 5, 2 and 16 (d) 2, 5 and 8

36. Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal M, is present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be : **[JEE (Main) 2013]**
(a) 6.05% (b) 5.08%
(c) 7.01% (d) 4.08%

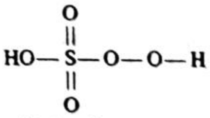
SOLUTIONS (One Answer Correct)

1. (b) No doubt Xe shows + 8 oxidation state XeF_8 does not exist because of crowding of 8 F-atoms.

2. (a) Oxidation no. of Xe in $[XeO_6]^{4-}$ is + 8.

3. (a) Pr_6O_{11}, $6 \times a + (11 \times -2) = 0$ (No O—O bond),
$a = +\frac{22}{6}$

4. (b) H_2SO_5 is



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

i.e., one peroxide bond.

5. (d) Carbon is also oxidised.

6. (d) Intramolecular redox change involve oxidation of one atom and reduction of other atom within a molecule.

7. (d) Disproportionation involves oxidation reduction of same atom in a molecule.

8. (d) Intermolecular redox change involves oxidation of one molecule and reduction of other molecule.

9. (d)

$$\begin{array}{c} 3Fe^{\circ} + 8e \longrightarrow (Fe^{+8/3})_3 \\ [(H^+)_2 \longrightarrow (H^{\circ})_2 + 2e] \times 4 \\ \hline 3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2 \end{array}$$

10. (c) $A_3(BC_4)_2$, $3 \times 2 + [5 + 4 \times (-2)] \times 2 = 0$

11. (b) Balance charge on two sides.

12. (a) $S_8 : a \times 8 = 0$ $\therefore a = 0$
$S_2F_2 : a \times 2 + 2 \times (-1) = 0$ $\therefore a = +1$
$H_2S : 2 \times 1 + a = 0$ $\therefore a = -2$

13. (b) $2N^{5+} \longrightarrow (N^+)_2 + 8e$
2 mole HNO_3 gives one mole of N_2O.

14. (c) $K_2Cr_2O_7 + 2KOH \longrightarrow 2K_2CrO_4 + H_2O$

15. (b) $Ag^+ + e \longrightarrow Ag$; hydroquinol reduces Ag^+ to Ag

16. (b) Rest all are true

17. (c) $(N^{2-})_2 \longrightarrow (2N^{+a}) + 10e$
$\therefore$ $2a - (-4) = 10$
$a = +3$

18. (c) $a + 2 \times (+1) - 2 \times 1 = 0$

19. (a) NO in iron complex has +1 oxidation state.

20. (c) $2 \times 1 + 2[2 \times 1 + a + 2 \times (-2)] = 0$
$\therefore$ $a = +1$

21. (b) Products are $BaSO_4$ and H_2C_2.

22. (a) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

23. (b) $C_3O_2 : 3 \times a + 2(-2) = 0$
$a = +\frac{4}{3}$
$Mg_2C_3 : 2 \times 2 + 3 \times a = 0$
$a = -\frac{4}{3}$

24. (d) $Na\overset{-1}{H} + \overset{+1}{H_2}O \longrightarrow NaOH + \overset{0}{H_2}$

25. (a) $Hg + O_3 \longrightarrow HgO + O_2$
HgO formed is responsible for tailing

26. (b) $HgO + H_2O_2 \longrightarrow Hg + H_2O + O_2$

27. (d) Each has +7 oxidation state of I.

28. (c) Highest oxidation state of an element is noticed with fluorine and oxygen.

29. (d) Cr in $CrO_2Cl_2 : a + 2 \times (-2) + 2 \times (-1) = 0$,
$\therefore$ $a = +6$

30. (b) $(Cr^{6+})_2 + 6e \longrightarrow 2Cr^{3+}$
$\therefore$ $E_{K_2Cr_2O_7} = \frac{M}{6}$

31. (c) Cl-atom is oxidised ($Cl^+ \longrightarrow Cl^{5+} + 4e$) as well as Cl is reduced. ($Cl^+ + 2e \longrightarrow Cl^-$) such reactions are called disproportionation or auto-redox changes.

32. (a) Cr has + 6 and Mn has + 7 oxidation state.

33. (c) The balanced disproportionation reaction involving white phosphorus with aq. NaOH is

Oxidation of P^0 to P^{+1} state

$$P_4^0 + 3NaOH + 3H_2O \longrightarrow \overset{-3}{P}H_3 + 3NaH_2\overset{+1}{P}O_2$$

Reduction of P^0 to P^{-3} state

34. (b) The oxidation state of N are +5, +2, 0 and –3 in HNO_3, NO, N_2 and NH_4Cl respectively.

35. (a) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

36. (d) Average oxidation no. of $M = +\frac{200}{98}$
(lies between 2 and 3)
Let % of M^{2+} be a and of M^{3+} be b
or $\frac{2 \times a + (100 - a) \times 3}{100} = 2.04 (\because a + b = 100)$
$\therefore$ $2a + 300 - 3a = \frac{200}{98}$
$\therefore$ $+a = 300 - 2.04 \times 100$
$= 300 - 204$
$= 96$
Thus $M^{2+} = 96\%$
$M^{3+} = 4\%$

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Which of the following are disproportionation redox changes?
   (a) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$
   (b) $5H_2O_2 + 2ClO_2 + 2OH^- \rightarrow 2Cl^- + 5O_2 + 6H_2O$
   (c) $3ClO^- \longrightarrow ClO_3^- + Cl^-$
   (d) $2HCuCl_2 \xrightarrow[\text{water}]{\text{Dilution with}} Cu + Cu^{2+} + 4Cl^- + 2H^+$
2. Which one are correct about the reaction?
   $HgS + HCl + HNO_3 \longrightarrow H_2HgCl_4 + NO + S + H_2O$
   (a) Hg is reduced (b) Sulphide is oxidised
   (c) N is reduced (d) HNO_3 is oxidant
3. Which of the followings are disproportionation reactions?
   (a) $2O_3 \longrightarrow 3O_2$
   (b) $4KClO_3 \longrightarrow 3KClO_4 + KCl$
   (c) $2H_2O_2 \longrightarrow 2H_2O + O_2$
   (d) $2KO_2 + 2H_2O \longrightarrow 4KOH + 3O_2$
4. For the reaction,
   $KO_2 + H_2O + CO_2 \longrightarrow KHCO_3 + O_2$; the mechanism of reaction suggests that:
   (a) acid-base reaction
   (b) disproportionation reaction
   (c) hydrolysis
   (d) redox change
5. Which of the following can be used as oxidant and reductant both?
   (a) HNO_2 (b) SO_2
   (c) O_2 (d) CO
6. Which molecules represented by the bold atoms show their highest oxidation state?
   (a) $H_2\underline{S_2}O_8$ (b) $\underline{P_4}O_{10}$
   (c) $\underline{F_2}O$ (d) $\underline{Mn_2}O_7$
7. Which molecules represented by the bold atoms show their lowest oxidation state?
   (a) $F_2\underline{O}$ (b) $H_2\underline{S}$
   (c) $\underline{P}H_3$ (d) $\underline{N_2}H_4$
8. Which one are not correct about $CH_2 = CCl_2$?
   (a) Both carbon are in +2 oxidation state
   (b) Both carbon are in −2 oxidation state
   (c) One carbon has +2 and other has −2 oxidation state
   (d) The average oxidation number of carbon is zero
9. Which is correct about tailing of Hg?
   (a) it is due to Hg_2O (b) it is due to HgO
   (c) it is removed by H_2O_2 (d) it is removed by O_3
10. Thermal decomposition of $(NH_4)_2Cr_2O_7$ involves :
    (a) Oxidation of N (b) Reduction of Cr
    (c) Intramolecular redox (d) Disproportionation
11. $LiAlH_4$ is used as :
    (a) an oxidant (b) a reductant
    (c) a mordant (d) water softner
12. Which of the following are disproportionation reaction:
    (a) $F_2 + H_2O \longrightarrow HOF + HF$
    (b) $2HCHO + NaOH \longrightarrow HCOONa + CH_3OH$
    (c) $P_{4(s)} + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$
    (d) $2NO_2 + 2KOH \longrightarrow KNO_2 + KNO_3 + H_2O$
13. In which of the following oxidation no. of nitrogen atom is correctly matched :
    (a) $HC\underline{N}$ −3
    (b) $H\underline{N}C$ −3
    (c) $HOC\underline{N}$ −3
    (d) $(C\underline{N})_2$ −2
14. Select the correct statements :
    (a) Oxidation number of oxygen in O_2^+ is $+\frac{1}{2}$
    (b) Oxidation number of oxygen in O_2^- is $-\frac{1}{2}$
    (c) Oxidation number of Cr in K_3CrO_8 is +5
    (d) Average oxidation number of Br in tribromo-octaoxide (Br_3O_8) is $+\frac{18}{3}$

SOLUTIONS (More Than One Answer Correct)

1. (c,d) $e + Cl^{+} \longrightarrow Cl^{-}$ $Cu^{+} \longrightarrow Cu^{2+} + e$
$Cl^{+} \longrightarrow Cl^{5+} + 4e$ $Cu^{+} + e \longrightarrow Cu$

2. (b,c,d) $S^{2-} \longrightarrow S^{\circ} + 2e,\ 3e + N^{5+} \longrightarrow N^{2+}$

3. (b,c,d) $Cl^{+5} \longrightarrow Cl^{+7} + Cl^{-}$
$O^{-} \longrightarrow O^{-2} + O_2^0$
$O_2^{-1/2} \longrightarrow O^{-2} + O_2^0$

4. (a,b,c,d) $4KO_2 + 2H_2O \longrightarrow 4KOH + 3O_2$
(Hydrolysis and disproportionation)
$4KOH + 4CO_2 \longrightarrow 4KHCO_3$ (Acid-base reaction)

5. (a,b,c,d) The element (in a molecule) having its oxidation state in the middle (*i.e.*, > minimum)
and < maximum) can be used as reductant and oxidant both.

6. (a,b,d) The highest oxidation state is given by the gp. number (except O, F).

7. (b,c) The lowest oxidation state is given by (gp. number – 8) except metals.

8. (a,b) Average is zero.

9. (a,c) Hg gets oxidised by O_3 to give sticking nature on glass
$$2Hg + O_3 \longrightarrow Hg_2O + O_2$$
$$Hg_2O + H_2O_2 \longrightarrow Hg_2 + H_2O + O_2$$

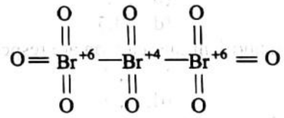
10. (a,b,c) $(\overset{-3}{N}H_4)_2\overset{+6}{Cr_2}O_7 \longrightarrow \overset{0}{N_2} + \overset{+3}{Cr_2}O_3 + 4H_2O$

11. (b) It is a fact.

12. (b,c,d) $\overset{0}{F_2} + H_2\overset{-2}{O} \longrightarrow H\overset{0}{O}\overset{-1}{F} + H\overset{-1}{F}$
$2H\overset{0}{C}HO + NaOH \longrightarrow H\overset{+2}{C}OONa + \overset{-2}{C}H_3OH$
$\overset{0}{P}_{4(s)} + 3NaOH + 3H_2O \longrightarrow \overset{-3}{P}H_3 + 3NaH_2\overset{+1}{P}O_2$
$2\overset{+4}{N}O_2 + 2KOH \longrightarrow K\overset{+3}{N}O_2 + K\overset{+5}{N}O_3 + H_2O$

13. (a,b,c) Oxidation no. of N in $(CN)_2$ is –3.

14. (a,b,c) In Br_3O_8 two Br atoms have +6 oxidation number and one has +4. The average oxidation no. is $+\frac{16}{3}$.



COMPREHENSION BASED PROBLEMS

Comprehension 1 : In the chemical change:
$aN_2H_4 + bBrO_3^- \longrightarrow aN_2 + bBr^- + 6H_2O$, answer the following questions:

[1] The element oxidised and reduced in the reaction are respectively:
(a) N_2H_4, BrO_3^- (b) N, Br
(c) H, Br (d) BrO_3^-, N_2H_4

[2] The number of electrons lost or gained during the redox change are:
(a) 8 (b) 10
(c) 12 (d) 6

[3] The equivalent mass of N_2H_4 in the above reaction is:
(a) 8 (b) 10.6
(c) 16 (d) 6.4

[4] The equivalent mass of $KBrO_3$ in the above reaction is:
(a) 167 (b) 27.83
(c) 55.67 (d) 83.5

[5] The values of *a* and *b* in the reaction are respectively:
(a) 3, 2 (b) 2, 3
(c) 4, 6 (d) 6, 4

[6] The species acting as oxidant and reductant respectively are:
(a) BrO_3^-, N_2H_4 (b) N_2H_4, BrO_3^-
(c) N_2, BrO_3^- (d) Br^-, N_2H_4

[7] The conjugate pair of oxidant-reductant is:
(a) BrO_3^-, Br^- (b) $N_2H_4^-, BrO_3^-$
(c) Br^-, N_2 (d) Br^-, BrO_3^-

[8] The reaction shows:
(a) intermolecular redox (b) auto redox
(c) intramolecular redox (d) either of these

Comprehension 2 : A redox reaction involves oxidation of reductant liberating electrons, which are then consumed by an oxidant. The sum of two half reactions give rise to net redox change. In half reaction charge and atoms are always conserved.

[1] Which of the following half reaction is correct for the redox change :
$$Fe_3O_4 \longrightarrow Fe_2O_3 + FeO$$
(a) $Fe^{+8/3} \longrightarrow Fe^{+3} + \frac{1}{3}e$
(b) $Fe^{+8/3} \longrightarrow Fe^{+2} - \frac{2}{3}e$
(c) $(Fe^{+8/3})_3 \longrightarrow 3Fe^{+2} + 2e$
(d) $2(Fe^{+8/3})_3 \longrightarrow 3(Fe^{+3})_2 + 2e$

[2] In the reaction :
$As_2S_3 + HNO_3 \longrightarrow H_3AsO_4 + H_2SO_4 + NO$ the element oxidised is :
(a) As only (b) S only
(c) N only (d) As and S both

[3] In the equation :
$NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + ne$, *n* stands for :
(a) 1 (b) 2
(c) 3 (d) 4

[4] In half reaction :
$S_2O_3^{2-} \longrightarrow S_4O_6^{2-}$, The number of electrons that must be added :
(a) 2, on right side (b) 2, on left side
(c) 3, on right side (d) 4, on left side

SOLUTIONS

Comprehension 1

[1] (b) $(N^{2-})_2 \longrightarrow N_2^0 + 4e$

$Br^{5+} + 6e \longrightarrow Br$

[2] (c) $(N^{2-})_2 \longrightarrow N_2^0 + 4e] \times 3$

$Br^{5+} + 6e \longrightarrow Br^-] \times 2$

[3] (a) $E_{N_2H_4} = \dfrac{\text{Molar mass of } N_2H_4}{\text{No. of } e \text{ lost by 1 molecule}} = \dfrac{32}{4} = 8$

[4] (b) $E_{KBrO_3} = \dfrac{\text{Molar mass of } KBrO_3}{6} = \dfrac{167}{6} = 27.83$

[5] (a)

$$\begin{array}{c} (N^{2-})_2 \longrightarrow N_2^0 + 4e] \times 3 \\ Br^{5+} + 6e \longrightarrow Br^-] \times 2 \\ \hline 3N_2H_4 + 2BrO_3^- \longrightarrow 3N_2 + 2Br^- \end{array}$$

Balancing H atoms

$3N_2H_4 + 2BrO_3^- \longrightarrow 3N_2 + 2Br + 6H_2O$

[6] (a) BrO_3^- acts as an oxidant and N_2H_4 as reductant

[7] (a) BrO_3^- is oxidant and its conjugate reductant is Br^-

[8] (a) It is intermolecular redox where one species is oxidised and the other is reduced.

Comprehension 2

[1] (d) Electrons and atoms are conserved in half reaction.

[2] (d) $(As^{+3})_2 \longrightarrow 2As^{+5} + 4e$

$(S^{-2})_3 \longrightarrow 3S^{+6} + 24e$

[3] (b) Balance charge on two sides.

[4] (a) $2(S^{+2})_2 \longrightarrow (S^{+5/2})_4 + 2e$

STATEMENT EXPLANATION PROBLEMS

Read the statement **(S)** and explanation **(E)** given below. Choose the correct choices (a), (b), (c) from (d) the options:

(a) S is correct but **E** is wrong

(b) S is wrong but **E** is correct

(c) Both S and **E** are correct and **E** is correct explanation of S

(d) Both S and E are correct but **E** is not correct explanation for S

1. S : Reaction of white phosphorus with NaOH(*aq*) gives PH_3.

E : The reaction is disproportionation of P in alkaline medium.

2. S : Na_2SO_3 solution is oxidised by air but Na_3AsO_3 not. However Na_3AsO_3 is oxidised in presence of Na_2SO_3 by air.

E : The reaction is called induced oxidation.

3. S : Copper forms complexes $[CuCl_4]^{2-}$ but not $[CuI_4]^{2-}$.

E : $[CuI_4]^{2-}$ is not stable because Cu^{2+} is oxidant and I^- is reductant.

4. S : The passage of H_2S through aqueous solution of SO_2 gives yellow turbidity of S in solution.

E : The yellow turbidity of S is in colloidal state due to oxidation of H_2S by SO_2 *aq*.

5. S : Bleaching action of SO_2 is temporary whereas bleaching action of Cl_2 is permanent.

E : Bleaching by SO_2 and Cl_2 is due to oxidation.

6. S : Conversion of black lead painting is made to white by the action of H_2O_2.

E : Sulphur is oxidised to SO_4^{2-}.

7. S : CrO_5 on decomposition undergoes disproportionation.

E : CrO_5 undergoes intermolecular redox reaction.

8. S : NH_4NO_3 on heating gives N_2O.

E : NH_4NO_3 on heating shows disproportionation.

9. S : In azide ion average oxidation number of N is $-1/3$.

E : In azide ion two N atoms have zero oxidation number and one has oxidation number -1.

10. S : $K_2[CuCl_4]$ exists but $K_2[CuI_4]$ does not exist.

E : I^- is strong oxidant.

11. S : Oxidation number of Cu in CuH is -1.

E : Cu is placed below H in electrochemical series.

12. S : Oxidation state of H is $+1$ in CuH and -1 in CaH_2.

E : Ca is strong electropositive metal.

13. S : Oxygen atom in both O_2 and O_3 has oxidation number zero.

E : In F_2O, oxidation number of O is +2.

14. S : N atom has two different oxidation states in NH_4NO_2.

E : One N atom has –ve oxidation number as it is attached with less electronegative H atom and other has +ve oxidation number as it is attached with more electronegative atom.

15. S : $2H_2O_2 \longrightarrow 2H_2O + O_2$ is a auto redox change.

E : One oxygen atom is oxidised and one oxygen atom is reduced.

16. S : Oxidation number of metals in metal carbonyls is zero.

E : The oxidation number of CO has been taken to be zero.

17. S : SO_2 can be used as reductant as well as oxidant.

E : The oxidation number of S is +4 in SO_2 which lies in between its minimum (–2) and maximum (+6) values.

18. S : $KMnO_4$ is strong oxidant whereas Mn^{2+} is weaker reductant.

E : Stronger is the oxidant weaker is its conjugate reductant.

19. S : VO_2^+ and VO^{2+} both are called vanadyl ions.

E : VO_2^+ is dioxovanadium (V) ion and VO^{2+} is oxovanadium (IV) ion.

20. S : In the reaction,

$$3As_2S_3 + 28HNO_3 + 4H_2O \longrightarrow 6H_3AsO_4 + 9H_2SO_4 + 28NO$$

electrons transferred are 84.

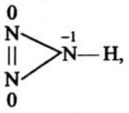
E : As is oxidised from +3 to +5 and sulphur from –2 to +6.

21. S : If a strong acid is added to a solution of potassium chromate it changes its colour from yellow to orange.

E : The colour change is due to the oxidation of potassium chromate.

ANSWERS (Statement Explanation Problems)

1. (c) $4P + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$
2. (c) Explanation is correct reason for statement.
3. (c) Explanation is correct reason for statement.
4. (c) $2H_2S + SO_2 \longrightarrow 2H_2O + 3S$
5. (a) $Cl_2 + H_2O \longrightarrow 2HCl + O;$

   $SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$
6. (c) $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$
7. (a) $CrO_5 \xrightarrow{\Delta} CrO_3 + O_2$ (Disproportionation of O^-)
8. (a) $NH_4NO_3 \longrightarrow N_2O + 2H_2O$ (intermolecular redox)
9. (c) 

   , Explanation is correct reason for statement.
10. (c) Explanation is correct reason for statement.
11. (c) The explanation is correct reason for statement.
12. (c) The explanation is correct reason for statement.
13. (d) The reason is that the sum of oxidation number of elements in a molecule is equal to zero.
14. (c) N in NH_4^+ is in −3 oxidation state and in NO_2^- it is in +3 oxidation state.
15. (c) The explanation is correct reason.

$$2O^- \longrightarrow O_2^0 + 2e$$
$$O^- + e \longrightarrow O^{2-}$$

16. (c) The explanation is correct reason for statement.
17. (c) The explanation is correct reason for statement.
18. (c) The explanation is correct reason for statement.
19. (d) Both statement and explanation are correct but explanation is not reason for statement.
20. (c)

$$\begin{array}{l} (As^{3+})_2 \longrightarrow 2As^{5+} + 4e \\ (S^{2-})_3 \longrightarrow 3S^{6+} + 24e \\ \hline [As_2S_3 \longrightarrow 2As^{5+} + 3S^{6+} + 28e] \times 3 \\ [3e + N^{5+} \longrightarrow N^{2+}] \times 28 \end{array}$$

21. (a) $\underset{\text{yellow}}{2CrO_4^{2-}} \xrightarrow{H^+} \underset{\text{orange}}{Cr_2O_7^{2-}}$

   Cr in +6 state.

MATCHING TYPE PROBLEMS

Type I : Only One Match Is Possible

1. Match the following :

List A	List B
(a) Intermolecular redox change	(i) $CO_2 + C \longrightarrow 2CO$
(b) Intramolecular redox change	(ii) $As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$
(c) Auto-redox change	(iii) $KClO_4 \longrightarrow KCl + 2O_2$
(d) Precipitation	(iv) $C_3O_2 \longrightarrow CO_2 + 2C$

Type II : More Than One Match Are Possible

2.

List A	List B
(a) HNO_2	(i) Oxidant
(b) HCN	(ii) Reductant
(c) CO	(iii) Complexing agent
(d) NaOCl	(iv) Acid
(e) $C_2O_4^{2-}$	(v) Base

3. Match the following with their minimum and maximum oxidation number if any as well as with respective variable oxidation number if any.

List A	List B
(a) N	(i) zero
(b) P	(ii) $-\frac{1}{3}$
(c) Mn	(iii) +3
	(iv) +5
(d) C	(v) +7
(e) Bi	(vi) +4
(f) Cl	(vii) −4

4.

Column-I	Column-II
(a) $O_2^- \rightarrow O_2 + O_2^{2-}$	(i) Redox reaction
(b) $CrO_4^{2-} + H^+ \rightarrow$	(ii) One of the products has trigonal planar structure
(c) $MnO_4^- + NO_2^- + H^+ \rightarrow$	(iii) Dimeric bridged tetra- hedral metal ion
(d) $NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow$	(iv) Disproportionation

Type III : Only One Match From Each List

5.

List-A	List-B	List-C
(a) CH_4	(i) E. mass $= M/8$	(A) $C^{2+} \longrightarrow C^{4+}$
(b) CO	(ii) E. mass $= M/2$	(B) $C^{-4} \longrightarrow C^{4+}$
(c) $C_2O_4^{2-}$	(iii) E. mass $= M/12$	(C) $C^{3+} \longrightarrow C^{4+}$
(d) C_2H_4		(D) $C^{-2} \longrightarrow C^{4+}$

ANSWERS

1. a–i; b–iii; c–iv; d–ii
2. a–i, ii, iv; b–ii, iii, iv; c–i, iii; d –i, ii; e–ii, iii, v
3. a–i, ii, iii, iv; b–i, iii, iv; c–i, iii, iv, v, vi; d–i, vi, vii; e–i, iii, iv; f–i, iii, iv, v, vi
4. a–i, iv; b–iii; c–i, ii; d–i
5. a–i–B; b–ii–A; c–ii–C; d–iii–D

7

Electrolysis and Electrochemical Cells

Electrolysis: The phenomenon in which passage of current through an electrolytic cell containing molten or aqueous solution brings in chemical changes involving electronation (reduction) as well as de-electronation (oxidation) of ions or atoms is known as electrolysis.

The products formed during electrolysis depend upon:

(1) Nature of electrolyte **See Examples I to III**

(2) Conc. of electrolyte **See Examples II (A and B)**

(3) Charge density flown during electrolysis **See Examples VIII (A and B)**

(4) Nature of electrodes used–attacked or non attacked electrode. **See Examples I to VII and IX**

Anode is the electrode at which oxidation occurs.

Cathode is the electrode at which reduction occurs.

Examples:

Case I. Electrolysis of molten NaCl using Pt electrodes:

At anode: $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e$

At cathode: $Na^+ + e \longrightarrow Na$

Thus, Cl_2 and Na are formed at anode and cathode respectively due to discharge of Cl^- and Na^+ at opposite electrodes.

Case II. Electrolysis of aq. NaCl using Pt electrodes:

A. Conc. NaCl(*aq.*) $NaCl \longrightarrow Na^+ + Cl^-$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

At anode: $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e$

At cathode: $H_3O^+ + e^- \longrightarrow H_2O + \frac{1}{2}H_2$

It is found experimentally that if a mixture of ions is electrolysed, certain ion gets discharged at an electrode in preference of other on the basis of preferential discharge theory. The more is the discharge potential (D.P.) of ion, lesser is its tendency to get discharged.

Discharge potential of Cl^- < Discharge potential of OH^-

Discharge potential of H_3O^+ < Discharge potential of Na^+

B. Dilute NaCl(*aq.*)

In case of very dilute solution of NaCl (*aq.*) following charges are noticed.

At anode: $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$

At cathode: $2H_3O^+ + 2e \longrightarrow 2H_2O + H_2$

Case III. Electrolysis of NaCl(*aq.*) using Hg as cathode:

At anode : $2Cl^- \longrightarrow Cl_2 + 2e$

At cathode: $2Na^+ + 2e \longrightarrow 2Na$

$$2Na + 2Hg \longrightarrow 2Na - Hg \text{ (amalgam)}$$

$$2Na - Hg + 2H_2O \longrightarrow 2NaOH + H_2 + 2Hg$$

The discharge potential of Na^+ <D.P. of H_3O^+ at Hg cathode.

Case IV. Electrolysis of HCl(*aq.*) using Pt electrodes:

At anode: $2Cl^- \longrightarrow Cl_2 + 2e$

At cathode: $2H_3O^+ + 2e \longrightarrow 2H_2O + H_2$

Case V. Electrolysis of $NaNO_3(aq.)$ or $Na_2SO_4(aq.)$ using Pt electrodes:

For $NaNO_3$(*aq.*)	**For Na_2SO_4 (*aq.*)**
At anode:	
$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$	$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$
At cathode:	
$2H_3O^+ + 2e \longrightarrow 2H_2O + H_2$	$2H_3O^+ + 2e \longrightarrow 2H_2O + H_2$
D.P. of NO_3^- > D.P. of OH^-	D.P. of SO_4^{2-} > D.P. of OH^-
D.P. of Na^+ > D.P. of H_3O^+	

Case VI. Electrolysis of $CuSO_4(aq.)$ or $AgNO_3(aq.)$ using Pt electrodes:

For $CuSO_4(aq.)$	**For $AgNO_3(aq.)$**
At anode:	
$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$	$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$
At cathode:	
$Cu^{2+} + 2e \longrightarrow Cu$	$Ag^+ + e \longrightarrow Ag$
D.P. of Cu^{2+} > D.P. of H_3O^+	D.P. of Ag^+ > D.P. of H_3O^+

Case VII: Electrolysis of $RCOONa(aq.)$ using Pt electrodes:

At anode: $2RCOO^- \longrightarrow R-R + 2CO_2 + 2e$

At cathode: $2H_3O^+ + 2e \longrightarrow 2H_2O + H_2$

D.P. of $RCOO^-$ < D.P. of OH^-

Case VIII: Electrolysis of H_2SO_4 using Pt electrodes:

Part A. Normal current density:

$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$ and $2H_2O \rightleftharpoons H_3O^+ + OH^-$

At anode: $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$

At cathode: $2H^+$ or $2H_3O^+ + 2e \longrightarrow 2H_2O + H_2$

$\because$ H^+ in solution exists as H_3O^+

Part B. High current density: Electrolysis of 50% H_2SO_4 using high current density gives:

At anode: $2HSO_4^- \longrightarrow H_2S_2O_8 + 2e$

At cathode: $2H^+ + 2e \longrightarrow H_2$

The distillation of $H_2S_2O_8$ with water yields H_2O_2

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$$
$$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$$

Note : All these examples were of non attacked electrodes.

Case IX: Attacked electrodes: The electrodes which themselves take part (dissolution or deposition occurs) in electronation or de-electronation, *e.g.*, electrolysis of $CuSO_4(aq.)$ using Cu electrodes.

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

At anode: Three reactions are possible

$Cu \longrightarrow Cu^{2+} + 2e \qquad E° = -0.34$ V

$SO_4^{2-} \longrightarrow SO_4 + 2e \qquad E° = -2.0$ V

$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e \qquad E° = -1.2$ V

It is clear that discharge potential of Cu^{2+} to get oxidized is lowest and thus Cu anode dissolves in preference to other process.

Thus in case of attacked electrodes:

(1) Metal dissolves at anode, *i.e.*, oxidation.

(2) Metal ions are reduced at cathode.

(3) No change in concentration of solution during electrolysis.

Note : 1. The phenomenon of electrolysis occurs only at the electrodes. Oxidation occurs at anode; reduction occurs at cathode.

2. Corrosion of metals is electrochemical phenomenon. It is defined as the process of slow oxidation of metals. *e.g.*, rusting of iron, tarnishing of silver, green deposits on copper.

3. Rusting of iron is favoured by H^+ (*i.e.*, water vapours in atmosphere), CO_2 and O_2.

4. Purest form of metal is not corroded. Strained articles of metals are easily corroded.

5. Rust is $Fe_2O_3 \cdot XH_2O$.

Faraday's laws of Electrolysis

I law: The mass, w of an ion oxidized or reduced at either electrodes during the passage of current (*i.e.*, electrolysis) is directly proportional to the quantity of charge passed through electrolyte, *i.e.*,

$$w \propto Q$$
$$\propto i\,t$$
$$w = Z\,i\,t \qquad ...(1)$$

Q is total charge passed through electrolyte

i is current strength in amperes

t is time in seconds for which current flows

Z is electrochemical equivalent, a characteristic constant for the given metal defined as the mass of ion oxidized or reduced by the passage of one coulomb charge. The unit of $Z = \text{kg C}^{-1}$.

Note : 1. One Faraday of charge = charge on one mole electron

= charge which discharges one g equivalent of ion

$= 1.602 \times 10^{-19} \times 6.023 \times 10^{23}$

= charge which deposits or discharges E g where, E is eq. mass

= 96514.8 C

≈ 96500 C

Thus, 96500 C discharge E g of ion

$\therefore$ 1 C discharge $\frac{E}{96500}$ g ion $= Z$

$\therefore$ By Eq. (1) $\qquad w = \frac{E \cdot i \cdot t}{96500} \qquad ...(2)$

2. Also, $\qquad F = N \times e \qquad ...(3)$

where, F is charge in Faraday, N is Avogadro's number, e is charge on one electron,

3. Equivalent of an ion discharged, $\left(\frac{w}{E}\right) = \frac{i \cdot t}{96500} \quad ...(4)$

II law: The passage of same charge through different electrolytes, brings in equal equivalents of ions to be oxidized or reduced at either electrodes as the case may be

$$\frac{w}{E} = \text{constant}$$

or $\qquad w \propto E \qquad ...(5)$

or $\qquad \frac{w_A}{E_A} = \frac{w_B}{E_B} = \frac{w_C}{E_C} \qquad ...(6)$

Chemical cells: (i) A class of cell in which chemical energy is converted into electrical energy.

(ii) The change in free energy = Electrical work done

$$-\Delta G = nFE \qquad ...(7)$$

$$\Delta G = (G_{\text{products}} - G_{\text{reactants}}) \text{ for a redox change}$$

Nernst equation for electrode potential

$$A \rightleftharpoons A^{+n} + ne$$

$$E_{OP} = E^{\circ}_{OP} - \frac{RT}{nF}\log_e \frac{a_{\text{oxidized state}}}{a_{\text{reduced state}}} \qquad ...(8)$$

and $$E_{RP} = E^{\circ}_{RP} + \frac{RT}{nF}\log_e \frac{a_{O.S.}}{a_{R.S.}} \qquad ...(9)$$

Also $$E^{\circ}_{OP} = -E_{RP} \qquad ...(10)$$

and $$E^{\circ}_{OP} = -E^{\circ}_{RP} \qquad ...(11)$$

where, E_{OP} and E_{RP} are oxidation potential and reduction potential respectively.

E°_{OP} and E°_{RP} are standard O.P. and standard R.P. defined as equal to E_{OP} and E_{RP} respectively when, $\frac{a_{O.S.}}{a_{R.S.}} = 1$

R is molar gas constant $= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ (MKS system, since E in volt)

T is temperature in Kelvin

n is no. of electrons lost or gained during oxidation or reduction in redox change

F is one Faraday, *i.e.*, 96500 C

$a_{O.S.}$ = active mass of oxidized state in solution

$a_{R.S.}$ = active mass of reduced state in solution

Since $a = fc$ where, f is activity coefficient

For dilute solutions $f = 1$

$\therefore$ a = concentration in molarity

Thus, Eq. (8) may be written as

$$E_{OP} = E^{\circ}_{OP} - \frac{RT}{nF}\log_e \frac{[O.S.]}{[R.S.]} \qquad ...(12)$$

$$E_{OP} = E^{\circ}_{OP} - \frac{2.303\,RT}{nF}\log_{10} \frac{[O.S.]}{[R.S.]} \qquad ...(13)$$

$\because$ Numerical value of $\frac{2.303\,RT}{F} = 0.058$ at 288 K

$= 0.059$ at 298 K

$= 0.060$ at 308 K

i.e., no significant change with temperature.

By Eq. (13)

$$\therefore \quad E_{OP} = E^{\circ}_{OP} - \frac{0.059}{n}\log_{10} \frac{[O.S.]}{[R.S.]} \qquad ...(14)$$

Similarly,

and $$E_{RP} = E^{\circ}_{RP} + \frac{0.059}{n}\log_{10} \frac{[O.S.]}{[R.S.]} \qquad ...(15)$$

Formation of equation for different electrodes

Case I. $M \mid M^{+n}$ (*aq.*), *i.e.*, $M \rightleftharpoons M^{+n} + ne$

$$E_{OP} = E^{\circ}_{OP} - \frac{0.059}{n}\log_{10} \frac{[M^{+n}]}{[M]}$$

or $$E_{OP} = E^{\circ}_{OP} - \frac{0.059}{n}\log_{10} [M^{+n}]$$

[$\therefore$ M in solid state = unity]

and $$E_{RP} = E^{\circ}_{RP} + \frac{0.059}{n}\log_{10} [M^{+n}]$$

Case II. $\underset{(P)}{\text{Pt}_{\text{H}_2}} \mid \text{H}^+ (aq.)$,

i.e., $\text{H}_2 \rightleftharpoons 2\text{H}^+ + 2e$ or $\frac{1}{2}\text{H}_2 \rightleftharpoons \text{H}^+ + e$

For gaseous phase concentration is reported as pressure, *i.e.*, $[\text{H}_2]$ as P_{H_2}

$$E_{OP} = E^{\circ}_{OP} - \frac{0.059}{2}\log_{10} \frac{[\text{H}^+]^2}{P_{\text{H}_2}} \qquad ...(16)$$

or $$E_{OP} = E^{\circ}_{OP} - \frac{0.059}{1}\log_{10} \frac{[\text{H}^+]}{(P_{\text{H}_2})^{1/2}} \qquad ...(17)$$

Note : Eqs. (16) and (17) are same and thus it is evident that stoichiometry of change in half cell emf has no effect on Nernst expression.

Similarly, $$E_{RP} = E^{\circ}_{RP} + \frac{0.059}{2}\log_{10} \frac{[\text{H}^+]^2}{P_{\text{H}_2}}$$

Case III. $\text{Pt}_{\text{Cl}_2} \mid \text{Cl}^- (aq.)$ *i.e.*, $2\text{Cl}^- \rightleftharpoons \text{Cl}_2 + 2e$

$$E_{OP} = E^{\circ}_{OP} - \frac{0.059}{2}\log_{10} \frac{P_{\text{Cl}_2}}{[\text{Cl}^-]^2} \qquad ...(18)$$

Similarly, $$E_{RP} = E^{\circ}_{RP} + \frac{0.059}{2}\log_{10} \frac{P_{\text{Cl}_2}}{[\text{Cl}^-]^2} \qquad ...(19)$$

Formulation of equation for emf of cell

A model question: *Given that*

$A \longrightarrow A^{2+} + 2e \qquad E^{\circ} = +0.76 \text{ V}$

$B \longrightarrow B^{2+} + 2e \qquad E^{\circ} = +0.44 \text{ V}$

Find out

- (*a*) *Anode of cell*
- (*b*) *Cathode of cell*
- (*c*) *Reaction at anode*
- (*d*) *Reaction at cathode*
- (*e*) *Redox change*
- (*f*) *No. of electrons used for redox change*
- (*g*) *Direction of flow of electron*
- (*h*) *Direction of flow of current*
- (*i*) E°_{cell}
- (*j*) E_{cell}
- (*k*) *Design of cell.*

Solution (1) First decide the nature of E° values given, *i.e.*, whether they are E°_{OP} or E°_{RP} by noting.

(a) Given directly, *i.e.*, mentioned as E°_{OP} or E°_{RP}

or

(b) See the change,

(i) If oxidation reaction is mentioned, then

$$E^\circ_{OP} \quad i.e., \quad E_{A/A^{2+}} \text{ then } E^\circ_{OP}$$

(ii) If reduction reaction is mentioned, then

$$E^\circ_{RP} \quad i.e., \quad E_{A^{2+}/A} \text{ then } E^\circ_{RP}$$

(2) Write E°_{OP} and E°_{RP} of both

$$E^\circ_{OP\, A/A^{2+}} = +0.76 \quad \text{then} \quad E^\circ_{RP\, A^{2+}/A} = -0.76$$

$$E^\circ_{OP\, B/B^{2+}} = +0.44 \qquad E^\circ_{RP\, B^{2+}/B} = -0.44$$

(3) Write the process for oxidation at the electrode having more or +ve value of E°_{OP} and reduction for other.

$$A \longrightarrow A^{2+} + 2e$$

Anode of cell; cell reaction at anode

$$B^{2+} + 2e \longrightarrow B$$

Cathode of cell; cell reaction at cathode

[Ans. to a, b, c, d]

(4) Now add these two after making electrons same on two sides.

$$A + B^{2+} = A^{2+} + B$$

This is cell reaction of redox change **[Ans. to e]**

Also no. of electrons lost or gained during process is 2. **[Ans. to f]**

Also, In a redox cell: Anode has negative polarity.
Cathode has positive polarity.

Thus, electrons flow from A to B **[Ans. to g]**

and Current flows from B to A **[Ans. to h]**

(5) $E^\circ_{cell} = E^\circ_{OP_A} + E^\circ_{RP_B}$ **[Ans. to i]**

$$= +0.76 + (-0.44) = +0.32 \text{ V}$$

Write E°_{OP} for one which show oxidation	Put a +ve sign in
Write E°_{RP} for one which show reduction	between two

Similarly, $E_{cell} = E_{OP_A} + E_{RP_B}$ **[Ans. to j]**

$$= E^\circ_{OP_A} - \frac{0.059}{2}\log_{10}[A^{2+}] + E^\circ_{RP_B} + \frac{0.059}{2}\log_{10}[B^{2+}]$$

$$= E^\circ_{OP_A} + E^\circ_{RP_B} + \frac{0.059}{2}\log_{10}\frac{[B^{2+}]}{[A^{2+}]}$$

$$E_{cell} = E^\circ_{cell} + \frac{0.059}{2}\log_{10}\frac{[B^{2+}]}{[A^{2+}]}$$

(6) For design of cell, keep electrode showing oxidation on left and other showing reduction on right. Put two vertical lines in between these two electrodes to show salt bridge in order to eliminate **liquid junction potential.**

	L.H.S.		R.H.S.
	$A \mid A^{2+}$	$\Vert$	$B^{2+} \mid B$
or	$A \mid A(NO_3)_2$ (Anode) (– ve polarity)	$\Vert$	$B(NO_3)_2 \mid B$ (Cathode) (+ve polarity)

Liquid junction potential is arised due to different ionic mobility of ions.

Some applications of Nernst equation

(1) In computation of E°_{cell} and E_{cell}: See model question.

$$E^\circ_{cell} = E^\circ_{OP} + E^\circ_{RP}, \quad E_{cell} = E_{OP} + E_{RP}$$

(2) In computation of equilibrium constant: When the cell reaction is at equilibrium, the system does no net work and the cell emf is zero.

i.e., $-\Delta G = nFE$ or $-\Delta G = 0$ $\quad (\because E = 0)$

Consider the following reaction in equilibrium

$$\text{Zn} + \text{Cu}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Cu}$$

At equilibrium $\quad K_C = \dfrac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$ ...(20)

As discussed in model question,

$$E_{cell} = E^\circ_{cell} + \frac{RT}{nF}\log_e\frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]} \qquad ...(21)$$

$\because$ Zn is oxidized and Cu^{2+} is reduced
At equilibrium $\quad E_{cell} = 0$

$\therefore$ By Eqs. (20) and (21), $\quad -E^\circ_{cell} = \dfrac{RT}{nF}\log_e\dfrac{1}{K_C}$

$$E^\circ_{cell} = \frac{RT}{nF}\log_e K_C$$

or $\quad n.F.E^\circ_{cell} = RT\log_e K_C$

or $\quad -\Delta G^\circ = RT\log_e K_C$

$$-\Delta G^\circ = 2.303\,RT\log_{10} K_C \qquad ...(22)$$

where, ΔG° is change in standard free energy.

(3) Heat of reaction for cell reaction: The heat of reaction for cell reaction (ΔH) at a temperature is calculated by Gibb's Helmholtz equation.

$$\Delta G = \Delta H + T\left(\frac{\delta}{\delta T}\Delta G\right)_P$$

$\because \quad -\Delta G = nEF$

$$-nEF = \Delta H + T\left[\frac{\delta}{\delta T}(-nEF)\right]_P$$

or $\quad E = -\dfrac{\Delta H}{nF} + T\left(\dfrac{\delta E}{\delta T}\right)_P$ ...(23)

or $\quad \Delta H = nF\left[T\left(\dfrac{\delta E}{\delta T}\right)_P - E\right]$ ...(24)

where, $\left(\dfrac{\delta E}{\delta T}\right)_P$ is called temperature coefficient of emf, *i.e.*, rate of change of emf with temperature.

(4) To decide spontaniety of cell reaction: Compute E°_{cell} for the given reaction, *e.g.*,

$$A + B^{2+} \longrightarrow A^{2+} + B$$

$$\therefore \quad E^\circ_{cell} = E^\circ_{OP_A} + E^\circ_{RP_B}$$

If E°_{cell} comes to be +ve, cell reaction is spontaneous and if E°_{cell} comes to be −ve, cell reaction is not spontaneous.

(5) To evaluate solubility product: See Solved Problems

(6) To evaluate pH of solution: See Solved Problems

Relation between standard potential of metal-metal ion electrode and the corresponding metal-insoluble salt anion electrode : Ag /AgCl, Cl$^-$

Consider and electrode Ag /Ag$^+$ with reaction :

$$Ag^+ + e \longrightarrow Ag$$

The electrode potential is :

$$E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} + \frac{0.059}{1}\log[Ag^+] \quad ...(25)$$

Now suppose excess of NaCl is added in this electrolyte chamber so that all of the Ag$^+$ ions are precipitated obeying :

$$K_{sp_{AgCl}} = [Ag^+][Cl^-] \quad ...(26)$$

By Eqs. (25) and (26),

$$E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} + \frac{0.059}{1}\log\frac{K_{sp}}{[Cl^-]} \quad ...(27)$$

Now at this stage electrode can be taken as Ag/AgCl(*s*), Cl$^-$. The half reaction for this electrode is

$$AgCl(s) + e \longrightarrow Ag(s) + Cl^-(aq.)$$

The electrode potential is :

$$E_{Cl^-/AgCl/Ag} = E^\circ_{Cl^-/AgCl/Ag} + \frac{0.0591}{1}\log\frac{1}{[Cl^-]} \quad ...(28)$$

Since, both the electrodes are same, thus Eqs. (27) and (28) are identical, therefore,

$$E^\circ_{Cl^-/AgCl/Ag} + \frac{0.0591}{1}\log\frac{1}{[Cl^-]} = E^\circ_{Ag^+/Ag} + \frac{0.059}{1}\log\frac{K_{sp}}{[Cl^-]}$$

$$E^\circ_{Cl^-/AgCl/Ag} = E^\circ_{Ag^+/Ag} + \frac{0.059}{1}\log K_{sp_{AgCl}} \quad ...(29)$$

Relation for metal amalgam-metal ion half cell :

Pt electrode : $M\,(Hg) \longrightarrow M^{n+}(aq.) + ne$

$$E_{M\,(Hg)Pt/M^{n+}} = E^\circ_{M\,(Hg)Pt/M^{n+}} + \frac{0.059}{n}\log[M^{n+}] ...(30)$$

Also for a cell PtM (Hg) / $M^{n+}(aq.)/M$

$$E_{cell} = E^\circ_{M\,(Hg)Pt/M^{n+}} - E^\circ_{M^{n+}/M} \quad ...(31)$$

Relation for oxidation-reduction in half cell :

(a) Pt / Fe^{2+}, Fe^{3+}

The half cell reaction is $Fe^{3+}(aq.) + e \longrightarrow Fe^{2+}(aq.)$

$$E_{Fe^{3+}/Fe^{2+}} = E^\circ_{Fe^{3+}/Fe^{2+}} + \frac{0.059}{1}\log\frac{[Fe^{3+}]}{[Fe^{2+}]}$$

(b) Pt / H$^+$, MnO$_4^-$, Mn^{2+}

The half cell reaction is ;

$$Mn^{7+} + 5e \longrightarrow Mn^{2+}$$

or $$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} 4H_2O$$

$$\therefore E_{MnO_4^-/Mn^{2+}} = E^\circ_{MnO_4^-/Mn^{2+}} + \frac{0.059}{5}\log\frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$$

Reference electrode : Normal hydrogen electrode (NHE) is used as primary reference electrode having $E^\circ_{H^+/H} = 0$, assigned arbitrarily.

$$\underset{P = 1\text{ atm}}{PtH_2}\ \text{gas} \left|\ \underset{a=1}{HCl} \right. \quad \text{at } 25^\circ C\ E^\circ = 0$$

The other reference electrodes such as calomel electrode [Hg$_2$Cl$_2$(*s*) + KCl(*aq.*)], Ag—AgCl(*s*) electrode are called secondary reference electrodes.

• NUMERICAL PROBLEMS •

1. Calculate the quantity of electricity that will be required to liberate 710 g of Cl_2 gas by electrolysing a conc. solution of NaCl. What mass of NaOH and what volume of H_2 at 27° C and 1 atm. pressure is obtained during this process?
2. How many kJ of energy is expended during the passage of 1 ampere current for 100 sec under a potential of 115 V?
3. Find the charge in coulomb on 1 g ion of N^{3-}.
4. Find out the volume of gases evolved by passing 0.965 A current for 1 hr through an aqueous solution of CH_3COONa at 25° C and 1 atm.
5. A current of 0.5 A is passed through acidulated water for 30 minute. Calculate mass of H_2 and O_2 evolved. Also calculate the volume of O_2 produced at 25° C and 760 mm of Hg if the gas is :
   (a) dry (b) saturated with water vapour (aqueous tension is 23.0 mm at 25° C).
6. Calculate the volume of Cl_2 at NTP produced during electrolysis of fused $MgCl_2$ which produces 6.50 g Mg. Atomic mass of Mg = 24.3.
7. How long would it take to deposit 100 g of Al from an electrolytic cell containing Al_2O_3 using a current of 125 ampere?
8. A metal wire carries a current of 1 ampere. How many electrons pass a point in the wire in one second?
9. How long will it take for a uniform current of 6.0 ampere to deposit 78.0 g gold from a solution of $AuCl_4^-$? What mass of chlorine gas will be formed simultaneously at the anode of the electrolytic cell?
10. An ammeter and copper voltameter are connected in series in an electric circuit through which a constant direct current flows. The ammeter shows 0.525 ampere. If 0.6354 g of Cu is deposited in one hour, what is percentage error of ammeter? Atomic mass of Cu = 63.54.
11. Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 minute. It was found that after electrolysis, the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with.
12. Calculate the number of electrons lost or gained during electrolysis of:
    (a) 2 g Cl^- ions. (b) 1 g Zn^{2+} ions.
13. 0.35 mole of electrons were passed through three electrolyte solutions connected in series. If the solutions are of Ag^+, Cu^{2+} and Au^{3+}, calculate the amount of each metal deposited at cathode of each cell.
14. Same quantity of electricity being used to liberate iodine (at anode) and a metal (at cathode) : The mass of metal liberated at cathode is 0.617 g and the liberated iodine completely reduced by 46.3 mL of 0.124 M sodium thiosulphate solution. What is equivalent mass of metal?
15. Cd amalgam is prepared by electrolysis of a solution of $CdCl_2$ using a mercury cathode. Find how long should a current of 5 ampere is passed in order to prepare 12% Cd-Hg amalgam on a cathode of 2 g mercury? Atomic mass of Cd = 112.40.
16. 10 g fairly concentrated solution of $CuSO_4$ is electrolysed using 0.01 Faraday of electricity. Calculate:
    (a) the mass of resulting solution.
    (b) the no. of equivalents of acid or alkali in solution. Atomic mass of Cu = 63.5.
17. A test for complete removal of Cu^{2+} ions from a solution of Cu^{2+} (*aq.*) is to add NH_3 (*aq.*). A blue colour signifies the formation of complex $[Cu(NH_3)_4]^{2+}$ having $K_f = 1.1 \times 10^{13}$ and thus confirms the presence of Cu^{2+} in solution. 250 mL of 0.1 *M* $CuSO_4$ (*aq.*) is electrolysed by passing a current of 3.512 ampere for 1368 second. After passage of this charge sufficient quantity of NH_3 (*aq.*) is added to electrolysed solution maintaining $[NH_3] = 0.10$ M. If $[Cu(NH_3)_4]^{2+}$ is detectable upto its concentration as low as 1×10^{-5}, would a blue colour be shown by the electrolysed solution on addition of NH_3?
18. A current of 3.7 ampere is passed for 6 hr between Ni electrodes in 0.5 litre of 2 M solution of $Ni(NO_3)_2$. What will be the molarity of solution at the end of electrolysis?
19. How much current is necessary to produce hydrogen gas at the rate of 1 cc per second at NTP conditions?
20. 3 ampere current was passed through an aqueous solution of an unknown salt of Pd for 1 hour. 2.977 g of Pd^{n+} was deposited at cathode. Find *n*. (Atomic mass of Pd = 106.4)
21. A Zn rod weighing 25 g was kept in 100 mL of 1 *M* $CuSO_4$ solution. After a certain time the molarity of Cu^{2+} in solution was 0.8. What was molarity of SO_4^{2-}? What was the mass of Zn rod after cleaning? (Atomic mass of Zn = 65.4)
22. Assume that impure copper contains only Fe, Au and Ag as impurities. After passage of 140 ampere for 482.5 sec. the mass of anode decreased by 22.260 g and the cathode increased in mass by 22.011 g. Calculate the

percentage of iron and percentage of copper originally present.

23. Chromium metal can be plated out from an acidic solution containing CrO_3 according to following equation,

$$CrO_3(aq.) + 6H^+ + 6e \longrightarrow Cr(s) + 3H_2O$$

Calculate:

(a) how many gram of chromium will be plated out by 24000 coulomb?

(b) how long will it take to plated out 1.5 g of Cr by using 12.5 ampere current? **(IIT 1993)**

24. In an electrolysis experiment, current was passed for 5 hour through two cells connected in series. The first cell contains a solution of gold and the second contains $CuSO_4$ solution. 9.85 g of gold was deposited in the first cell. If the oxidation no. of gold is +3, find the amount of Cu deposited on cathode in second cell. Also calculate the current strength in ampere. Atomic mass of Au = 197 and atomic mass of Cu = 63.5.

25. An electric current is passed through two solutions of (i) $AgNO_3$ and (ii) a solution of $10\,g\ CuSO_4 \cdot 5H_2O$ crystals in 500 mL H_2O, platinum electrodes being used in each case. After 30 minute it is found that 1.307 g Ag has been deposited. What was the conc. of Cu expressed in g of Cu per litre in solution after electrolysis?
(Atomic mass of Cu = 63.54, Ag = 108)

26. Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2 as per reaction,

$$Mn^{2+}(aq.) + 2H_2O \longrightarrow MnO_2(s) + 2H^+(aq.) + H_2(g)$$

Passing a current of 27 A for 24 hours gives one kg of MnO_2. What is the value of current efficiency? Write the reaction taking place at the cathode and at the anode. **(IIT May 1997)**

27. A constant current was flown for 2 hour through a KI solution oxidising iodide ion to iodine ($2I^- \rightarrow I_2 + 2e$). At the end of experiment liberated iodine consumed 21.75 mL of 0.0831 M solution of sodium thiosulphate following the redox change $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$. What was the average rate of current flown in ampere?

28. 50 mL of 0.1 $M\,CuSO_4$ solution is electrolysed using Pt electrodes with a current of 0.965 ampere for a period of 1 minute. Assuming that volume of solution does not change during electrolysis, calculate $[Cu^{2+}]$, $[H^+]$ and $[SO_4^{2-}]$ after electrolysis. What will be the concentration of each species if current is passed using Cu electrodes?

29. An electric current is passed through two electrolytic cells connected in series, one containing $AgNO_3(aq.)$ and other $H_2SO_4(aq.)$. What volume of O_2 measured at 25°C and 750 mm in Hg would be liberated from H_2SO_4 if :

(a) 1 mole of Ag^+ are deposited from $AgNO_3$ solution?

(b) 8×10^{22} ions of Ag^+ are deposited from $AgNO_3$ solution?

30. In a fuel cell H_2 and O_2 react to produce electricity. In the process H_2 gas is oxidized at the anode and O_2 at cathode. If 67.2 litre of H_2 at STP reacts in 15 minutes, what is average current produced? If the entire current is used for electro deposition of Cu from Cu^{2+}, how many gram of Cu are deposited?

31. A 200 W, 110V incandescent lamp is connected in series with an electrolytic cell of negligible resistance containing a solution of $ZnCl_2$. What mass of Zn will be deposited from the solution on passing current for 30 minutes? (Atomic mass of Zn = 65.4)

32. By passing a certain amount of charge through NaCl solution, 9.2 litre of Cl_2 were liberated at STP. When the same charge is passed through a nitrate solution of metal M, 7.467 g of the metal was deposited. If the specific heat of metal is 0.216 cal/g, what is formula of metal nitrate?

33. An oxide of metal (atomic mass = 112) contains 12.5% O_2 by mass. The oxide was converted into chloride by treatment with HCl and electrolysed. Calculate the amount of metal that would be deposited at cathode if a current of 0.965 ampere was passed for a period of 5 hr. What is valency of metal?

34. A current of 3 ampere was passed for 2 hour through a solution of $CuSO_4 \cdot 3g$ of Cu^{2+} ions were discharged at cathode. Calculate current efficiency. (atomic mass of Cu = 63.5)

35. An aqueous solution of NaCl on electrolysis gives $H_2(g)$, $Cl_2(g)$ and NaOH according to reaction:

$$2Cl^-(aq.) + 2H_2O \longrightarrow 2OH^-(aq.) + H_2(g) + Cl_2(g)$$

A direct current of 25 ampere with a current efficiency of 62% is passed through 20 litre of NaCl solution (20% by mass).

(a) Write down the reactions taking place at the electrodes.

(b) How long will it take to produce 1 kg of Cl_2?

(c) What will be the molarity of solution with respect to OH^-?

Assume no loss in volume due to evaporation. **(IIT 1992)**

36. A current of 1.70 A is passed through 300 mL of 0.160 M solution of $ZnSO_4$ for 230 sec. with a current efficiency of 90%. Find the molarity of Zn^{2+} after the deposition of Zn. Assume the volume of the solution remains constant during electrolysis. **(IIT 1991)**

37. 19g fused $SnCl_2$ was electrolysed using inert electrodes. 0.119 g Sn was deposited at cathode. If nothing was given out during electrolysis, calculate the ratio of mass of $SnCl_2$ and $SnCl_4$ in fused state after electrolysis (Atomic mass of Sn = 119).

38. After electrolysis of a sodium chloride solution with inert electrodes for a certain period of time, 600 mL of the 1N solution was left which was found to be NaOH. During the same time 31.80 g Cu was deposited in copper voltameter in series with the electrolytic cell. Calculate the % of NaOH obtained. (Atomic mass of Cu = 63.6).

39. Per disulphuric acid ($H_2S_2O_8$) can be prepared by electrolytic oxidation of H_2SO_4 as

$$2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e.$$

Oxygen and hydrogen are byproducts. In such an electrolysis 9.72 litre of H_2 and 2.35 litre of O_2 were generated at STP. What is the mass of $H_2S_2O_8$ formed?

40. An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed until all the Cu is deposited. The electrolysis is containued for seven more minutes with the volume of solution kept at 100 mL and the current at 1.2 ampere. Calculate volume of gases evolved at NTP during entire electrolysis. (Atomic mass of Cu = 63.6)

41. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if current efficiency is 50%. If the potential drops across the cell is 3.0 volt, how much energy will be consumed? **(IIT 1990)**

42. Calculate the quantity of electricity required to reduce 6.15 g of nitrobenzene to aniline if the current efficiency is 68 per cent. If potential drops across the cell is 7.0 volt, calculate the energy consumed in the process.

43. In the manufacture of Al, Al_2O_3 is dissolved in Na_3AlF_6 at 300 K and electrolysed between Al and carbon electrodes following the net reaction,

$$2Al_2O_3\ (\text{solution}) + 3C \longrightarrow 4Al(l) + 3CO_2(g)$$

write the reaction of each electrode. Calculate the minimum voltage required between the electrodes if the Gibbs free energy change for the above reaction is $-1370\ \text{kJ mol}^{-1}$.

44. During the discharge of a lead storage battery, the density of sulphuric acid fell from $1.294\ \text{g mL}^{-1}$ to $1.139\ \text{g mL}^{-1}$. Sulphuric acid of density $1.294\ \text{g mL}^{-1}$ is 39% by mass and that of density $1.139\ \text{g mL}^{-1}$ is 20% by mass. The battery holds 3.5 litre of acid and the volume practically remained constant during the discharge. Calculate the no. of ampere hour for which the battery must have been used. The charging and discharging reactions are:

$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e \qquad \text{charging}$$

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e \longrightarrow PbSO_4 + 2H_2O$$

discharging

45. A lead storage cell is discharged which causes the H_2SO_4 electrolyte to change from a concentration of 34.6% by mass (density $1.261\ \text{g mL}^{-1}$ at 25°C) to one of 27% by mass. The original volume of electrolyte is one litre. How many Faraday have left the anode of battery? Note the water is produced by the cell reaction as H_2SO_4 is used up. Overall reaction is:

$$Pb(s) + PbO_2 + 2H_2SO_4(l) \longrightarrow 2PbSO_4(s) + 2H_2O$$

46. The electrolytic reduction of 300 mL of 0.01 *M* nitroalkane was carried out in acidic buffer medium of pH 5.0 following the change :

$$RNO_2 + 4H_3O^+ + 4e \longrightarrow RNHOH + 5H_2O$$

If the total concentration of weak acid and its conjugate base was 0.50*M*, calculate the pH of solution after completion of reduction. K_a for weak acid is 1.8×10^{-5}.

47. Two litre solution of a buffer mixture containing 1.0 *M* NaH_2PO_4 and 1.0 *M* Na_2HPO_4 is placed in two compartments (one litre in each) of an electrolytic cell. The platinum electrodes are inserted in each compartment and 1.25 ampere current is passed for 212 minute. Assuming electrolysis of water only at each compartment. What will be pH in each compartment after passage of above charge? (pK_a for $H_2PO_4^- = 2.15$).

48. The density of copper is $8.94\ \text{g mL}^{-1}$. Find out the number of coulomb needed to plate an area of $10 \times 10\ \text{cm}^2$ to a thickness of 10^{-2} cm using $CuSO_4$ solution as electrolyte. (Atomic mass of Cu = 63.6)

49. How many grams of silver could be plated out on a serving tray by electrolysis of solution containing silver in +1 oxidation state for a period of 8.0 hour at a current of 8.46 ampere? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? (Density of silver is $10.5\ \text{g / cm}^3$). **(IIT July 1997)**

50. A current of 40 microampere is passed through a solution of $AgNO_3$ for 32 minutes using Pt electrodes. A uniform single atom thick layer of Ag is deposited covering 43% cathode surface. What is the total surface area of cathode if each Ag atom covers $5.4 \times 10^{-16}\ \text{cm}^2$?

51. Calculate emf of half cells given below:

(a) $\underset{2\ \text{atm}}{Pt_{H_2}} \Big| \underset{a = 0.02}{HCl}$ $\qquad E^{\circ}_{OP} = 0V$

(b) $Fe \Big| \underset{a = 0.1}{FeSO_4}$ $\qquad E^{\circ}_{OP} = 0.44\,V$

(c) $\underset{10\ \text{atm}}{Pt_{Cl_2}} \Big| \underset{a = 0.1}{HCl}$ $\qquad E^{\circ}_{OP} = -1.36V$

52. Calculate the pH of the following half cells solutions:

(a) $\begin{array}{c|l} \text{Pt}_{\text{H}_2} & \text{HCl} \\ 1\text{ atm} & \end{array}$ $\qquad E = 0.25V$

(b) $\begin{array}{c|l} \text{Pt}_{\text{H}_2} & \text{H}_2\text{SO}_4 \\ 1\text{ atm} & \end{array}$ $\qquad E = 0.3V$

(c) A solution containing 4.5 mM of $Cr_2O_7^{2-}$ and 15 mM of Cr^{3+} shows a pH of 2.0. Calculate the potential of half reaction. (Standard potential of the reaction $Cr_2O_7^{2-} \rightarrow Cr^{3+}$ is 1.33 V.)

(Roorkee 2001)

53. Consider the reaction: $2Ag^+ + Cd \rightarrow 2Ag + Cd^{2+}$. The standard reduction potential of $Ag^+ - Ag$ and $Cd^{2+} - Cd$ couples are +0.80 and –0.40 volt respectively.

(a) What is the standard cell emf, $E°$?

(b) Will the total emf of the reaction be more +*ve* or –*ve*, if conc. of Cd^{2+} is 0.10*M* rather than 1*M*?

54. Calculate the values for cell

$$Zn \mid Zn^{2+}(aq.) \mid\mid Cu^{2+}(aq.) \mid Cu$$

(i) cell reaction and (ii) emf of cell if Zn^{2+} and Cu^{2+} are 1 *M* each, (iii) the minimum concentration of Cu^{2+} at which the cell reaction,

$$Zn + Cu^{2+}(aq.) \longrightarrow Zn^{2+}(aq.) + Cu$$

will be spontaneous if Zn^{2+} is 1 *M* (iv) does the displacement of $Cu^{2+}(aq.)$ by Zn goes to completion.

Given, $E^{\circ}_{RP_{Cu^{2+}/Cu}} = +0.35$ V

$E^{\circ}_{RP_{Zn^{2+}/Zn}} = -0.76$ V

55. Two students use same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The emf of one cell is 0.03 V higher than the other. The conc. of $CuSO_4$ in the cell with higher emf value is 0.5 *M*. Find out the conc. of $CuSO_4$ in the other cell $\left(\frac{2.303\,RT}{F} = 0.06\right)$. **(IIT 2003)**

56. A graph is plotted between E_{cell} and $\log_{10}\frac{[Zn^{2+}]}{[Cu^{2+}]}$. The curve was linear with intercept on E_{cell} axis equal to 1.10 V. Calculate E_{cell} for

$$\begin{array}{c|c||c|c} Zn & Zn^{2+} & Cu^{2+} & Cu \\ & 0.1\,M & 0.01\,M & \end{array}$$

57. If $NO_3^- \longrightarrow NO_2$ (acidic medium); $E° = 0.790$ V and $NO_3^- \longrightarrow NH_2OH$ (acidic medium); $E° = 0.731$ V. At what pH the above two half reactions will have same *E* values? Assume the concentrations of all the species to the unity.

58. The following electrochemical cell has been set up.

$Pt_{(I)} \mid Fe^{3+}, Fe^{2+}\,(a = 1) \mid\mid Ce^{4+}, Ce^{3+}\,(a = 1) \mid Pt_{(II)}$

$E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.77$ V and $E^{\circ}_{Ce^{4+}/Ce^{3+}} = 1.61$ V

If an ammeter is connected between the two platinum electrode, predict the direction of flow of current. Will the current increase or decrease with time? **(IIT 2000)**

59. The standard oxidation potential of Ni / Ni^{2+} electrode is 0.236 V. If this is combined with a hydrogen electrode in acid solution, at what pH of the solution will the measured emf be zero at 25°C? (Assume $[Ni^{2+}] = 1M$ and $P_{H_2} = 1$ atm).

60. Calculate the equilibrium constant for the reaction:

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$$

Given, $E^{\circ}_{Ce^{4+}/Ce^{3+}} = 1.44$ V and $E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.68$ V

(IIT July 1997)

61. Calculate the equilibrium constant for the reaction, $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$. The standard reduction potentials in acidic conditions are 0.77 and 0.54V respectively for Fe^{3+} / Fe^{2+} and I_3^- / I^- couples.

(IIT 1998)

62. Find the equilibrium constant for the reaction:

$$In^{2+} + Cu^{2+} \longrightarrow In^{3+} + Cu^+ \text{ at } 298\text{ K}$$

Given, $E^{\circ}_{Cu^{2+}/Cu^+} = 0.15$ V, $E^{\circ}_{In^{3+}/In^+} = -0.42$ V, $E^{\circ}_{In^{2+}/In^+} = -0.40$ V **(IIT 2004)**

63. Construct a cell in which the disproportionation reaction

$$2CuCl \longrightarrow CuCl_2 + Cu$$

takes place. Also calculate the equilibrium constant for the reaction if Cu^{2+} / Cu^+ and Cu^+ / Cu are 0.153 V and 0.518V respectively.

64. Zinc granules are added in excess to 500 mL of 1*M* $Ni(NO_3)_2$ solution at 25°C until the equilibrium is reached. If $E^{\circ}_{Zn^{2+}/Zn}$ and $E^{\circ}_{Ni^{2+}/Ni}$ are –0.75 V and –0.24 V respectively, find out the $[Ni^{2+}]$ at equilibrium.

(IIT 1991)

65. The standard reduction potential for Cu^{2+} / Cu is +0.34 V. Calculate the reduction potential at pH = 14 for the above couple, K_{sp} of $Cu(OH)_2$ is 1.0×10^{-19}.

(IIT 1996)

66. The emf of cell $Ag \mid AgI(s)$, 0.05*M KI*||0.05*M* $AgNO_3 \mid Ag$ is 0.788 V. Calculate solubility product of AgI.

67. If it is desired to construct the following voltaic cell to have $E_{cell} = 0.0860$ V, what $[Cl^-]$ must be present in the cathodic half cell to achieve the desired emf. Given K_{sp} of AgCl and AgI are 1.8×10^{-10} and 8.5×10^{-17} respectively?

$Ag(s) \mid Ag^+$ [Sat. AgI (*aq.*)]||

Ag^+ (Sat. $AgCl \cdot xMCl^-$)| $Ag(s)$

68. The standard reduction potential of $Cu^{2+}|Cu$ and $Ag^+|Ag$ electrodes are 0.337V and 0.799V respectively. Construct a galvanic cell using these electrodes so that its E°_{cell} is +ve. For what $[Ag^+]$ will the emf of cell at 25°C be zero if $[Cu^{2+}]$ is $0.01M$?

(IIT 1990)

69. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298K if the emf of the cell $Ag\,|\,Ag^+$ (satd. Ag_2CrO_4 sol.)$||\,Ag^+\,(0.1M)|\,Ag$ is 0.164V at 298K. **(IIT 1998)**

70. A silver electrode is immersed in saturated $Ag_2SO_4(aq.)$. The potential difference between the silver and the standard hydrogen electrode is found to be 0.711V. Determine $K_{sp}\,(Ag_2SO_4)$. Given, $E^\circ_{Ag^+/Ag} = 0.799V$. **(Roorkee 2000)**

71. The emf of the cell obtained by combining Zn and Cu electrodes of a Daniel cell with N calomel electrodes are 1.083V and −0.018V respectively at 25°C. If the potential of N calomel electrode is −0.28V, find emf of Daniel cell.

72. The standard reduction potential at 25°C for the reaction $2H_2O + 2e \longrightarrow H_2 + 2OH^-$ is −0.8277V. Calculate the equilibrium constant for the reaction $2H_2O \rightleftharpoons H_3O^+ + OH^-$ at 25°C. **(IIT 1989)**

73. An excess of liquid Hg was added to $10^{-3}\,M$ acidified solution of Fe^{3+} ions. It was found that only 5% of the ions remained as Fe^{3+} at equilibrium at 25°C. Calculate E° for $2Hg\,|\,Hg_2^{2+}$ at 25°C for $2Hg + 2Fe^{3+} \rightleftharpoons Hg_2^{2+} + 2Fe^{2+}$ and $E^\circ_{Fe^{2+}/Fe^{3+}} = -0.77\,V$. **(IIT 1995)**

74. Calculate the potential of an indicator electrode versus the standard hydrogen electrode, which originally contains $0.1\,M\,MnO_4^-$ and $0.8\,M\,H^+$ and which was treated with Fe^{2+} necessary to reduce 90% of MnO_4^- to Mn^{2+} $E^\circ_{MnO_4^-/Mn^{2+}} = 1.51V$.

75. Calculate the minimum mass of NaOH required to be added in R.H.S. to consume all the H^+ present in R.H.S. of cell of emf +0.701V at 25°C before its use. Also report the emf of cell after addition of NaOH.

$$Zn\left|\begin{matrix}Zn^{2+}\\0.1M\end{matrix}\right\|\begin{matrix}HCl\\1\text{ litre}\end{matrix}\left|\begin{matrix}Pt_{H_2}(g)\\1\text{ atm}\end{matrix}\right.$$

$E^\circ_{Zn/Zn^{2+}} = +0.760V$

76. A zinc electrode is dipped in a $0.1M$ solution at 25°C. Assuming that salt is dissociated to 20% at this dilution, calculate the electrode potential. $E^\circ_{Zn^{2+}/Zn} = -0.76\,V$.

77. A cell is containing two H electrodes. The negative electrode is in contact with a solution of $10^{-6}\,M\,H^+$ ion. The emf of the cell is 0.118 volt at 25°C. Calculate $[H^+]$ at positive electrode.

78. For the galvanic cell

$$Ag\,|\,AgCl(s),\ \underset{0.2M}{KCl}\ ||\ \underset{0.001M}{KBr}\ ,AgBr(s)\,|\,Ag$$

Calculate the emf generated and assign correct polarity to each electrode for a spontaneous process after taking an account of cell reaction at 25°C. Given, $K_{sp\,AgCl} = 2.8\times10^{-10}; K_{sp\,AgBr} = 3.3\times10^{-13}$. **(IIT 1992)**

79. Consider the cell $Ag\,|\,AgBr(s)Br^-\,||\,AgCl(s)Cl^-\,|\,Ag$ at 25°C. The solubility product of AgCl and AgBr are 1×10^{-10} and 5×10^{-13} respectively. For what ratio of concentration of Br^- and Cl^- ions would the emf of cell be zero?

80. Calculate E° of redox change : $Ag_2S + 2e \rightleftharpoons 2Ag + S^{2-}$ if the reaction occurs at pH = 3 and saturated with $0.1\,M\,H_2S$. K_1 and K_2 for H_2S are 1×10^{-8} and 1.1×10^{-13} respectively. $K_{sp\,Ag_2S} = 2\times10^{-49}$ and $E^\circ_{Ag^+/Ag} = 0.8V$.

81. The pK_{sp} of AgI is 16.07. If the E° value for Ag^+/Ag is 0.7991V, find out the E° for half reaction:

$$AgI(s) + e \longrightarrow Ag + I^-$$

82. Determine potential for the cell

$$Pt\left|\begin{matrix}Fe^{2+}\\Fe^{3+}\end{matrix}\right\|Cr_2O_7^{2-}, Cr^{3+}, H^+\big|\,Pt$$

in which $[Fe^{2+}]$ and $[Fe^{3+}]$ are $0.5\,M$ and $0.75\,M$ respectively and $[Cr_2O_7^{2-}]$, $[Cr^{3+}]$ and $[H^+]$ are $2\,M$, $4\,M$ and $1\,M$ respectively.

Given, $Fe^{3+} + e \longrightarrow Fe^{2+}$ $E^\circ = 0.770V$

$$14H^+ + 6e + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O \qquad E^\circ = 1.35V$$

83. The voltage of the cell given below is −0.46 V

$$Pt_{H_2}\left|\begin{matrix}NaHSO_3\\0.4M\end{matrix}\quad\begin{matrix}Na_2SO_3\\6.44\times10^{-3}M\end{matrix}\right\|\begin{matrix}Zn^{2+}\\0.3M\end{matrix}\Big|\,Zn(s)$$

Also, $Zn^{2+} + 2e \longrightarrow Zn(s)$, $E^\circ = -0.763V$. Calculate the value of K_2, where $K_2 = \dfrac{[H^+][SO_3^{2-}]}{[HSO_3^-]}$.

84. What ratio of Pb^{2+} to Sn^{2+} concentration is needed to reverse the following cell reaction?

$$Sn(s) + Pb(aq.)^{2+} \rightleftharpoons Sn(aq.)^{2+} + Pb(s)$$

$E^\circ_{Sn^{2+}/Sn} = -0.136V$ and $E^\circ_{Pb^{2+}/Pb} = -0.126V$

85. The Edison storage cell is represented as,

$$\mathrm{Fe}(s)|\mathrm{FeO}(s)|\mathrm{KOH}(aq.)|\mathrm{Ni_2O_3}(s)|\mathrm{Ni}(s)$$

The half cell reactions are:

$$\mathrm{Ni_2O_3}(s)+\mathrm{H_2O}(l)+2e^- \longrightarrow 2\mathrm{NiO}(s)+2\mathrm{OH}^-; \quad E^\circ=+0.40\mathrm{V}$$

$$\mathrm{FeO}(s)+\mathrm{H_2O}(l)+2e^- \longrightarrow \mathrm{Fe}(s)+2\mathrm{OH}^-; \quad E^\circ=-0.87\mathrm{V}$$

(i) What is the cell reaction?

(ii) What is the cell emf ? How does it depend on the concentration of KOH?

(iii) What is the maximum amount of electrical energy that can be obtained from one mole of $\mathrm{Ni_2O_3}$?

(IIT 1994)

86. For the electrode reaction,

$$\underset{1\,M}{\mathrm{CH_3CHO}}+2\mathrm{H}^+ +2e \longrightarrow \underset{1\,M}{\mathrm{CH_3CH_2OH}},$$

the half cell potential is $-0.197\mathrm{V}$ at $\mathrm{pH}=7$. Calculate the half cell potential when $\mathrm{pH}=6$ and ethanol and acetaldehyde each has concentration $10^{-5}\,M$.

87. For the cell $\mathrm{Mg(s)}|\mathrm{Mg}(aq.)^{2+}||\mathrm{Ag}(aq.)^+|\mathrm{Ag}(s)$, calculate the equilibrium constant at 25°C and the maximum work that can be obtained during operation of cell. Given,

$$E^\circ_{\mathrm{Mg/Mg^{2+}}}=+2.37\,\mathrm{V} \quad \text{and} \quad E^\circ_{\mathrm{Ag^+/Ag}}=+0.80\,\mathrm{V},$$

$R=8.314\,\mathrm{J}$

88. The standard reduction potential for the half cell

$$\mathrm{NO_3^-}(aq.)+2\mathrm{H}^+(aq.)+e \longrightarrow \mathrm{NO_2}(g)+\mathrm{H_2O}$$

is 0.78V.

(i) Calculate the reduction potential in $8\,M\ \mathrm{H}^+$.

(ii) What will be the reduction potential of the half cell in a neutral solution? Assume all the other species to be at unit concentration. **(IIT 1993)**

89. The standard reduction potential of $E^\circ_{\mathrm{Bi^{3+}/Bi}}$ and $E^\circ_{\mathrm{Cu^{2+}/Cu}}$ are 0.226 V and 0.344 V respectively. A mixture of salts of Bi^{3+} and Cu^{2+} at unit concentration each is electrolysed at 25°C. To what value can $[\mathrm{Cu}^{2+}]$ be brought down before bismuth starts to deposit during electrolysis?

90. How much is the oxidizing power of $(1M, \mathrm{MnO_4^-/Mn^{2+}}, 1M)$ couple decreased if the H^+ concentration is decreased from $1M$ to $10^{-4}\,M$ at 25°C?

91. An alloy weighing 1.05 g of Pb — Ag was dissolved in desired amount of $\mathrm{HNO_3}$ and the volume was made 350 mL. An Ag electrode was dipped in solution and E_{cell} of the cell $\mathrm{Pt}\ \underset{1\,atm}{\mathrm{H_2}}\,|\,\underset{1\,M}{\mathrm{H^+}}\,||\,\mathrm{Ag^+}\,|\,\mathrm{Ag}$ was 0.503 V at 298 K. Calculate the percentage of lead in alloy. Given $E^\circ_{\mathrm{Ag^+/Ag}}=0.80\mathrm{V}$.

92. Calculate the emf of given cell reaction and

$$\mathrm{Pb}(s)+\mathrm{Hg_2SO_4} \rightleftharpoons \mathrm{PbSO_4}(s)+2\mathrm{Hg}(l)$$

design the cell if both electrolytes are present in their saturated solution state. Given $E^\circ_{\mathrm{Pb/Pb^{2+}}}$ and $E^\circ_{\mathrm{Hg/Hg_2^{2+}}}$ are 0.126 and $-0.789\mathrm{V}$ respectively and K_{sp} of $\mathrm{PbSO_4}$ and $\mathrm{Hg_2SO_4}$ are 2.43×10^{-8} and 1.46×10^{-6} respectively.

93. The standard reduction potential of the $\mathrm{Ag^+/Ag}$ electrode at 298K is 0.799V. Given that for AgI. $K_{sp}=8.7\times10^{-17}$, evaluate the potential of the $\mathrm{Ag^+/Ag}$ electrode in a saturated solution of AgI. Also calculate the standard reduction potential of the $\mathrm{I^-/AgI/Ag}$ electrode. **(IIT 1994)**

94. For the reaction $\mathrm{Ag}^+(aq.)+\mathrm{Cl}^-(aq.) \rightleftharpoons \mathrm{AgCl}(s)$; the ΔG° values for $\mathrm{Ag}^+(aq.)$, $\mathrm{Cl}^-(aq.)$ and $\mathrm{AgCl}(s)$ are $+77, -129$ and $-109\,\mathrm{kJ\,mol^{-1}}$. Write the cell representation of above reaction and calculate E° at 298 K. Also calculate K_{sp} of AgCl at 298K.

If 6.539×10^{-2} g of metallic zinc is added to 100 mL saturated solution of AgCl, find the value of $\log_{10}\dfrac{[\mathrm{Zn}^{2+}]}{[\mathrm{Ag}^+]^2}$. How many mole of Ag will be precipitated in this reaction? Given, $E^\circ_{\mathrm{Zn^{2+}/Zn}}=-0.76\mathrm{V}$.

(IIT 2005)

95. The standard potential of the following cell is 0.23 V at 15°C and 0.21 V at 35°C.

$$\mathrm{Pt}_{\mathrm{H_2}}(g)\,|\,\mathrm{HCl}(aq.)\,||\,\mathrm{AgCl}(s)\,|\,\mathrm{Ag}(s)$$

(i) Write the cell reaction.

(ii) Calculate ΔH° and ΔS° for the cell reaction by assuming that these quantities remain unchanged in the range 15°C to 35°C.

(iii) Calculate the solubility of AgCl in water at 25°C. Given, the standard reduction potential of the $\mathrm{Ag}^+(aq.)/\mathrm{Ag}(s)$ couple is 0.80 V at 25°C.

(IIT 2001)

96. Show that the potentials are additive for the process in which half reactions are added to yield an overall reaction but they are not additive when added to yield a third half reaction.

97. What is the standard electrode potential for the electrode $\mathrm{MnO_4^-/MnO_2}$ in solution? Given:

$$E^\circ_{\mathrm{MnO_4^-/Mn^{2+}}}=1.51\mathrm{V} \text{ and } E^\circ_{\mathrm{MnO_2/Mn^{2+}}}=1.23\mathrm{V}$$

98. The reduction potential diagram for Cu in acid solution is:

$$\begin{tikzcd}
\mathrm{Cu}^{2+} \arrow[r, "+0.15\text{ volt}"] \arrow[rr, bend right, "E^\circ = X\text{ volt}"'] & \mathrm{Cu}^{+} \arrow[r, "+0.50\text{ volt}"] & \mathrm{Cu}
\end{tikzcd}$$

Calculate X. Does Cu^+ disproportionate in solution?

99. If E_1° is standard electrode potential for Fe / Fe^{2+} and E_2° is for Fe^{2+}/ Fe^{3+} and E_3° for Fe / Fe^{3+}. Derive a relation between E_1°, E_2° and E_3°.

100. The following galvanic cell was

$$\mathrm{Zn}\left|\begin{array}{c}\mathrm{Zn(NO_3)_2}(aq.)\\ 100\ \mathrm{mL}, 1M\end{array}\right\|\begin{array}{c}\mathrm{Cu(NO_3)_2}(aq.)\\ 100\ \mathrm{mL}, 1M\end{array}\Bigg|$$

operated as an electrolytic cell using Cu as anode and Zn as cathode. A current of 0.48 ampere was passed for 10 hour and then the cell was allowed to function as galvanic cell. What would be the emf of the cell at 25°C? Assume that the only electrode reactions occurring were those involving Cu / Cu^{2+} and Zn / Zn^{2+}. Given $E^\circ_{Cu^{2+}/Cu} = +0.34$ V and $E^\circ_{Zn^{2+}/Zn} = -0.76$ V.

101. A cell $Ag|Ag^+||Cu^{2+}|Cu$ initially contains $1\,M$ Ag^+ and $1\,M$ Cu^{2+} ions. Calculate the change in the cell potential after the passage of 9.65 A of current for 1 hour. **(IIT 1999)**

102. Estimate the cell potential of a Daniel cell having $1.0\,M$ Zn^{2+} and originally having $1.0\,M$ Cu^{2+} after sufficient ammonia has been added to the cathode compartment to make the NH_3 concentration 2.0 *M*. Given $E^\circ_{Zn/Zn^{2+}}$ and $E^\circ_{Cu/Cu^{2+}}$ are 0.76 and –0.34 V respectively. Also equilibrium constant for the $[Cu(NH_3)_4]^{2+}$ formation is 1×10^{12}.

103. Two electrochemical cells are assembled in which the following reactions occur.

$$V^{2+} + VO^{2+} + 2H^+ \longrightarrow 2V^{3+} + H_2O \quad E^\circ_{cell} = 0.616\text{V}$$

$$V^{3+} + Ag^+ + H_2O \longrightarrow VO^{2+} + 2H^+ + Ag(s)$$

$$E^\circ_{cell} = 0.439\text{V}$$

Calculate $E°$ for half reaction $V^{3+} + e \rightarrow V^{2+}$. Given, $E^\circ_{Ag^+/Ag} = 0.799$ volt.

104. The emf of cell $Zn| ZnSO_4||CuSO_4|Cu$ at 25°C is 0.03V and the temperature coefficient of emf is -1.4×10^{-4} V per degree. Calculate heat of reaction for the change taking place inside the cell.

105. For the reaction,

$$H_2(g) + 2AgCl(s) + 2H_2O(l) \longrightarrow 2Ag(s) + 2H_3O^+(aq.) + 2Cl^-(aq.).$$

At 25°C, the standard free energy of formation of $AgCl(s)$, $H_2O(l)$ and $(H_3O^+ + Cl^-)$ $(aq.)$ are –109.7, –237.2 and –368.4 kJ / mol. Calculate what will be the cell voltage if this reaction is run at 25°C and one atmosphere in a cell in which H_2 activity is unity and $H_3O^+(aq.)$ and $Cl^-(aq.)$ activities are each at $0.01M$?

106. E°_{cell} for reaction,

$$4Al(s) + 3O_2(g) + 6H_2O + 4OH^- \longrightarrow 4[Al(OH)_4]^-$$

is 2.73V. If G_f° for OH^- and H_2O are –157 k J mol^{-1} and –237.2 k J mol^{-1}, determine G_f° for $[Al(OH)_4]^-$.

107. Calculate the emf of cell:

$$\begin{array}{c}\mathrm{Pt}_{\mathrm{H_2}}\\ 1\ \mathrm{atm}\end{array}\left|\begin{array}{c}\mathrm{CH_3COOH}\\ 0.1M\end{array}\right\|\begin{array}{c}\mathrm{NH_4OH}\\ 0.01\,M\end{array}\left|\begin{array}{c}\mathrm{Pt}_{\mathrm{H_2}}\\ 1\ \mathrm{atm}\end{array}\right.$$

K_a for $CH_3COOH = 1.8 \times 10^{-5}$; K_b for $NH_4OH = 1.8 \times 10^{-5}$.

108. Two weak acid solutions HA_1 and HA_2 each with the same concentration and having pK_a values 3 and 5 are placed in contact with hydrogen electrode (1 atm, 25°C) and are interconnected through a salt bridge. Find emf of cell.

109. Dissociation constant for $Ag(NH_3)_2^+$ into Ag^+ and NH_3 is 6×10^{-14}. Calculate $E°$ for the half reaction,

$$Ag(NH_3)_2^+ + e \longrightarrow Ag + 2NH_3$$

Given, $Ag^+ + e \longrightarrow Ag$ has $E° = 0.799$V.

110. The overall formation constant for the reaction of 6 mole of CN^- with cobalt (II) is 1×10^{19}. Calculate the formation constant for the reaction of 6 mole of CN^- with cobalt (II). Given that,

$$Co(CN)_6^{3-} + e \longrightarrow Co(CN)_6^{4-};\ E^\circ_{RP} = -0.83\text{ V}$$

$$Co^{3+} + e \longrightarrow Co^{2+};\quad E^\circ_{RP} = 1.82\text{ V}$$

111. The voltage of the cell :

$$Zn(s)|\underset{0.45\,M}{Zn(CN)_4^{2-}}(aq.),\ \underset{2.65\times10^{-3}\,M}{CN^-}\ ||\ \underset{3.84\times10^{-4}}{Zn^{2+}}|Zn(s)$$

is +0.099 V. Calculate the instability constant for $Zn(CN)_4^{2-}$ if only complexation resulting is $Zn^{2+} + 4CN^- \longrightarrow Zn(CN)_4^{2-}$.

112. Calculate the equilibrium constant at 25°C for the disproportionation of 3 mole of aqueous HNO_2 to yield NO and NO_3^- ions. The $E°$ for reduction of HNO_2 to NO is 0.99V and $E°$ for reduction of NO_3^- to HNO_2 is 0.94V.

113. The standard electrode potential corresponding to the reaction,

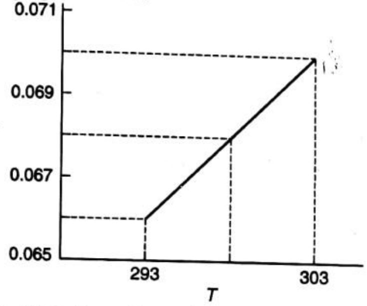
$$Au^{3+}(aq.) + 3e \longrightarrow Au(s)$$

is 1.42V. Predict if gold can be dissolved in $1M$ HCl solution and on passing hydrogen gas through gold salt solution, metallic gold will be precipitated or not.

114. For the cell:

$$As(s) \mid AgBr(s) \mid KBr(aq.) \mid Hg_2Br_2(s) \mid Hg(l),$$

the variation of emf with temperature is shown by the graph given below:



(a) Write the cell reaction.

(b) Calculate ΔG, ΔH and ΔS at 298K.

115. Determine the degree of hydrolysis and hydrolysis constant of aniline hydrochloride if:

$$Pt.(H_2) \underset{1\,M}{\mid H^+} \| \underset{\frac{1}{32}M}{C_6H_5NH_3Cl} \mid H_2\, Pt; \quad E_{cell} = -0.188\text{V at}$$

$\underset{1\,atm}{(H_2)}$ and $\underset{1\,atm}{H_2}$

300K.

116. Peroxodisulphate salts (*e.g.*, $Na_2S_2O_8$) are strong oxidising agents used as bleaching agents for fats, oils and fabrics. Can oxygen gas oxidise sulphate ion to peroxide sulphate ion $S_2O_8^{2-}$ in acidic solution with $O_2(g)$ being reduced to water? Given,

$$O_2(g) + 4H^+(aq.) + 4e \longrightarrow 2H_2O; \quad E° = 1.23\text{V}$$

$$S_2O_8^{2-}(aq.) + 2e \longrightarrow 2SO_4^{2-}; \quad E° = 2.01\text{V}$$

117. $E°$ of some elements are given as:

$$I_2 + 2e \longrightarrow 2I^-; \qquad E° = +0.54\text{V}$$

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O; \quad E° = +1.52\text{V}$$

$$Fe^{3+} + e \longrightarrow Fe^{2+}; \qquad E° = +0.77\text{V}$$

$$Sn^{4+} + 2e \longrightarrow Sn^{2+}; \qquad E° = +0.1\text{V}$$

(a) Select the strongest reductant and oxidant in these.

(b) Select the weakest reductant and oxidant in these.

(c) Select the spontaneous reaction from the changes given below:

(i) $Sn^{4+} + 2Fe^{2+} \longrightarrow Sn^{2+} + 2Fe^{3+}$

(ii) $2Fe^{2+} + I_2 \longrightarrow 2Fe^{3+} + 2I^-$

(iii) $Sn^{4+} + 2I^- \longrightarrow Sn^{2+} + I_2$

(iv) $Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$

118. Two metals A and B have $E^{\circ}_{RP} = -0.76\text{V}$ and $+0.80\text{V}$ respectively, which will liberate H_2 from H_2SO_4?

SOLUTIONS (Numerical Problems)

1. $2Cl^- \longrightarrow Cl_2 + 2e \quad \therefore \; E_{Cl_2} = \frac{\text{Molar mass}}{2}$

$$w = \frac{E \cdot i \cdot t}{96500} = \frac{E \cdot Q}{96500}$$

$$\therefore \quad Q = \frac{96500w}{E} = \frac{96500 \times 710}{35.5} = 20\,\text{F}$$

$$Q = \mathbf{1930000\ coulomb}$$

$\because$ 1 F gives 1 g eq. or 40 g NaOH

$\therefore$ 20 F gives 20 g eq. or 40×20 g NaOH = **800 g NaOH**

$\because$ 1 F gives 1 g eq. or 1 g H_2

$\therefore$ 20 F gives 20 g eq. or 20 g H_2

from $\quad PV = \frac{w}{M}RT$

$$1 \times V = \frac{20}{2} \times 0.0821 \times 300$$

$$\therefore \quad V_{H_2} = \mathbf{246.3\ litre}$$

2. Energy = charge × potential $= 1 \times 100 \times 115 =$ **11.5 kJ**

3. The electronic charge on $1\,N^{3-}$ is $= 3 \times 1.602 \times 10^{-19}$ C

$\therefore$ The electronic charge on 1 g eq. N^{3-}

$$= 3 \times 1.602 \times 10^{-19} \times \text{N C}$$

$$= 3 \times 1.602 \times 10^{-19} \times 6.023 \times 10^{23}\ \text{C}$$

$$= \mathbf{2.89 \times 10^5\ coulomb}$$

4. $2CH_3COONa(aq.) \xrightarrow{\text{Electrolysis}} \overset{\text{Anode}}{C_2H_6 + 2CO_2} + \overset{\text{Cathode}}{2NaOH + H_2}$

$$2CH_3COO^- \longrightarrow C_2H_6 + 2CO_2 + 2e$$

$$2H^+ \longrightarrow H_2 + 2e$$

$$\text{Equivalent}\left(\frac{W}{E}\right) = \frac{i \cdot t}{96500} = \frac{0.965 \times 1 \times 60 \times 60}{96500} = 0.036$$

Thus total equivalent of $C_2H_6 + CO_2 + H_2$

$$= 0.036 + 0.036 + 0.036$$

$\therefore$ Total mole of gases

$$(n) = \frac{0.036}{2} + \frac{0.036}{1} + \frac{0.036}{2} = 0.072$$

$$\left[\because E_{C_2H_6} = \frac{M}{2}; \quad E_{H_2} = \frac{M}{2}; \quad E_{CO_2} = \frac{M}{1}\right]$$

$$\therefore \quad V = \frac{nRT}{P} = \frac{0.072 \times 0.0821 \times 298}{1} = \mathbf{1.762\ litre}$$

5. $2H^+ + 2e \longrightarrow H_2 \qquad 4OH^- \longrightarrow 2H_2O + O_2 + 4e$

$$\because E_{H_2} = \frac{\text{Molar mass}}{2} = \frac{2}{2} = 1 \because E_{O_2} = \frac{\text{Molar mass}}{4} = \frac{32}{4} = 8$$

$$w_{H_2} = \frac{E \cdot i \cdot t}{96500} \qquad w_{O_2} = \frac{E \cdot i \cdot t}{96500}$$

$$= \frac{1 \times 0.5 \times 30 \times 60}{96500} \qquad = \frac{8 \times 0.5 \times 30 \times 60}{96500}$$

$$w_{H_2} = \mathbf{9.33 \times 10^{-3}\ g} \qquad w_{O_2} = \mathbf{7.46 \times 10^{-2}\ g}$$

(a) Using $\quad PV = \frac{w}{M}RT$

$$\frac{760}{760} \times V = \frac{7.46 \times 10^{-2}}{32} \times 0.0821 \times 298$$

$$\therefore \quad V_{O_2} = \mathbf{5.7 \times 10^{-2}\ litre}$$

(b) $\quad P_{O_2} = P_T - P'_{H_2O} = 760 - 23 = 737$ mm

$$\therefore \quad \frac{737}{760} \times V = \frac{7.46 \times 10^{-2}}{32} \times 0.0821 \times 298$$

$$\therefore \quad V_{O_2} = \mathbf{5.88 \times 10^{-2}\ litre}$$

6. **At cathode:** $Mg^{2+} + 2e \longrightarrow Mg$

At anode: $\quad 2Cl^- \longrightarrow Cl_2 + 2e$

$\because$ Equivalent of Mg at cathode = Equivalent of Cl_2 at anode

$$\therefore \quad \frac{6.5}{24.3/2} = \frac{w_{Cl_2}}{35.5}$$

$$\therefore \quad w_{Cl_2} = 18.99\,\text{g}$$

At NTP $\quad PV = \frac{w}{M}RT$

$$1 \times V = \frac{18.99}{71} \times 0.0821 \times 273$$

Volume of Cl_2 = **5.99 litre**

7. $\because \quad Al_2^{3+} + 6e \longrightarrow 2Al$

$$\therefore \quad E_{Al} = \frac{\text{Atomic mass}}{3} = \frac{27}{3} = 9$$

Now $\quad w = \frac{E \cdot i \cdot t}{96500}$

$$100 = \frac{27 \times 125 \times t}{3 \times 96500}$$

$$\therefore \quad t = \mathbf{8577.77\ second}$$

8. Total charge passed in one sec. $= 1 \times 1 = 1$ coulomb

$(\because Q = i \times t)$

$\because$ 1 Faraday or 96500 C current carried by

$= 6.023 \times 10^{23}$ electrons

$\therefore$ 1 coulomb current carried by

$$= \frac{6.023 \times 10^{23}}{96500} = \mathbf{6.24 \times 10^{18}\ electrons}$$

9. $AuCl_4^- + 3e \longrightarrow Au + 4Cl^-$

$$Cl^- \longrightarrow \frac{1}{2}Cl_2 + e$$

$$\therefore \quad w_{Au} = \frac{E \cdot i \cdot t}{96500} = \frac{197 \times 6 \times t}{3 \times 96500} = 78.0$$

$$\therefore \quad t = \mathbf{19104\ sec.}$$

Also $\quad$ Eq. of Au = Eq. of Cl_2

$$\frac{78}{197/3} = \frac{w}{71/2}$$

$$\therefore \quad w_{Cl_2} = \mathbf{42.16\ g}$$

10. Current flown = 0.525 ampere as shown by ammeter

Actual current flown $(i) = \frac{w}{E \times t} \times 96500$

$$= \frac{0.6354 \times 96500}{(63.54/2) \times 60 \times 60}$$

$(\because t = 60 \times 60$ sec.$)$

$$\therefore \quad i = 0.536\ \text{ampere}$$

Thus, error in (i) = 0.536 − 0.525 = 0.011

$\therefore$ % error in ammeter $= \frac{0.011 \times 100}{0.536} = \mathbf{2.05\%}$

11. Equivalent of Cu^{2+} lost during electrolysis

$$= \frac{i \times t}{96500} = \frac{2 \times 10^{-3} \times 16 \times 60}{96500} = 1.989 \times 10^{-5}$$

or Mole of Cu^{2+} lost during electrolysis $= \frac{1.989 \times 10^{-5}}{2}$

This value is 50% of the initial concentration of solution

Thus, initial mole of $CuSO_4$

$$= \frac{2 \times 1.989 \times 10^{-5}}{2} = 1.989 \times 10^{-5}$$

Thus, initial concentration of $CuSO_4$

$$= \frac{1.989 \times 10^{-5} \times 1000}{250}$$

$[CuSO_4] = \mathbf{7.95 \times 10^{-5}}$ ***M***

12. (a) Eq. of Cl^- used $= \frac{2}{35.5}$ for $2Cl^- \longrightarrow Cl_2 + 2e$

$\because$ 1 eq. of an element = 1 Faraday charge

$= 6.023 \times 10^{23}$ electrons

$\therefore$ $\frac{2}{35.5}$ eq. of $Cl^- = \frac{6.023 \times 10^{23} \times 2}{35.5}$

$= \mathbf{3.39 \times 10^{22}}$ **electrons lost**

(b) Similarly, calculate for $Zn^{2+} + 2e \longrightarrow Zn$

Electrons gained $= \mathbf{1.85 \times 10^{22}}$ **electrons**

13. $\because$ 1 mole of electrons deposits 108 of Ag

$\therefore$ 0.35 mole of electrons deposits $108 \times 0.35 =$ **37.8 g Ag**

Similarly, w_{Cu} = **11.113 g,** w_{Au} = **22.98 g**

14. $I_2 + 2e \longrightarrow 2I^-$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e \quad \left[\therefore E_{Na_2S_2O_3} = \frac{M}{1}\right]$$

Eq. of metal = Eq. of I_2 = Eq. of hypo

$$\frac{0.617}{E} = \frac{46.3 \times 0.124}{1000}$$

$\therefore$ $\boldsymbol{E = 107.47}$ **g eq^{-1}**

15. $\because$ 88 g Hg has 12 g Cd

$\therefore$ 2 g Hg require $= \frac{12 \times 2}{88}$ g Cd = 0.273 g Cd

$\because$ $Cd^{2+} + 2e \longrightarrow Cd \quad \left[\therefore E_{Cd} = \frac{112.40}{2}\right]$

Now, $w = \frac{E \cdot i \cdot t}{96500}$

$$0.273 = \frac{112.4 \times 5 \times t}{2 \times 96500}$$

$\therefore$ $\boldsymbol{t = 93.75}$ **second**

16. (a) **At anode:** $2H_2O \longrightarrow 4H^+ + O_2 + 4e$

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

$\therefore$ Mass loss at anode = mass of O_2 formed $= \frac{E \cdot i \cdot t}{96500}$

$$= \frac{32 \times 0.01 \times 96500}{4 \times 96500} = 0.08\,g$$

$\therefore$ Mass loss at cathode = mass of Cu formed $= \frac{E \cdot i \cdot t}{96500}$

$$= \frac{63.5 \times 0.01 \times 96500}{2 \times 96500} = 0.3175\,g$$

$\therefore$ Mass of resulting solution

= Initial mass − mass loss of O_2 − mass loss of Cu

= 10 − 0.08 − 0.3175 = **9.6025 g**

(b) $\because$ 1 Faraday will produce 1 equivalent of acid or H^+

$\therefore$ 0.01 Faraday will produce $\frac{1 \times 0.01}{1}$

= **0.01 equivalent of acid**

17. $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$

$\therefore$ $$K_f = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}$$

The blue colour will be noticed upto

$[Cu(NH_3)_4]^{2+} = 1 \times 10^{-5}$.

Thus, at this stage,

$\therefore$ m mole of Cu^{2+} present = $250 \times 0.1 = 25$

m mole of Cu^{2+} removed $= \frac{w}{E} \times \frac{1000}{2} = \frac{i \cdot t \times 1000}{96500 \times 2}$

$$= \frac{3.512 \times 1368 \times 1000}{96500 \times 2} = 24.89$$

$\therefore$ $[Cu^{2+}]_{left} = \frac{(25 - 24.89)}{250} = 4.4 \times 10^{-4}\,M$

Since, K_f is very high (1.1×10^{13}) thus almost whole of the $[Cu^{2+}]_{left}$ will be used to form $[Cu(NH_3)_2]^{2+}$,

or $[Cu(NH_3)_2]^{2+} = 4.4 \times 10^{-4}\,M > 1 \times 10^{-5}\,M$ detectable limit

Thus, solution **will show blue colour** as it will provide appreciable Cu^{2+} to form complex.

18. The electrolysis of $Ni(NO_3)_2$ in presence of Ni electrode will bring in following changes:

At anode: $Ni \longrightarrow Ni^{2+} + 2e$

At cathode: $Ni^{2+} + 2e \longrightarrow Ni$

$\because$ Eq. of Ni^{2+} formed = Eq. of Ni^{2+} lost

Thus, there will be no change in conc. of $Ni(NO_3)_2$ solution during electrolysis, *i.e.*, **it will remain 2 *M*.**

19. 1 Eq. or 11200 mL H_2 gas involves = 96500 coulomb

$\therefore$ 1 mL H_2 gas involves $= \frac{96500}{11200}$ coulomb

= 8.616 coulomb

Now time to produce 1 mL gas is 1 second and thus, 8.616 coulomb charge should be passed in one sec. to bring the change.

Therefore, $Q = i \times t$

$8.616 = i \times t$ or $i =$ **8.616 ampere**

20. $\because$ $Pd^{n+} + ne \longrightarrow Pd$

For Pd, $\frac{w}{E} = \frac{i \times t}{96500}$

$$\frac{2.977}{106.4 / n} = \frac{3 \times 1 \times 60 \times 60}{96500}$$

$\therefore$ $n = 4$

21. $\because \quad \text{Meq.} = N \times V$

Meq. of Cu^{2+} before reaction $= 100 \times 1 \times 2 = 200$

Meq. of Cu^{2+} after reaction $= 100 \times 0.8 \times 2 = 160$

$\therefore \quad \text{Meq. of } Cu^{2+} \text{ lost} = 200 - 160 = 40$

$\therefore \quad \text{Meq. of Zn lost} = 40$

$$\therefore \quad \frac{w}{65.4/2} \times 1000 = 40$$

$$w_{Zn} = 1.308\,\text{g}$$

$\therefore$ Net mass of Zn rod $= 25 - 1.308\,\text{g} = \mathbf{23.692\ g}$

Also the reactions are $Zn \longrightarrow Zn^{2+} + 2e$

$$Cu^{2+} + 2e \longrightarrow Cu$$

$\therefore$ **No change in molarity of SO_4^{2-}**

22. The increase in mass at the cathode is due to deposition of Cu ($Cu^{2+} + 2e \rightarrow Cu$). The loss in mass of anode is due to loss of Cu and Fe because of their oxidation because only these two are active metals and will oxidise as

$$Cu \longrightarrow Cu^{2+} + 2e$$

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

and loss of Ag and Au to fall in anode mud.

Thus, gain in mass at cathode is due to deposition of $Cu = 22.011\,\text{g}$

$\therefore$ Mole of Cu deposited at cathode $= \dfrac{22.011}{63.5} = 0.3466$

Equivalent of Cu and Fe dissolved at anode $= \dfrac{i \cdot t}{96500}$

$$= \frac{140 \times 482.5}{96500} = 0.70$$

$\therefore$ Mole of Cu and Fe dissolved at anode $= \dfrac{0.70}{2} = 0.35$

(both Cu and Fe are bivalent losing two electrons)

Mole of Fe dissolved at anode $= 0.3500 - 0.3466 = 0.0034$

$\therefore$ Mass of Fe dissolved at anode $= 0.0034 \times 56 = 0.190\,\text{g}$

Thus, anode mass loss of 22.260 g contains 22.011 g Cu, 0.190 g Fe and (Au + Ag) $= (22.260 - 22.011 - 0.190)$

$$= 0.059\,\text{g}$$

[$Fe \longrightarrow Fe^{2+} + 2e$; Fe^{2+} exist in solution]

$$\therefore \quad \%\,Cu = \frac{22.011}{22.26} \times 100 = \mathbf{98.88\%}$$

$$\%\,Fe = \frac{0.190}{22.26} \times 100 = \mathbf{0.85\%}$$

23. Eq. mass of Cr

$$= \frac{\text{Atomic mass}}{\text{No. of electrons lost or gained by one molecule of Cr}}$$

$$= \frac{52}{6}$$

(a) $\because$ 96500 coulomb deposit $= \dfrac{52}{6}$ g Cr

$\therefore$ 24000 coulomb deposit $= \dfrac{52}{6} \times \dfrac{24000}{96500}$ g Cr

$$= \mathbf{2.1554\ g\ of\ Cr}$$

(b) Also given, $w_{Cr} = 1.5\,\text{g}$, $i = 12.5\,\text{ampere}$, $t = ?$, $E_{Cr} = 52/6$

$$\therefore \quad w = \frac{E \cdot i \cdot t}{96500}$$

$$1.5 = \frac{52 \times 12.5 \times t}{6 \times 96500}$$

$$\therefore \quad \mathbf{t = 1336.15\ second}$$

24. $Au^{3+} + 3e \longrightarrow Au$

$$Cu^{2+} + 2e \longrightarrow Cu$$

Equivalent of gold formed = Eq. of Cu formed

$$\frac{9.85}{197/3} = \frac{w_{Cu}}{63.5/2}$$

$$\therefore \quad w_{Cu} = \mathbf{4.763\ g}$$

Also $\quad w = \dfrac{E \cdot i \cdot t}{96500}$

$$\therefore \quad 4.763 = \frac{63.5 \times i \times 5 \times 60 \times 60}{2 \times 96500}$$

$$\therefore \quad \mathbf{i = 0.804\ ampere}$$

25. Eq. of Ag deposited $= \dfrac{1.307}{108} = 0.0121$

$\therefore \quad$ Eq. of Cu^{2+} lost $= 0.0121$

Initial Eq. of $CuSO_4 \cdot 5H_2O = \dfrac{10 \times 2}{249.54} = 0.0802$

$= \text{Initial Eq. of } Cu^{2+}$

$\therefore$ Eq. of Cu^{2+} left $= 0.0802 - 0.0121 = 0.0681$

$\therefore$ Mass of Cu^{2+} left $= \dfrac{0.0681 \times 63.54}{2}$

$= 2.164$ g in 500 mL

$\therefore$ Mass of Cu^{2+} left in 1 litre $H_2O = 2.164 \times 2$

$= \mathbf{4.328\ g/litre}$

26. $w = \dfrac{E \cdot i \cdot t}{96500}$

$$\therefore \quad 1000 = \frac{87 \times i \times 24 \times 60 \times 60}{2 \times 96500}$$

$$i = 25.6\,\text{ampere}$$

$\therefore$ Current efficiency $= \dfrac{25.6}{27} \times 100 = \mathbf{94.8\%}$

Reactions

Anode : $\quad Mn^{2+} \longrightarrow Mn^{4+} + 2e$

Cathode : $\quad 2H^{+} + 2e \longrightarrow H_2$

27. $\because \quad N_{Na_2S_2O_3} = M_{Na_2S_2O_3} \times$ no. of electrons lost or gained by 1 molecule of $Na_2S_2O_3$ (*i.e.*, 1)

$$\because \quad 2S_2^{2+} \longrightarrow S_4^{5/2+} + 2e$$

Meq. of I_2 formed = Meq. of $Na_2S_2O_3$ used

$= 21.75 \times 0.0831 \times 1 = 1.807$

or $\quad \dfrac{w}{E} \times 1000 = 1.807 \quad$ or $\quad \dfrac{w}{E} = \dfrac{1.807}{1000} \quad$ ...(1)

Also, $\quad \dfrac{w}{E} = \dfrac{i \cdot t}{96500}$

Thus, $\quad \dfrac{1.807}{1000} = \dfrac{i \times 2 \times 60 \times 60}{96500}$

$$\therefore \quad \mathbf{i = 0.0242\ ampere}$$

28. Meq. of $CuSO_4 = 50 \times 0.1 \times 2 = 10 \quad$ (Meq. $= N \times V$ mL)

or $\quad$ Meq. of $Cu^{2+} = 10$

Anode: $\quad 2H_2O \longrightarrow 4H^{+} + O_2 + 4e$

Cathode: $\quad Cu^{2+} + 2e \longrightarrow Cu$

Now, $\frac{w}{E}=\frac{i\cdot t}{96500}$

and Equivalent of Cu^{2+} lost

$$=\text{Equivalent of } H^+ \text{ formed}=\frac{i\cdot t}{96500}$$

$$=\frac{0.965\times1\times60}{96500}=6\times10^{-4}$$

$\therefore$ Meq. of Cu^{2+} lost = Meq. of H^+ formed = 0.6

$\therefore$ Meq. of Cu^{2+} left in solution or Meq. of $CuSO_4$ left in solution = 10 − 0.6 = 9.4

$$\therefore \quad [Cu^{2+}]=\frac{N_{Cu^{2+}}}{2}=\frac{9.4}{50\times2}=\mathbf{0.094}\boldsymbol{M}$$

$$\left[\because \; N=\frac{\text{Meq.}}{\text{Volume (mL)}}\right]$$

$$[H^+]=\frac{N_{H^+}}{1}=\frac{0.6}{50}=\mathbf{0.012}\boldsymbol{M}$$

$$[SO_4^{2-}]=\mathbf{0.1}\boldsymbol{M}$$

Since SO_4^{2-} does not take part in redox change.

Also if Cu electrodes are used, no change will be in the molarity of electrolyte, *i.e.*, 0.1*M*.

Since, the reactions are $Cu^{2+}+2e\longrightarrow Cu$

$$Cu\longrightarrow Cu^{2+}+2e$$

29. (a) Eq. of O_2 = Eq. of Ag

$$\frac{w_{O_2}}{8}=1 \qquad (\because \; 1 \text{ mole Ag}=1 \text{ Eq. Ag})$$

$\therefore$ $w_{O_2}=8\text{ g}$

$\because$ $T=298\text{ K},\quad P=\frac{750}{760}\text{ atm.}$

Now $PV=\frac{w}{M}RT$

$$\therefore \quad V_{O_2}=\frac{8}{32}\times\frac{0.0821\times298\times760}{750}=\textbf{6.20 litre}$$

(b) Eq. of O_2 = Eq. of Ag $=\frac{w_{Ag}}{108}$

$$=\frac{8\times10^{22}\times108}{6.023\times10^{23}\times108}=0.133$$

$(\because \; 6.023\times10^{23}$ atoms or ions$)=108\text{ g Ag}$

$$w_{O_2}=8\times0.133=1.064\text{ g}$$

$$\therefore \quad V_{O_2}=\frac{1.064\times0.0821\times298\times760}{32\times750}=\textbf{0.824 litre}$$

30. Mole of H_2 reacting $=\frac{67.2}{22.4}=3$

$\therefore$ Eq. of H_2 used = 3 × 2 = 6

Now $\frac{w}{E}=\frac{i\cdot t}{96500};\quad 6=\frac{i\times15\times60}{96500}$

$\therefore$ $i=$ **643.33 ampere**

Also Eq. of H_2 = Eq. of Cu formed

$\therefore$ Eq. of Cu deposited = 6

$\therefore$ $w_{Cu}=6\times\frac{63.5}{2}=190.5\text{ g}$

Mass of Cu deposited = **190.5 g**

31. Watt = ampere × volt

$\therefore$ Ampere $=\frac{200}{110}$

Now $w=\frac{E\cdot i\cdot t}{96500}$

$$\therefore \quad w_{Zn}=\frac{65.4\times200\times30\times60}{2\times110\times96500}=\mathbf{1.109\ g}$$

32. $\because$ Sp. heat × atomic mass = 6.4

$\therefore$ Atomic mass of metal $=\frac{6.4}{0.216}=29.63$

After electrolysis;

Eq. of metal = Eq. of Cl_2

$$\therefore \quad \frac{w}{\text{atomic mass}/n}=\frac{\text{mass of } Cl_2}{\text{Eq. mass of } Cl_2}$$

$$\frac{7.467\times n}{29.63}=\frac{71\times9.2}{22.4\times35.5}$$

$\because$ 22.4 litre of Cl_2 at STP weigh = 71g

$\because$ Eq. mass of metal $=\frac{\text{Atomic mass}}{\text{Valency}}=\frac{29.63}{n}$

$\therefore$ $n=3.25$

$n=3$ $\qquad (\because \; n$ is integer)

$\therefore$ **Metal nitrate is $M(NO_3)_3$.**

33. Eq. of O_2 = Eq. of metal

$$\frac{12.5}{8}=\frac{87.5}{E}$$

$$\therefore \quad E_{\text{metal}}=\frac{87.5\times8}{12.5}=56$$

$$\therefore \quad \text{Valency of metal}=\frac{\text{Atomic mass}}{\text{Eq. mass}}=\frac{112}{56}=\mathbf{2}$$

Now by electrolysis: $w=\frac{E\cdot i\cdot t}{96500}$

$$w=\frac{56\times5\times60\times60\times0.965}{96500}=\mathbf{10.08\ g}$$

34. $w_{Cu}=\frac{E\cdot i\cdot t}{96500}$

$$3=\frac{63.5\times i\times2\times60\times60}{2\times96500}$$

$\therefore$ $i=1.266$ ampere

Current efficiency

$$=\frac{\text{Current passed actually}}{\text{Total current passed experimentally}}\times100$$

$$=\frac{1.266}{3}\times100=\mathbf{42.2\%}$$

35. (a) **Anode:** $2Cl^-\longrightarrow Cl_2+2e$

Cathode: $2e+2H_2O\longrightarrow 2OH^-+H_2$

(b) $w=\frac{E\cdot i\cdot t}{96500}$

$10^3=\frac{35.5\times25\times62\times t}{100\times96500}$

$t=175374.83$ sec.

$\therefore$ $t=$ **48.71 hr**

$\because$ $w_{Cl_2}=10^3$ g, $E_{Cl_2}=35.5$

$\because$ Current efficiency = 62%

$\therefore$ $i=\frac{25\times62}{100}$ ampere

(c) Eq. of OH^- formed = Eq. of Cl_2 formed

$$= \frac{10^3}{35.5} = 28.17$$

∴ Mole of OH^- formed = 28.17 (∵ monovalent)

∴ $[OH^-] = \frac{\text{mole}}{\text{Volume in litre}} = \frac{28.17}{20}$

$= \mathbf{1.408\ mol\ litre^{-1}}$

36. $i = \frac{1.70 \times 90}{100}$ ampere

∴ Eq. of Zn^{2+} lost $= \frac{i \cdot t}{96500}$

$= \frac{1.70 \times 90 \times 230}{100 \times 96500} = 3.646 \times 10^{-3}$

∴ Meq. of Zn^{2+} lost = 3.646

Initial Meq. of $Zn^{2+} = 300 \times 0.160 \times 2$

$= 48 \times 2 = 96$ [∵ $M \times 2 = N$ for Zn^{2+} Meq. $= N \times V_{(\text{in mL})}$]

∴ Meq. of Zn^{2+} left in solution $= 96 - 3.646 = 92.354$

∴ $[ZnSO_4] = \frac{92.354}{2 \times 300} = \mathbf{0.154}\ \boldsymbol{M}$

37. Electrolysis of $SnCl_2$ yields:

Anode: $2Cl^- \longrightarrow Cl_2 + 2e$

Cathode: $Sn^{2+} + 2e \longrightarrow Sn$

Further Cl_2 formed at anode reacts with $SnCl_2$ to give $SnCl_4$

$SnCl_2 + Cl_2 \longrightarrow SnCl_4$

During electrolysis

Eq. of $SnCl_2$ lost = Eq. of Cl_2 formed

= Eq. of Sn formed

Eq. of Cl_2 formed $= \frac{0.119}{119/2} = 2 \times 10^{-3}$

∴ Eq. of $SnCl_4$ formed $= 2 \times 10^{-3}$

or Eq. of $SnCl_2$ lost during electrolysis $= 2 \times 10^{-3}$

Now total loss in Eq. of $SnCl_2$ during complete course = Eq. of $SnCl_2$ lost during electrolysis + Eq. of $SnCl_2$ lost during reaction with Cl_2

$= 2 \times 10^{-3} + 2 \times 10^{-3} = 4 \times 10^{-3}$

Initial Eq. of $SnCl_2 = \frac{19}{190/2} = 2 \times 10^{-1}$

∴ Eq. of $SnCl_2$ left in solution $= 2 \times 10^{-1} - 4 \times 10^{-3} = 0.196$

Eq. of $SnCl_4$ formed $= 2 \times 10^{-3} = 0.002$

$$\therefore \frac{\text{Mass of } SnCl_2 \text{ left}}{\text{Mass of } SnCl_4 \text{ formed}} = \frac{0.196 \times \frac{190}{2}}{0.002 \times \frac{261}{2}} = \frac{18.62}{0.261} = \mathbf{71.34}$$

38. Eq. of Cu deposited $= \frac{31.8}{63.6/2} = 1$

∴ Eq. of NaOH formed = 1

or Meq. of NaOH formed = 1000

However, 600 mL of 1*N* NaOH is formed

i.e., Experimental yield of Meq. of NaOH $= 600 \times 1 = 600$

∴ % yield $= \frac{600}{1000} \times 100 = \mathbf{60\%}$

39. Anode reaction:

(i) $2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H^+ + 2e$

(ii) $2H_2O \longrightarrow 4H^+ + O_2 + 4e$

Cathode reaction: $2H_2O + 2e \longrightarrow 2OH^- + H_2$

∴ Equivalent of $H_2S_2O_8$ + Equivalent of O_2

= Equivalent of H_2

∵ 22.4 litre H_2 = 1 mole = 2 Eq.

∴ 9.72 litre $H_2 = \frac{2 \times 9.72}{22.4}$ Eq. = 0.868 Eq. H_2

∵ 22.4 litre O_2 = 1 mole = 4 Eq.

∴ 2.35 litre $O_2 = \frac{4 \times 2.35}{22.4}$ Eq. = 0.42 Eq. O_2

∴ Eq. of $H_2S_2O_8$ = Eq. of H_2 − Eq. of O_2

$= 0.868 - 0.420 = 0.448$

∴ $\frac{w_{H_2S_2O_8}}{194/2} = 0.448$

$w_{H_2S_2O_8} = \frac{0.448 \times 194}{2} = \mathbf{43.456\ g}$

40. For I part of electrolysis :

Anode: $2H_2O \longrightarrow 4H^+ + O_2 + 4e$

Cathode: $Cu^{2+} + 2e \longrightarrow Cu$

∴ Eq. of O_2 formed = Eq. of Cu

$= \frac{0.4 \times 2}{63.6} = 12.58 \times 10^{-3}$

For II part of electrolysis : Since Cu^+ ions are discharged completely and thus further passage of current through solution will lead the following changes.

Anode: $2H_2O \longrightarrow 4H^+ + O_2 + 4e$

Cathode: $2H_2O + 2e \longrightarrow H_2 + 2OH^-$

Eq. of H_2 = Eq. of $O_2 = \frac{i \cdot t}{96500} = \frac{1.2 \times 7 \times 60}{96500} = 5.22 \times 10^{-3}$

∴ Total Eq. of O_2

$= 5.22 \times 10^{-3} + 12.58 \times 10^{-3}$

$= 17.8 \times 10^{-3}$

∵ 4 Eq. of O_2 at NTP

= 22.4 litre

∴ 17.8×10^{-3} Eq. O_2 at NTP

$= \frac{22.4 \times 17.8 \times 10^{-3}}{4}$ litre

$= \mathbf{99.68\ mL}$

Eq. of $H_2 = 5.22 \times 10^{-3}$

∵ 2 Eq. of H_2 at NTP

= 22.4 litre

∴ 5.22×10^{-3} Eq. at NTP

$= \frac{22.4 \times 5.22 \times 10^{-3}}{2}$ litre

$= \mathbf{58.46\ mL}$

∴ Total volume of $O_2 + H_2 = 99.68 + 58.46 = \mathbf{158.14\ mL}$

Note : If Cu^{2+} is as $CuCl_2$, then $\mathbf{Cl_2}$ will come out in I step and $\mathbf{H_2}$ and $\mathbf{O_2}$ in II step. Calculate their volumes.

41. $C_6H_5NO_2 + 6H^+ + 6e \longrightarrow C_6H_5NH_2 + 2H_2O$

$N^{3+} + 6e \longrightarrow N^{3-}$

∴ Eq. mass of nitrobenzene $= \frac{M}{6} = \frac{123}{6}$

Now $w = \frac{E \cdot i \cdot t}{96500}$

(∵ current efficiency is 50% ∴ $i = \frac{50 i_0}{100}$)

$$12.3 = \frac{123 \times i \times t \times 50}{6 \times 100 \times 96500}$$

$\therefore$ $i \times t = \mathbf{115800\ coulomb}$

Now energy used $= Q \times V = 115800 \times 3 = \mathbf{347.4\ kJ}$

42. **[Ans. 42573.5 coulomb, 298.014 kJ]**

43. **Anode:** $2Al_2^{3+} + 12e \longrightarrow 4Al^0$

Cathode: $3C \longrightarrow 3C^{4+} + 12e$

(no. of electrons involved in change = 12)

$$-\Delta G^\circ = nFE^\circ$$

$$1370 \times 10^3 = 12 \times 96500 \times E^\circ$$

$\therefore$ $E^\circ = \mathbf{1.1830\ V}$

44. Adding the charging and discharging reactions

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O$$

$N_{H_2SO_4} = M_{H_2SO_4}$ (since $2SO_4^{2-}$ requires 2 electrons)

i.e., Normality = Molarity

Before discharge	After discharge
$M_{H_2SO_{4_I}} = \frac{39 \times 1.294 \times 1000}{98 \times 100}$	$M_{H_2SO_{4_{II}}} = \frac{20 \times 1.139 \times 1000}{98 \times 100}$
$= 5.15$	$= 2.325$
Mole of $H_2SO_4 = 5.15 \times 3.5$	Mole of $H_2SO_4 = 2.325 \times 3.5$
$= 18.025$	$= 8.1375$

$\therefore$ Mole or equivalents of H_2SO_4 used

$$= 18.025 - 8.1375 = 9.8875$$

$\because$ $\frac{w}{E} = \frac{i \cdot t}{96500}$

$\therefore$ $i \cdot t = 9.8875 \times 96500$

$= 954143.75$ ampere sec. $=$ **265.04 ampere hr**

45. Before electrolysis:

Volume of solution = 1 litre = 1000 mL

$\therefore$ Mass of solution $= 1000 \times 1.261 = 1261\,g$

($\because$ $w = V \times d$)

$\therefore$ Mass of $H_2SO_4 = \frac{34.6 \times 1261}{100} = 436.306\,g$

$\therefore$ Mass of water $= 1261 - 436.306 = 824.694\,g$

After electrolysis:

Now during reaction mass of H_2O formed $= X$ g

$\therefore$ Mole of H_2O formed $= \frac{X}{18}$

$\therefore$ Mole of H_2SO_4 used $= \frac{X}{18}$

($\because$ mole ratio of $H_2SO_4 : H_2O :: 1 : 1$)

$\therefore$ Mass of H_2SO_4 used $= \frac{98X}{18} = 5.44X$ g

$\therefore$ Mass of H_2SO_4 left $= (436.306 - 5.44X)$ g

Net mass of solution = mass of old solution + mass of H_2O formed − mass of H_2SO_4 lost

$$= 1261 + X - 5.44X$$

$\therefore$ % by mass of new solution $= \frac{436.306 - 5.44X}{(1261 + X - 5.44X)} = \frac{27}{100}$

$\therefore$ $X = 22.59\,g$

$\therefore$ $\frac{22.59}{18}$ mole of H_2O are formed

$\because$ Mole of H_2O = Eq. of H_2O

($\because$ $2H_2O$ consume 2 electrons)

Now 1 mole of H_2O formed by the passage of 1 Faraday

$\therefore$ $\frac{22.59}{18}$ mole of H_2O formed by the passage of

$$= \frac{22.59}{18} \text{ Faraday}$$

$= \mathbf{1.255\ Faraday}$

46. Milli equivalent of $RNO_2 = 300 \times 0.01 \times 4 = 12$

$\therefore$ Milli equivalent of $[H^+]$ consun.ed = 12

or Milli equivalent of $[OH^-]$ generated = 12

Let a mole of weak acid and b mole of its conjugate base are present, then

$$a + b = 0.50$$

Also, $$pH = -\log K_a + \log \frac{[Salt]}{[Acid]}$$

$$5.0 = +4.7442 + \log \frac{b}{a}$$

$\therefore$ $\frac{b}{a} = 1.8$

$\therefore$ $a = 0.1786$

$b = 0.3214$

OH^- generated will increase the concentration of A^- ion

$$OH^- + HA \longrightarrow H_2O + A^-$$

	OH^-	HA	H_2O	A^-
Meq. before reaction	12	178.6	0	321.4
Meq. after reaction	0	(178.6 − 12)		(321.4 + 12)
	0	166.6		333.4

$\therefore$ $pH = 4.7442 + \log \frac{333.4}{166.6}$

$= 4.7442 + 0.3013 = \mathbf{5.0455}$

47. **At cathode:** $2H^+ + 2e \longrightarrow H_2$

At anode: $2OH^- \longrightarrow H_2O + 2e + \frac{1}{2}O_2$

Equal equivalent of H^+ and OH^- will be discharged at anode and cathode respectively.

$$\frac{w}{E} = \frac{i \cdot t}{96500}$$

$$\frac{w}{E} = \frac{1.25 \times 212 \times 60}{96500} = 1.65 \times 10^{-1}\ M$$

Now for buffer mixture at anode, $[H^+]$ will increase by 1.65×10^{-1} M.

$$HPO_4^{2-} + H^+ \rightleftharpoons H_2PO_4^-$$

HPO_4^{2-}	H^+	$H_2PO_4^-$
1	0.165	1
0.835	—	1.165

$\therefore$ $pH = pKa + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$

$pH = 2.15 \log \frac{0.835}{1.165} = \mathbf{2.005}$

For buffer mixture at cathode, $[OH^-]$ will increase by 1.65×10^{-1} M.

$$H_2PO_4^- + OH^- \rightleftharpoons HPO_4^{2-} + H_2O$$

$H_2PO_4^-$	OH^-	HPO_4^{2-}
1	0.165	1
0.835	—	1.165

$$\therefore \quad pH = 2.15 + \log \frac{1.165}{0.835} = \mathbf{2.295}$$

48. Volume of Cu^{2+} ion deposited on plate

$$(\text{Area} \times \text{thickness}) = 10 \times 10 \times 10^{-2} = 1\,cm^3$$

$$\therefore \quad \text{Mass of } Cu^{2+} \text{ deposited} = 1 \times 8.94\,g$$

Now

$$w = \frac{E \cdot i \cdot t}{96500}$$

$$8.94 = \frac{63.6 \times Q}{2 \times 96500}$$

$$\therefore \quad Q = \mathbf{27129.2\ coulomb}$$

49. $w_{Ag} = \frac{E \cdot i \cdot t}{96500} = \frac{107.8 \times 8.46 \times 8 \times 60 \times 60}{96500} = \mathbf{272.18\ g}$

Volume of $Ag = \frac{272.18}{10.5} = 25.92\,mL$

$\therefore$ Surface area $= \frac{25.92}{0.00254} = \mathbf{1.02 \times 10^4\ cm^2}$

50. $w_{Ag} = \frac{E \cdot i \cdot t}{96500} = \frac{108 \times 40 \times 10^{-6} \times 32 \times 60}{96500} = 85.95 \times 10^{-6}\,g$ ...(1)

Now covered area is 43% of cathode surface. Let total area of cathode be $a\,cm^2$.

$\therefore$ Covered area $= \frac{43a}{100}\,cm^2$

$\because$ $5.4 \times 10^{-16}\,cm^2$ is covered by one atom of Ag

$\therefore$ $\frac{43a}{100}\,cm^2$ is covered by $= \frac{43a}{100 \times 5.4 \times 10^{-16}}$ atoms of Ag

$\therefore$ Mass of Ag atoms covering this area

$$= \frac{43a \times 108}{100 \times 5.4 \times 10^{-16} \times 6.023 \times 10^{23}} \quad ...(2)$$

By Eqs. (1) and (2), on equating, $a = \mathbf{601.65\ cm^2}$

51. (a) $H_2 \longrightarrow 2H^+ + 2e$

$$\therefore \quad E_{OP} = E^{\circ}_{OP} - \frac{0.059}{2} \log_{10} \frac{[H^+]^2}{P_{H_2}}$$

$$= 0 - \frac{0.059}{2} \log_{10} \frac{(0.02)^2}{2}$$

$$E_{OP_{H_2/H^+}} = \mathbf{+0.109\ volt}$$

(b) $Fe \longrightarrow Fe^{2+} + 2e$

$$\therefore \quad E_{OP} = E^{\circ}_{OP} - \frac{0.059}{2} \log_{10} [Fe^{2+}]$$

$$= 0.44 - \frac{0.059}{2} \log_{10} [0.1]$$

$$E_{OP_{Fe/Fe^{2+}}} = \mathbf{+0.4695\ volt}$$

(c) $2Cl^- \longrightarrow Cl_2 + 2e$

$$\therefore \quad E_{OP} = E^{\circ}_{OP} - \frac{0.059}{2} \log_{10} \frac{P_{Cl_2}}{[Cl^-]^2}$$

$$= -1.36 - \frac{0.059}{2} \log_{10} \frac{10}{(0.1)^2}$$

$$E_{OP_{Cl^-/Cl_2}} = \mathbf{-1.4485\ volt}$$

52. (a) $H_2 \longrightarrow 2H^+ + 2e$

$$\therefore \quad E_{OP_{H/H^+}} = E^{\circ}_{OP_{H/H^+}} - \frac{0.059}{2} \log_{10} \frac{[H^+]^2}{P_{H_2}}$$

$$0.25 = 0 - \frac{0.059}{2} \log_{10} \frac{[H^+]^2}{1}$$

$\therefore$ $-\log [H^+] = 4.237$ $\quad \therefore$ $pH = \mathbf{4.237}$

(b) Solve accordingly: $pH = \mathbf{5.08}$

Note : No change in calculation if any strong acid producing H^+ is given.

(c) $Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$

$$E = E^{\circ}_{Cr_2^{6+}/Cr^{3+}} + \frac{0.059}{6} \log \frac{[Cr_2O_7^{2-}][H^+]^{14}}{[Cr^{3+}]^2}$$

$$E = 1.33 + \frac{0.059}{6} \log \frac{\left[\frac{4.5}{1000}\right] \times [10^{-2}]^{14}}{\left[\frac{15}{1000}\right]^2}$$

$$= 1.33 + \frac{0.059}{6} \log 20 \times 10^{-28}$$

$$= 1.33 + \frac{0.059}{6} [\log 20 - 28 \log 10]$$

$$= 1.33 + \frac{0.059}{6} [1.3010 - 28]$$

$$= 1.33 - 0.26 = \mathbf{1.07\ V}$$

53. (a) For $2Ag^+ + Cd \longrightarrow 2Ag + Cd^{2+}$

$\because$ Ag^+ shows reduction and Cd shows oxidation:

$$\therefore \quad E^{\circ}_{cell} = E^{\circ}_{OP_{Cd/Cd^{2+}}} + E^{\circ}_{RP_{Ag^+/Ag}}$$

$$= +0.40 + 0.80$$

$$= \mathbf{1.2\ volt}$$

Given,

$$E^{\circ}_{RP_{Ag^+/Ag}} = +0.80\,V$$

$$E^{\circ}_{RP_{Cd^{2+}/Cd}} = -0.40\,V$$

$$\therefore \quad E^{\circ}_{OP_{Cd/Cd^{2+}}} = 0.40\,V$$

(b) Also $E_{cell} = E_{OP_{Cd}} + E_{RP_{Ag}}$

$$= E^{\circ}_{OP_{Cd/Cd^{2+}}} - \frac{0.059}{2} \log_{10} [Cd^{2+}] + E^{\circ}_{RP_{Ag^+/Ag}} + \frac{0.059}{2} \log_{10} [Ag^+]^2$$

or $E_{cell} = E^{\circ}_{OP_{Cd}} + E^{\circ}_{RP_{Ag}} + \frac{0.059}{2} \log_{10} \frac{[Ag^{2+}]}{[Cd^{2+}]}$

Thus, if $[Cd^{2+}]$ is reduced from $1M$ to $0.1\,M$, the net value of E_{cell} will increase or become **more +ve.**

Most important: For solving the problems on emf of cell, one should see E°_{OP} values for two changes and should write oxidation at the electrode having more or +ve E°_{OP} and reduction for other.

Also

$$E_{cell} = \underset{\text{(one which shows oxidation)}}{E^{\circ}_{OP}} + \underset{\text{(one which shows reduction)}}{E^{\circ}_{RP}}$$

54. (i) $\therefore$ E°_{OP} for $\mathrm{Cu/Cu^{2+}} = -0.35\ \mathrm{V}$

E°_{OP} for $\mathrm{Zn/Zn^{2+}} = +0.76\ \mathrm{V}$

More is E°_{OP}, more is tendency to show oxidation and thus Zn will oxidise and $\mathrm{Cu^{2+}}$ will reduce.

Anode: $\mathrm{Zn} \longrightarrow \mathrm{Zn^{2+}} + 2e$

Cathode: $\mathrm{Cu^{2+}} + 2e \longrightarrow \mathrm{Cu}$

Cell reaction $\mathrm{Zn} + \mathrm{Cu^{2+}} \longrightarrow \mathrm{Zn^{2+}} + \mathrm{Cu}$

(ii) Also $E_{cell} = E_{OP_{\mathrm{Zn/Zn^{2+}}}} + E_{RP_{\mathrm{Cu^{2+}/Cu}}}$

$$= E^\circ_{OP_{\mathrm{Zn/Zn^{2+}}}} - \frac{0.059}{2}\log_{10}[\mathrm{Zn^{2+}}] + E^\circ_{RP_{\mathrm{Cu^{2+}/Cu}}} + \frac{0.059}{2}\log_{10}[\mathrm{Cu^{2+}}]$$

$$= E^\circ_{OP_{\mathrm{Zn/Zn^{2+}}}} + E^\circ_{RP_{\mathrm{Cu^{2+}/Cu}}} + \frac{0.059}{2}\log_{10}\frac{[\mathrm{Cu^{2+}}]}{[\mathrm{Zn^{2+}}]}$$

$$= 0.76 + 0.35 + \frac{0.059}{2}\log_{10}\frac{1}{1}$$

E_{cell} = **1.11 volt**

(iii) Also $E_{cell} = 1.11 + \frac{0.059}{2}\log_{10}\frac{[\mathrm{Cu^{2+}}]}{[\mathrm{Zn^{2+}}]}$

To make cell reaction spontaneous; $E_{cell} = +\mathrm{ve}$

or $\frac{0.059}{2}\log_{10}\frac{[\mathrm{Cu^{2+}}]}{[\mathrm{Zn^{2+}}]} > -1.11$

or $\log_{10}\frac{[\mathrm{Cu^{2+}}]}{1} > -\frac{2.22}{0.059}$

or $\log_{10}[\mathrm{Cu^{2+}}] > -37.627$

$[\mathrm{Cu^{2+}}] > \mathbf{2.36 \times 10^{-38}}\ M$

(iv) The displacement will almost go to completion.

55. Given,

Cell I : $\mathrm{Zn}\,\Big|\underset{C_1}{\mathrm{ZnSO_4}}\Big\|\underset{C_2}{\mathrm{CuSO_4}}\Big|\,\mathrm{Cu}$

$$E_{cell} = E^\circ_{cell} + \frac{0.06}{2}\log\frac{[\mathrm{Cu^{2+}}]}{[\mathrm{Zn^{2+}}]}$$

$$E_{cell} = E^\circ_{cell} + \frac{0.06}{2}\log\frac{C_2}{C_1} \qquad \text{...(1)}$$

Cell II : $\mathrm{Zn}\,\Big|\underset{C_1'}{\mathrm{ZnSO_4}}\Big\|\underset{C_2'}{\mathrm{CuSO_4}}\Big|\,\mathrm{Cu}$

$$E'_{cell} = E^\circ_{cell} + \frac{0.06}{2}\log\frac{C_2'}{C_1} \qquad \text{...(2)}$$

If $E_{cell} > E'_{cell}$, then $E_{cell} > E'_{cell} = 0.03\ \mathrm{V}$ and $C_2 = 0.5\ M$

$\therefore$ By Eqs. (1) and (2) $0.03 = \frac{0.06}{2}\log\frac{0.5}{C_2'}$

or $C_2' = \mathbf{0.05}\ M$

56. For the given cell,

Anode: $\mathrm{Zn} \longrightarrow \mathrm{Zn^{2+}} + 2e$

Cathode: $\mathrm{Cu^{2+}} + 2e \longrightarrow \mathrm{Cu}$

and $E_{cell} = E^\circ_{cell} + \frac{0.059}{2}\log_{10}\frac{[\mathrm{Cu^{2+}}]}{[\mathrm{Zn^{2+}}]}$ ...(1)

$$y = c + mx \qquad \text{...(2)}$$

Eq. (1) represents a straight line equation like Eq. (2)

Thus, E°_{cell} = intercept = 1.10 V

Now from Eq. (1),

$$E_{cell} = 1.10 + \frac{0.059}{2}\log_{10}\frac{0.01}{0.1}$$

$$= 1.10 - 0.0295 = \mathbf{1.0705\ V}$$

57. $2\mathrm{H^+} + \mathrm{NO_3^-} + e \longrightarrow \mathrm{NO_2} + \mathrm{H_2O}$; $E^\circ = 0.790\ \mathrm{V}$

$7\mathrm{H^+} + \mathrm{NO_3^-} + 6e \longrightarrow \mathrm{NH_2OH} + 2\mathrm{H_2O}$; $E^\circ = 0.731\ \mathrm{V}$

Since E_{RP} of both are same

$\therefore$ $E_{RP_{\mathrm{NO_3^-/NO_2}}} = E_{RP_{\mathrm{NO_3^-/NH_2OH}}}$

or $E^\circ_{RP_{\mathrm{NO_3^-/NO_2}}} + \frac{0.059}{1}\log\frac{[\mathrm{H^+}]^2[\mathrm{NO_3^-}]}{[\mathrm{NO_2}]}$

$$= E^\circ_{RP_{\mathrm{NO_3^-/NH_2OH}}} + \frac{0.059}{6}\log\frac{[\mathrm{H^+}]^7[\mathrm{NO_3^-}]}{[\mathrm{NH_2OH}]}$$

or $0.790 + \frac{0.059}{1}\log[\mathrm{H^+}]^2 = 0.731 + \frac{0.059}{6}\log[\mathrm{H^+}]^7$

or $0.790 + 0.118\log[\mathrm{H^+}] = 0.731 + 0.0688\log[\mathrm{H^+}]$

or $-\log[\mathrm{H^+}] = \frac{0.059}{0.0492} = 1.1992$

$\therefore$ pH = **1.1992**

58. The emf of given cell $= E_{OP_{\mathrm{Fe^{2+}/Fe^{3+}}}} + E_{RP_{\mathrm{Ce^{3+}/Ce^{4+}}}}$

or $E_{cell} = E^\circ_{OP_{\mathrm{Fe^{2+}/Fe^{3+}}}} - \frac{0.059}{1}\log\frac{[\mathrm{Fe^{3+}}]}{[\mathrm{Fe^{2+}}]} + E^\circ_{RP_{\mathrm{Ce^{3+}/Ce^{4+}}}} + \frac{0.059}{1}\log\frac{[\mathrm{Ce^{4+}}]}{[\mathrm{Ce^{3+}}]}$

$$= E^\circ_{OP_{\mathrm{Fe^{2+}/Fe^{3+}}}} E^\circ_{RP_{\mathrm{Ce^{4+}/Ce^{3+}}}} + \frac{0.059}{1}\log\frac{[\mathrm{Ce^{4+}}][\mathrm{Fe^{2+}}]}{[\mathrm{Ce^{3+}}][\mathrm{Fe^{3+}}]}$$

$$= -0.77 + 1.61 + \frac{0.059}{1}\log 1$$

$\therefore$ $E_{cell} = 0.84\ \mathrm{V}$

Thus, $\mathrm{Pt_{(I)}Fe^{3+}/Fe^{2+}}$ acts as anode and $\mathrm{Pt_{(II)}Ce^{4+}/Ce^{3+}}$ acts as cathode. The electrons flow from left to right and thus current will flow from right to left. The current strength will decrease with time.

59. $\mathrm{Ni} \longrightarrow \mathrm{Ni^{2+}} + 2e$ $E^\circ_{OP} = 0.236\ \mathrm{V}$

$2\mathrm{H^+} + 2e \longrightarrow \mathrm{H_2}$ $E^\circ_{RP} = 0$

$\therefore$ $E^\circ_{cell} = 0.236$

$\therefore$ $E_{cell} = E^\circ_{cell} + \frac{0.059}{2}\log_{10}\frac{[\mathrm{H^+}]^?}{[\mathrm{Ni^{2+}}]}$

$$0 = 0.236 + \frac{0.059}{2}\log_{10}[\mathrm{H^+}]^2$$

or $-\log \mathrm{H^+} = 4$ $\therefore$ **pH = 4**

60. $E^\circ_{cell} = \frac{0.059}{1}\log_{10}K_C$

$E^\circ_{cell} = E^\circ_{OP_{\mathrm{Fe^{2+}/Fe^{3+}}}} + E^\circ_{RP_{\mathrm{Ce^{4+}/Ce^{3+}}}}$

$= -0.68 + 1.44 = 0.76\ \mathrm{V}$

$$\therefore \quad \log_{10} K_C = \frac{0.76}{0.059} = 12.8814$$

$$\therefore \quad K_C = \mathbf{7.6 \times 10^{12}}$$

61. For the change $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$, at equilibrium, $E = 0$

$$E = E^\circ - \frac{0.059}{2} \log_{10} K_C$$

or
$$E^\circ = \frac{0.059}{2} \log_{10} K_C$$

Also

$$E^\circ_{cell} = E^\circ_{RP_{Fe^{3+}/Fe^{2+}}} + E^\circ_{OP_{I^-/I_3^-}} = 0.77 - 0.54 = 0.23\text{ V}$$

Thus, $0.23 = \frac{0.059}{2} \log_{10} K_C \qquad \therefore K_C = \mathbf{6.26 \times 10^7}$

62. Given,

$$In^{3+} + 2e \longrightarrow In^+; \qquad E^\circ_1 = -0.42\text{ V} \quad ...(1)$$

$$In^{2+} + e \longrightarrow In^+; \qquad E^\circ_2 = -0.40\text{ V} \quad ...(2)$$

By subtracting Eq. (2) from Eq. (1) a third half-cell reaction can be obtained as:

$$\left[\begin{array}{ll} \text{where } E^\circ_3 \times 1 \times F = E^\circ_1 \times 2 \times F - E^\circ_2 \times 1 \times F & \\ \text{or} \qquad E^\circ_3 = 2 \times (-0.42) - 1 \times (-0.40) & \\ \qquad\qquad = -0.44\text{ V} & \end{array}\right]$$

$$In^{3+} + e \longrightarrow In^{2+}; \qquad E^\circ_3 = -0.44\text{ V}$$

For the reactions: $Cu^{2+} + e \longrightarrow Cu^+; \qquad E^\circ_4 = 0.15$

$$In^{2+} \longrightarrow In^{3+} + e; \qquad E^\circ_3 = +0.44$$

The net redox change:

$$Cu^{2+} + In^{2+} \longrightarrow Cu^+ + In^{3+};$$

$$E^\circ_{cell} = E^\circ_4 + E^\circ_3 = 0.15 + 0.44 = 0.59\text{ V}$$

Also
$$E^\circ_{cell} = \frac{0.059}{1} \log K_C$$

$$0.59 = \frac{0.059}{1} \log K_C \qquad \therefore K_C = \mathbf{10^{10}}$$

63.
$$Pt|CuCl||CuCl_2|Pt$$

Anode: $Cu^+ \longrightarrow Cu^{2+} + e; \qquad E^\circ_{OP} = -0.153\text{ V}$

Cathode: $Cu^+ + e \longrightarrow Cu; \qquad E^\circ_{RP} = 0.518\text{ V}$

Redox: $2Cu^+ \longrightarrow Cu^{2+} + Cu$

$$E^\circ_{cell} = E^\circ_{OP_{Cu^+/Cu^{2+}}} + E^\circ_{RP_{Cu^+/Cu}} = -0.153 + 0.518 = 0.365\text{ V}$$

Also
$$E^\circ = \frac{0.059}{1} \log K_C$$

$$0.365 = \frac{0.059}{1} \log K_C \quad \therefore K_C = \mathbf{1.50 \times 10^6}$$

64. The redox change is

	$Zn + Ni^{2+}$	$\rightleftharpoons Zn^{2+} + Ni$
mM before equilibrium	500	0
mM at equilibrium	a	$(500 - a)$

$$\therefore \quad E_{cell} = E_{OP_{Zn/Zn^{2+}}} + E_{RP_{Ni^{2+}/Ni}}$$

$$E_{cell} = E^\circ_{Zn/Zn^{2+}} + E^\circ_{RP_{Ni^{2+}/Ni}} + \frac{0.059}{2} \log_{10} \frac{[Ni^{2+}]}{[Zn^{2+}]}$$

At equilibrium $E_{cell} = 0$

$$\therefore \quad E^\circ_{OP_{Zn/Zn^{2+}}} + E^\circ_{RP_{Ni^{2+}/Ni}} = -\frac{0.059}{2} \log_{10} \frac{[Ni^{2+}]}{[Zn^{2+}]}$$

or
$$0.75 + (-0.24) = -\frac{0.059}{2} \log_{10} \frac{[Ni^{2+}]}{[Zn^{2+}]}$$

$$\frac{[Ni^{2+}]}{[Zn^{2+}]} = \text{antilog}\left(-\frac{0.51 \times 2}{0.059}\right) = 5.15 \times 10^{-18}$$

$$\therefore \quad \frac{a}{500 - a} = 5.15 \times 10^{-18}$$

$$\therefore \quad a = 500 \times 5.15 \times 10^{-18}$$

$$\therefore \quad [Ni^{2+}] = \frac{mM}{V} = \frac{500 \times 5.15 \times 10^{-18}}{500} = \mathbf{5.15 \times 10^{-18}}\ M$$

65. For $Cu(OH)_2$, $\qquad K_{sp} = [Cu^{2+}][OH^-]^2$

$$\because \quad [H^+] = 10^{-14} \quad ; \quad \text{thus } [OH^-] = 10^0 = 1$$

Therefore, $[Cu^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1.0 \times 10^{-19}}{1} = 1.0 \times 10^{-19}$

Now E_{RP} for the couple Cu^{2+}/Cu is

$$E_{RP} = E^\circ_{RP} + \frac{0.059}{2} \log_{10} [Cu^{2+}]$$

$$= 0.34 + \frac{0.059}{2} \log_{10} [1 \times 10^{-19}] = \mathbf{-0.2205\text{ V}}$$

66. K_{sp} of $AgI = [Ag^+][I^-] = [Ag^+][0.05] \qquad ...(1)$

For given cell $E_{cell} = E_{OP_{Ag}} + E_{RP_{Ag}}$

$$= E^\circ_{OP_{Ag/Ag^+}} - \frac{0.059}{1} \log_{10}[Ag^+]_{L.H.S.} + E^\circ_{RP_{Ag^+/Ag}} + \frac{0.059}{1} \log_{10} [Ag^+]_{R.H.S.}$$

$$E_{cell} = \frac{0.059}{1} \log_{10} \frac{[Ag^+]_{R.H.S.}}{[Ag^+]_{L.H.S.}}$$

$$\because \quad E^\circ_{OP_{Ag/Ag^+}} = -E^\circ_{RP_{Ag^+/Ag}}$$

$$0.788 = \frac{0.059}{1} \log_{10} \frac{0.05}{[Ag^+]_{L.H.S.}}$$

$$\therefore \quad [Ag^+]_{L.H.S.} = 2.203 \times 10^{-15}$$

$\therefore$ By Eq. (1), $\quad K_{sp} = [2.203 \times 10^{-15}][0.05]$

$$K'_{sp_{AgI}} = \mathbf{1.10 \times 10^{-16}}$$

67. $E_{cell} = E^\circ_{OP_{Ag/Ag^+}} + E^\circ_{RP_{Ag^+/Ag}} + \frac{0.059}{1} \log \frac{[Ag^+]_{R.H.S.}}{[Ag^+]_{L.H.S.}}$

or
$$0.0860 = \frac{0.059}{1} \log \frac{[Ag^+]_{R.H.S.}}{[Ag^+]_{L.H.S.}}$$

Also, $[Ag^+]_{L.H.S.}$ can be derived as

$$[Ag^+] = \sqrt{K_{sp_{AgI}}} = \sqrt{8.5 \times 10^{-17}} = 9.22 \times 10^{-9}\ M$$

$$\therefore \quad 0.0860 = \frac{0.059}{1} \log \frac{[Ag^+]_{R.H.S.}}{9.22 \times 10^{-9}}$$

or
$$\frac{[Ag^+]_{R.H.S.}}{9.22 \times 10^{-9}} = 28.68$$

$$\therefore \quad [Ag^+]_{R.H.S.} = 28.68 \times 9.22 \times 10^{-9}\ M$$

Also for R.H.S.,

$$[Ag^+][Cl^-] = K_{sp_{AgCl}}$$

$$\therefore \quad [Cl^-] = \frac{K_{sp_{AgCl}}}{[Ag^+]} = \frac{1.8\times10^{-10}}{28.68\times9.22\times10^{-9}}$$

$$\text{or} \quad [MCl^-] = \mathbf{6.8\times10^{-4}}\ \boldsymbol{M}$$

68. Given, $E^\circ_{RP_{Cu^{2+}/Cu}} = 0.337\text{ V} \ \therefore \ E^\circ_{OP_{Cu/Cu^{2+}}} = -0.337\text{ V}$

$E^\circ_{RP_{Ag^+/Ag}} = 0.799\text{ V} \ \therefore \ E^\circ_{OP_{Ag/Ag^+}} = -0.799\text{ V}$

For E°_{cell} to be +ve; oxidation of Cu and reduction of Ag^+ because

$$E^\circ_{OP_{Cu/Cu^{2+}}} > E^\circ_{OP_{Ag/Ag^+}}$$

$$\therefore \quad Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$$

The cell is, $Cu\,|\,CuSO_4(aq.)\,||\,AgNO_3(aq.)\,|\,Ag$

Now, $E_{cell} = E_{OP_{Cu/Cu^{2+}}} + E_{RP_{Ag^+/Ag}}$

$$= E^\circ_{OP_{Cu/Cu^{2+}}} - \frac{0.059}{2}\log_{10}[Cu^{2+}] + E^\circ_{RP_{Ag^+/Ag}} + \frac{0.059}{2}\log_{10}[Ag^+]^2$$

$$= E^\circ_{OP_{Cu/Cu^{2+}}} + E^\circ_{RP_{Ag^+/Ag}} + \frac{0.059}{2}\log_{10}\frac{[Ag^+]^2}{[Cu^{2+}]}$$

$$= E_{cell} = -0.337 + 0.799 + \frac{0.059}{2}\log_{10}\frac{[Ag^+]^2}{[Cu^{2+}]}$$

$$\because \quad E_{cell} = 0 \quad \text{at } [Cu^{2+}] = 0.01M$$

$$\therefore \quad 0 = 0.462 + \frac{0.059}{2}\log_{10}\frac{[Ag^+]^2}{0.01}$$

$$\therefore \quad [Ag^+] = \mathbf{1.477\times10^{-9}\ mol\ litre^{-1}}$$

69. For the cell

$$Ag\,\Big|\,Ag^+\ (Ag_2CrO_4\text{ sol. saturated})\,\Big\|\,\begin{matrix}Ag^+\\0.1\,M\end{matrix}\,\Big|\,Ag;$$

$$E_{cell} = 0.164\text{ V at } 298\text{ K}$$

We have $E_{cell} = E^\circ_{OP_{Ag/Ag^+}} + E^\circ_{RP_{Ag^+/Ag}} + \dfrac{0.059}{1}\log_{10}\dfrac{[Ag^+]_{R.H.S.}}{[Ag^+]_{L.H.S.}}$

$$\text{or} \quad 0.164 = 0 + \frac{0.059}{1}\log_{10}\frac{0.1}{[Ag^+]_{L.H.S.}}$$

$$\therefore \quad [Ag^+]_{L.H.S.} = 1.66\times10^{-4}\ M$$

Now $\quad K_{sp}$ for $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

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

Since, $\quad [Ag^+]_{L.H.S.} = 1.66\times10^{-4}\ M$

$$\therefore \quad [CrO_4^{2-}]_{L.H.S.} = \frac{1.66\times10^{-4}}{2}\ M$$

$$\therefore \quad K_{sp} = [1.66\times10^{-4}]^2\left[\frac{1.66\times10^{-4}}{2}\right]$$

$$K_{sp} = \mathbf{2.287\times10^{-12}\ mol^3\ litre^{-3}}$$

70. The given cell is $PtH_2\,\Big|\begin{matrix}H^+\\1\,M\end{matrix}\Big\|\begin{matrix}Ag_2SO_4(aq.)\\\text{saturated}\end{matrix}\Big|\,Ag$

The reaction are, $\quad H_2 \longrightarrow 2H^+ + 2e$

$$2Ag^+ + 2e \longrightarrow 2Ag$$

Thus, $\quad E_{cell} = E_{OP_H} + E_{RP_{Ag}}$

$$0.711 = 0.799 + \frac{0.059}{2}\log[Ag^+]^2$$

$$\therefore \quad \log\frac{1}{[Ag^+]^2} = \frac{[0.799-0.711]\times2}{0.059} = 3$$

$$\therefore \quad [Ag^+]^2 = 10^{-3} \quad \therefore [Ag^+] = 3.2\times10^{-2}$$

Now the solubility equilibrium is,

$$Ag_2SO_4 \rightleftharpoons 2Ag^+ + SO_4^{2-}$$

$$\therefore \quad K_{sp} = (Ag^+)^2\,(SO_4^{2-})$$

$$= (3.2\times10^{-2})^2\left(\frac{3.2\times10^{-2}}{2}\right) = \mathbf{1.6\times10^{-5}}$$

[**Note :** That if $[Ag^+] = 3.2\times10^{-2}$, then

$$[SO_4^{2-}] = \frac{1}{2}\times3.2\times10^{2-}]$$

71. For Zn electrode || calomel electrode

$$E_{OP_{calomel}} = -0.28\text{ V}; \quad E_{RP_{calomel}} = +0.28\text{ V}$$

$$\therefore \quad E_{cell} = E_{OP_{Zn/Zn^{2+}}} + E_{RP_{Calomel}}$$

$$1.083 = E_{OP_{Zn/Zn^{2+}}} + 0.28$$

$$\therefore \quad E_{OP_{Zn/Zn^{2+}}} = 1.083 - 0.28 = +0.803\text{ volt}$$

Now for Cu electrode || calomel electrode

$$E_{cell} = E_{OP_{Cu/Cu^{2+}}} + E_{RP\,Calomel}$$

$$-0.018 = E_{OP_{Cu/Cu^{2+}}} + E_{RP\,Calomel}$$

$$\therefore \quad E_{OP_{Cu/Cu^{2+}}} = -0.018 - 0.28 = -0.298\text{ volt}$$

Now for Zn electrode || Cu electrode, *i.e.*, Daniel cell

$$E_{cell} = E_{OP_{Zn/Zn^{2+}}} + E_{RP_{Cu^{2+}/Cu}}$$

$$= +0.803 + 0.298 = \mathbf{1.101\ volt}$$

72. Consider an electrode of H as

$$2H^+ + 2e \longrightarrow H_2; \quad E^\circ_{RP_H} = 0$$

Given electrode is $\quad 2H_2O + 2e \longrightarrow H_2 + 2OH^-; \quad E^\circ_{RP} = -0.8277\text{ V}$

$\because E^\circ_{OP}$ for $H_2O > E^\circ_{OP}$ for H.

$\therefore$ The cell reactions are:

Anode: $\quad H_2 + 2OH^- \longrightarrow 2H_2O + 2e; \quad E^\circ_{OP} = +0.8277\text{ V}$

Cathode: $\quad 2H^+ + 2e \longrightarrow H_2; \quad E^\circ_{RP} = 0$

$\therefore$ Net reaction is

$$2H^+ + 2OH^- \rightleftharpoons 2H_2O$$

and $K = \dfrac{[H_2O]^2}{[H^+]^2[OH^-]^2}$

Thus, for $2H_2O \rightleftharpoons [H_3O^+][OH^-]$

$K_w = [H_3O^+][OH^-]$

$\therefore \quad K = \left[\dfrac{1}{K_w}\right]^2 \qquad \text{...(1)}$

Also, $E_{cell} = E_{OP_{H_2O}} + E_{RP_H}$

$$= E^\circ_{OP_{H_2O}} - \frac{0.059}{2}\log_{10}\frac{[H_2O]^2}{[P_{H_2}][OH^-]^2}$$

$$+E^\circ_{RP_{H^+/H}} + \frac{0.059}{2}\log_{10}\frac{[H^+]^2}{P_{H_2}}$$

$$E_{cell} = 0.8277 + \frac{0.059}{2}\log_{10}\frac{[H^+]^2\cdot P_{H_2}\cdot[OH^-]^2}{P_{H_2}\cdot[H_2O]^2}$$

$$E_{cell} = 0.8277 + \frac{0.059}{2}\log_{10}\frac{[H^+]^2\,[OH^-]^2}{[H_2O]^2}$$

$$= 0.8277 + \frac{0.059}{2}\log_{10}\frac{1}{K}$$

$$E_{cell} = 0.8277 + \frac{0.059}{2}\log_{10}[K_w]^2 \qquad \text{by Eq. (1)}$$

At equilibrium, $E_{cell} = 0$

$\therefore \quad -0.8277 = 0.059\log_{10} K_w$

or $\log_{10} K_w = -\dfrac{0.8277}{0.059}$

or $K_w = \mathbf{9.35 \times 10^{-15}}$

73. For $2Hg + 2Fe^{3+} \rightleftharpoons Hg_2^{2+} + 2Fe^{2+}$

Before reaction	Excess	10^{-3}	0	0
After reaction	Excess	$10^{-3}\times\frac{5}{100}$	$\frac{95}{2\times100}\times10^{-3}$	$\frac{95}{100}\times10^{-3}$

For cell at equilibrium

$$E_{cell} = 0 = E_{OP_{Hg/Hg_2^{2+}}} + E_{RP_{Fe^{3+}/Fe^{2+}}}$$

$$0 = E^\circ_{OP_{Hg/Hg_2^{2+}}} - \frac{0.059}{2}\log_{10}[Hg_2^{2+}] + E^\circ_{RP_{Fe^{3+}/Fe^{2+}}} +$$

$$\frac{0.059}{2}\log_{10}\frac{[Fe^{3+}]^2}{[Fe^{2+}]^2}$$

$$0 = E^\circ_{OP_{Hg/Hg_2^{2+}}} + 0.77 + \frac{0.059}{2}\log_{10}\frac{[Fe^{3+}]^2}{[Fe^{2+}]^2\,[Hg_2^{2+}]}$$

$(\because E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} = -0.77\text{ V} \therefore E^\circ_{RP_{Fe^{3+}/Fe^{2+}}} = +0.77\text{ V})$

or $E^\circ_{OP_{Hg/Hg_2^{2+}}} = -0.77 - \dfrac{0.059}{2}\log_{10}$

$$\frac{\left[\frac{5}{100}\times10^{-3}\right]^2}{\left[\frac{95\times10^{-3}}{100}\right]^2\left[\frac{95\times10^{-3}}{2\times100}\right]} = \mathbf{-\,0.792\ V}$$

74. $MnO_4^- + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+}$

Initial conc.	$0.1\,M$	
Final conc.	$\frac{0.1\times10}{100}$	$\frac{0.1\times90}{100}$

$E_{cell} = E_{OP_H} + E_{RP_{Mn^{2+}/MnO_4^-}} = 0 + E_{RP_{Mn^{2+}/MnO_4^-}}$

The electrode reaction is :

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O\ \text{(cathode)}$$

$$\therefore \quad E_{RP} = E^\circ_{RP_{Mn^{2+}/MnO_4^-}} + \frac{0.059}{5}\log\frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$$

$$= 1.51 + \frac{0.059}{5}\log\frac{\frac{0.1\times10}{100}\times(0.8)^8}{\frac{0.1\times90}{100}}$$

$$= 1.51 - 0.099 = \mathbf{1.411\ V}$$

75. For given cell $\because \ E^\circ_{OP_{Zn/Zn^{2+}}} > E^\circ_{OP_{H/H^+}}$

$\therefore$ Redox changes will be: $Zn \longrightarrow Zn^{2+} + 2e$

$2H^+ + 2e \longrightarrow H_2$

$$E_{cell} = E_{OP_{Zn/Zn^{2+}}} + E_{RP_{H^+/H}}$$

$$= E^\circ_{OP_{Zn/Zn^{2+}}} - \frac{0.059}{2}\log_{10}[Zn^{2+}] + E^\circ_{RP_{H^+/H}}$$

$$+\frac{0.059}{2}\log_{10}\frac{[H^+]^2}{[P_{H_2}]}$$

$$0.701 = 0.760 + \frac{0.059}{2}\log_{10}\frac{[H^+]^2}{[Zn^{2+}]}$$

$$= 0.760 + \frac{0.059}{2}\log_{10}\frac{[H^+]^2}{[0.1]}$$

$[H^+] = 0.0316\text{ mol litre}^{-1}$

Since, H^+ must be used by NaOH

$\therefore$ Meq. of NaOH = Meq. of $[H^+]$

$$\frac{w}{40}\times1000 = 0.0316\times1000 \quad (\because V = 1\text{ litre})$$

$\therefore \quad \mathbf{w = 1.264\ g}$

After addition of NaOH to cathode solution $[H^+]$ becomes 10^{-7} since both acid and base are neutralized completely. Thus, new emf of cell,

$$E_{cell} = E^\circ_{cell} + \frac{0.059}{2}\log_{10}\frac{[H^+]^2}{(0.1)}$$

$$= 0.760 + \frac{0.059}{2}\log_{10}\frac{(10^{-7})^2}{0.1}$$

$E_{cell} = \mathbf{0.3765\ V}$

76. $Zn \longrightarrow Zn^{2+} + 2e \quad E^\circ_{OP} = +0.76\text{ V}$

$[Zn^{2+}] = \left[\dfrac{0.1\times20}{100}\right]$ ($\because$ Salt gives 20% of ions)

$$E_{OP_{Zn/Zn^{2+}}} = E^\circ_{OP_{Zn/Zn^{2+}}} - \frac{0.059}{2}\log_{10}[Zn^{2+}]$$

$$= +0.76 - \frac{0.059}{2}\log_{10}\left[\frac{0.1\times20}{100}\right]$$

$E_{OP_{Zn/Zn^{2+}}} = \mathbf{0.81\ V} \qquad (Zn \longrightarrow Zn^{2+} + 2e)$

$\therefore \ E_{RP_{Zn^{2+}/Zn}} = \mathbf{-\,0.81\ V} \qquad (Zn^{2+} + 2e \longrightarrow Zn)$

77. **Anode:** $H_2 \longrightarrow 2H^+ + 2e$

(negative polarity)

$$[H^+] = 10^{-6}\ M$$

Cathode: $2H^+ + 2e \longrightarrow H_2$

(positive polarity) $[H^+] \longrightarrow aM$

$$\therefore\ E_{cell} = E_{OP_{H/H^+}} + E_{RP_{H^+/H}}$$

$$= E^\circ_{OP_{H/H^+}} - \frac{0.059}{2}\log_{10}[H^+]^2_{\text{Anode}} + E^\circ_{RP_{H^+/H}} + \frac{0.059}{2}\log_{10}[H^+]^2_{\text{Cathode}}$$

$$= \frac{0.059}{2}\log_{10}\frac{[H^+]^2_{\text{Cathode}}}{[H^+]^2_{\text{Anode}}}$$

$$0.118 = \frac{0.059}{2}\log_{10}\frac{[H^+]^2_{\text{Cathode}}}{(10^{-6})^2} = \frac{0.059}{1}\log_{10}\frac{[H^+]_{\text{Cathode}}}{10^{-6}}$$

$$\therefore\ [H^+]_{\text{Cathode}} = \mathbf{10^{-4}}\ M$$

78.

$$E_{cell} = E_{OP_{Ag/Ag^+}} + E_{RP_{Ag^+/Ag}}$$

L.H.S. R.H.S.

$$= E^\circ_{OP_{Ag/Ag^+}} - \frac{0.059}{1}\log_{10}[Ag^+]_{\text{L.H.S.}} + E^\circ_{RP_{Ag^+/Ag}} + \frac{0.059}{1}\log_{10}[Ag^+]_{\text{R.H.S.}}$$

$$E_{cell} = \frac{0.059}{1}\log_{10}\frac{[Ag^+]_{\text{R.H.S.}}}{[Ag^+]_{\text{L.H.S.}}} \qquad \text{...(1)}$$

Now for L.H.S. $K_{sp_{AgCl}} = 2.8\times10^{-10}$

$$\therefore\ [Ag^+][Cl^-] = 2.8\times10^{-10}$$

$$\therefore\ [Ag^+] = \frac{2.8\times10^{-10}}{[Cl^-]} = \frac{2.8\times10^{-10}}{0.2} = 1.4\times10^{-9}\ M$$

For R.H.S. $K_{sp_{AgBr}} = 3.3\times10^{-13}$

$$[Ag^+][Br^-] = 3.3\times10^{-13}$$

$$\therefore\ [Ag^+] = \frac{3.3\times10^{-13}}{[Br^-]} = \frac{3.3\times10^{-13}}{0.001} = 3.3\times10^{-10}\,M$$

$$\therefore\ \text{By Eq. (1)}\quad E_{cell} = \frac{0.059}{1}\log_{10}\frac{3.3\times10^{-10}}{1.4\times10^{-9}} = -0.037\ \text{V}$$

Thus, to get E_{cell} positive, polarity of cells should be reversed.

i.e., **cell is Ag | AgBr(*s*) KBr||AgCl, KCl | Ag and *E* = +0.037 V**

0.001*M* **0.2*M***

79. Let a and b are the concentrations of Br^- and Cl^- at equilibrium when $E_{cell} = 0$.

$$\therefore\ [Ag^+]_{\text{L.H.S.}} = \frac{K_{sp_{AgBr}}}{[Br^-]} = \frac{5\times10^{-13}}{a}$$

$$[Ag^+]_{\text{R.H.S.}} = \frac{K_{sp_{AgCl}}}{[Cl^-]} = \frac{1\times10^{-10}}{b}$$

Also $E_{cell} = \underset{\text{R.H.S.}}{E^\circ_{Ag/Ag^+}} + \underset{\text{L.H.S.}}{E^\circ_{Ag^+/Ag}} + \dfrac{0.059}{1}\log\dfrac{[Ag^+]_{\text{R.H.S.}}}{[Ag^+]_{\text{L.H.S.}}}$

$$0 = 0 + \frac{0.059}{1}\log\frac{1\times10^{-10}\times a}{5\times10^{-13}\times b}$$

$$\therefore\ \frac{a}{b} = \frac{\mathbf{1}}{\mathbf{200}}$$

80.

$$Ag_2S + 2e \longrightarrow 2Ag + S^{2-}$$

$$(Ag^{+1})_2 + 2e \longrightarrow 2Ag$$

$$\therefore\ E_{RP} = E^\circ_{RP} + \frac{0.059}{2}\log[Ag^+]^2 \qquad \text{...(1)}$$

Also $K_1 \times K_2 = \dfrac{[H^+]^2[S^{2-}]}{[H_2S]}$

$$\therefore\ 1.1\times10^{-13}\times1.0\times10^{-8} = \frac{[10^{-3}]^2[S^{2-}]}{[0.1]}$$

or $[S^{2-}] = 1.1\times10^{-16}$

Also $K_{sp_{Ag_2S}} = 2\times10^{-49} = [Ag^+]^2[S^{2-}]$

$$= [Ag^+]^2[1.1\times10^{-16}]$$

$$\therefore\ [Ag^+]^2 = 1.818\times10^{-33} \qquad \text{...(2)}$$

$\therefore$ By Eqs. (1) and (2)

$$E_{RP} = 0.8 + \frac{0.059}{2}\log[1.818\times10^{-33}]$$

$$= 0.8 - 0.9658 = -0.1658\ \text{V}$$

81.

$$Ag \longrightarrow Ag^+ + e; \qquad E^\circ = -0.7991\ \text{V}$$

$$\underline{AgI(s) + e \longrightarrow Ag + I^-;} \qquad E^\circ = ?$$

$$AgI(s) \longrightarrow Ag^+ + I^-$$

$$\therefore\ E_{cell} = E^\circ_{OP_{Ag/Ag^+}} - \frac{0.059}{1}\log[Ag^+] + E^\circ_{RP_{I^-/AgI/Ag}} + \frac{0.059}{1}\log\frac{1}{[I^-]}$$

$\because\ E_{cell} = 0$ for $AgI \longrightarrow Ag^+ + I^-$

$$\therefore\ 0 = -0.7991 + E^\circ_{RP_{I^-AgI/Ag}} + \frac{0.059}{1}\log\frac{1}{[Ag^+][I^-]}$$

$$\therefore\ E^\circ_{RP_{I^-/AgI/Ag}} = 0.7991 + \frac{0.059}{1}\log K_{sp_{AgI}}$$

$$= 0.7991 - 0.059\times16.07$$

$$= +0.7991 - 0.9481 = \mathbf{-0.1490\ V}$$

82. $\because\ E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} > E_{Cr^{3+}/Cr_2^{6+}}$

$\therefore$ Redox changes will be

Anode: $Fe^{2+} \longrightarrow Fe^{3+} + e$

(L.H.S.)

Cathode: $14H^+ + 6e + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

(R.H.S.)

$$E_{cell} = E_{OP_{Fe^{2+}/Fe^{3+}}} + E_{RP_{\text{R.H.S.}}}$$

$$= E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} - \frac{0.059}{6}\log_{10}\frac{[Fe^{3+}]^6}{[Fe^{2+}]^6} + E^\circ_{RP_{\text{R.H.S.}}} + \frac{0.059}{6}\log_{10}\frac{[Cr_2O_7^{2-}][H^+]^{14}}{[Cr^{3+}]^2}$$

$$= -0.770 - \frac{0.059}{1}\log_{10}\frac{0.75}{0.5} + 1.35 + \frac{0.059}{6}\log_{10}\frac{(2)\times(1)^{14}}{(4)^2}$$

$$= -0.770 - 0.0104 + 1.35 + (-0.0089) = \mathbf{+0.56\ volt}$$

83. $$E_{cell} = E^\circ_{OP_H} + E^\circ_{RP_{Zn^{2+}/Zn}} + \frac{0.059}{2}\log_{10}\frac{[Zn^{2+}]}{[H^+]^2}$$

$$-0.46 = 0 - 0.763 + \frac{0.059}{2}\log_{10}\frac{[0.3]}{[H^+]^2}$$

$\therefore$ $[H^+] = 4.0\times10^{-6}$

Now $$K_2 = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]}$$

$\because$ $$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$$

The dissociation of HSO_3^- is suppressed in presence of SO_3^{2-} due to common ion effect. Thus $[SO_3^{2-}] = 6.44\times10^{-3}\ M$ and $[HSO_3^-] = 0.4\ M$

$\therefore$ $$K_2 = \frac{4\times10^{-6}\times6.44\times10^{-3}}{0.4} = \mathbf{6.44\times10^{-8}}$$

84. $$E_{cell} = E_{OP_{Sn}} + E_{RP_{Pb}}$$

$$= E^\circ_{OP_{Sn}} - \frac{0.059}{2}\log_{10}[Sn^{2+}] + E^\circ_{RP_{Pb}} + \frac{0.059}{2}\log_{10}[Pb^{2+}]$$

$$= E^\circ_{OP_{Sn}} + E^\circ_{RP_{Pb}} + \frac{0.059}{2}\log_{10}\frac{[Pb^{2+}]}{[Sn^{2+}]}$$

$$= 0.136 - 0.126 + \frac{0.059}{2}\log_{10}\frac{[Pb^{2+}]}{[Sn^{2+}]}$$

$$= 0.01 + \frac{0.059}{2}\log_{10}\frac{[Pb^{2+}]}{[Sn^{2+}]}$$

At equilibrium, $E_{cell} = 0$ $\therefore$ $\frac{[Pb^{2+}]}{[Sn^{2+}]} = 0.458$

Thus, till $\frac{[Pb^{2+}]}{[Sn^{2+}]} > 0.458$, cell reaction exists,

and it will be reversed when $\mathbf{\frac{[Pb^{2+}]}{[Sn^{2+}]} < 0.458}$

i.e., $E_{cell} = -\text{ve}$

85. Given, $E^\circ_{FeO/Fe} = -0.87\ V$; $\therefore$ $E^\circ_{Ni_2O_3/NiO} = +0.40\ V$

$\therefore$ $E^\circ_{Fe/FeO} = +0.87\ V$; $\therefore$ $E^\circ_{NiO/Ni_2O_3} = -0.40\ V$

Since, E°_{OP} for Fe/FeO > E°_{OP} for NiO/Ni_2O_3 and thus, redox changes are,

At anode: $Fe(s) + 2OH^- \longrightarrow FeO(s) + H_2O(l) + 2e$ (oxidation)

At cathode:

$$Ni_2O_3(s) + H_2O(l) + 2e \longrightarrow 2NiO(s) + 2OH^- \quad \text{(reduction)}$$

Redox reaction:

$$Fe(s) + Ni_2O_3(s) \longrightarrow FeO(s) + 2NiO(s)$$

(i) $$E_{cell} = E^\circ_{OP_{Fe/FeO}} - \frac{0.059}{2}\log_{10}\frac{[H_2O]}{[OH^-]^2} + E^\circ_{RP_{Ni_2O_3/NiO}} + \frac{0.059}{2}\log_{10}\frac{[H_2O]}{[OH^-]^2}$$

$$= E^\circ_{OP_{Fe/FeO}} + E^\circ_{RP_{Ni_2O_3/NiO}} = 0.87 + 0.40 = \mathbf{1.27\ V}$$

(ii) The E_{cell} is independent of OH^- ion concentration.

(iii) $-\Delta G^\circ = nE^\circ F = 2\times1.27\times96500$

$$= 245110\text{J} = \mathbf{245.11\ kJ}$$

86. At pH = 7: $$E_{RP} = E^\circ_{RP} + \frac{0.059}{2}\log\frac{[CH_3CHO][H^+]^2}{[CH_3CH_2OH]}$$

$$-0.197 = E^\circ_{RP} + \frac{0.059}{2}\log\frac{(10^{-7})^2\times1}{1}$$

$$-0.197 = E^\circ_{RP} + \frac{0.059}{2}\times(-14)$$

$\therefore$ $E^\circ_{RP} = 0.216$

Again when pH = 6

$$E_{RP} = E^\circ_{RP} + \frac{0.059}{2}\log\frac{(10^{-6})^2\times10^{-5}}{10^{-5}}$$

$$= 0.216 + \frac{0.059}{2}\times(-12) = 0.216 - 0.354 = \mathbf{-0.138\ V}$$

87. For the given cell, at equilibrium, the reaction is

$$Mg + 2Ag^+ \rightleftharpoons Mg^{2+} + 2Ag$$

$$E_{cell} = 0 = E_{OP_{Mg/Mg^{2+}}} + E_{RP_{Ag^+/Ag}}$$

$$0 = E^\circ_{OP_{Mg/Mg^{2+}}} - \frac{0.059}{2}\log_{10}[Mg^{2+}] + E^\circ_{RP_{Ag^+/Ag}} + \frac{0.059}{2}\log_{10}[Ag^+]^2$$

$$0 = E^\circ_{OP_{Mg/Mg^{2+}}} + E^\circ_{RP_{Ag^+/Ag}} + \frac{0.059}{2}\log_{10}\frac{[Ag^+]^2}{[Mg^{2+}]}$$

$$0 = 2.37 + 0.80 + \frac{0.059}{2}\log_{10}\frac{1}{K_C}$$

$\therefore$ $\log_{10}\frac{1}{K_C} = -107.457$

or $\log_{10}K_C = \mathbf{107.457}$

and $E^\circ_{cell} = 2.37 + 0.80 = \mathbf{3.17\ V}$

Now maximum work that can be obtained by cell is given by

$$-\Delta G^\circ = W_{max}$$

$\therefore$ $W_{max} = -\Delta G^\circ$

$$= nE^\circ F = 2\times96500\times3.17 = 6.118\times10^5 \text{ joule}$$

$$= \mathbf{6.118\times10^2\ kJ}$$

88. (i) In $8M\ H^+$ solution, conc. of all other species is unity.

$$E_{RP} = E^\circ_{RP} + \frac{0.059}{1}\log_{10}[H^+]^2$$

$$= 0.78 + 0.059\log_{10}(8)^2 = 0.78 + 0.1062$$

$$= \mathbf{0.8862\ V}$$

(ii) In case of neutral solution; concentration of $[H^+] = 10^{-7}\ M$ and conc. of all other species are unity, then

$$E_{RP} = E^\circ_{RP} + \frac{0.059}{1}\log_{10}[\mathrm{H}^+]^2$$
$$= 0.78 + \frac{0.059}{1}\log_{10}(10^{-7})^2 = 0.78 + (-0.826)$$
$$= \mathbf{-0.046\ V}$$

89. Initially $E_{\mathrm{Cu}^{2+}/\mathrm{Cu}} = E^\circ_{\mathrm{Cu}^{2+}/\mathrm{Cu}} + \frac{0.059}{2}\log[\mathrm{Cu}^{2+}]$

$$= 0.344 + \frac{0.059}{2}\log[1] = 0.344\ \mathrm{V}$$
$$E_{\mathrm{Bi}^{3+}/\mathrm{Bi}} = 0.226 + \frac{0.059}{3}\log[\mathrm{Bi}^{3+}]$$
$$= 0.226 + \frac{0.059}{3}\log 1 = 0.266\ \mathrm{V}$$

Thus, passage of current would initially deposits Cu^{2+} till $E_{\mathrm{Cu}^{2+}/\mathrm{Cu}}$ becomes 0.266 V because then only, Bi^{3+} will be deposited.

Thus, $E_{\mathrm{Cu}^{2+}/\mathrm{Cu}} = E^\circ_{\mathrm{Cu}^{2+}/\mathrm{Cu}} + \frac{0.059}{2}\log[\mathrm{Cu}^{2+}]$

$$0.266 = 0.344 + \frac{0.059}{2}\log[\mathrm{Cu}^{2+}]$$

$\therefore$ $[\mathrm{Cu}^{2+}] = \mathbf{10^{-4}}\ \boldsymbol{M}$

90. The half cell reaction is,

$$\mathrm{MnO_4^-} + 8\mathrm{H}^+ + 5e \longrightarrow \mathrm{Mn}^{2+} + 4\mathrm{H_2O}$$

$$\therefore E_{\mathrm{MnO_4^-/Mn^{2+}}} = E^\circ_{\mathrm{MnO_4^-/Mn^{2+}}} + \frac{0.059}{5}\log_{10}\frac{[\mathrm{MnO_4^-}][\mathrm{H}^+]^8}{[\mathrm{Mn}^{2+}]}$$

or $E_{RP} = E^\circ_{RP} + 0.0118\log_{10}\frac{1\times 1}{1}$

$\therefore$ $E_{RP} = E^\circ_{RP}$

If $\mathrm{H}^+ = 10^{-4}$

Then $E_{RP} = E^\circ_{RP} + 0.0118\log_{10}\frac{1\times(10^{-4})^8}{1}$

$$E_{RP} = E^\circ_{RP} - \mathbf{0.38\ V}$$

i.e., the couple $\mathrm{MnO_4^-}/\mathrm{Mn}^{2+}$ shows a decrease in its E_{RP} by 0.38 volt or an increase in its E_{OP} by 0.38 V and thus less oxidizing power.

91. The cell reactions are:

Anode: $\mathrm{H_2} \longrightarrow 2\mathrm{H}^+ + 2e$

Cathode: $2\mathrm{Ag}^+ + 2e \longrightarrow 2\mathrm{Ag}$

Thus, $E_{cell} = E^\circ_{OP_{\mathrm{H_2}}} + E^\circ_{RP_{\mathrm{Ag}}} + \frac{0.059}{2}\log_{10}\frac{[\mathrm{Ag}^+]^2\cdot P_{\mathrm{H_2}}}{[\mathrm{H}^+]^2}$

or $0.503 = 0 + 0.80 + \frac{0.059}{2}\log_{10}[\mathrm{Ag}^+]^2$

or $[\mathrm{Ag}^+] = 9.25\times 10^{-6}\ M$

$\therefore$ Mole of Ag^+ in 350 mL $= 9.25\times 10^{-6}\times\frac{350}{1000}$

$\therefore$ Mass of Ag^+ in 350 mL $= 9.25\times 10^{-6}\times\frac{350}{1000}\times 108$

$$= 3.497\times 10^{-4}\ \mathrm{g}$$

$\therefore$ % of Ag in 1.05 g alloy $= \frac{3.497\times 10^{-4}}{1.05}\times 100 = 0.033\%$

$\therefore$ % of lead in alloy $=$ **99.967%**

92. E°_{OP} is more for Pb and thus,

Anode: $\mathrm{Pb} \longrightarrow \mathrm{Pb}^{2+} + 2e$

Cathode: $\mathrm{Hg_2^{2+}} + 2e \longrightarrow \mathrm{Hg_2}$

$$\text{Cell is Pb}\left|\begin{matrix}\mathrm{PbSO_4}\\ \text{saturated}\end{matrix}\right|\left|\begin{matrix}\mathrm{Hg_2SO_4}\\ \text{saturated}\end{matrix}\right|\mathrm{Hg}$$

Also, $E_{cell} = E^\circ_{OP_{\mathrm{Pb}}} + E^\circ_{RP_{\mathrm{Hg}}} + \frac{0.059}{2}\log\frac{[\mathrm{Hg_2^{2+}}]}{[\mathrm{Pb}^{2+}]}$

$\therefore$ $E^\circ_{OP_{\mathrm{Pb}}} = 0.126\ \mathrm{V}$ and $E^\circ_{RP_{\mathrm{Hg}}} = +0.789\ \mathrm{V}$

and for $\mathrm{PbSO_4} \rightleftharpoons \mathrm{Pb}^{2+} + \mathrm{SO_4^{2-}}$

$\therefore$ $K_{sp} = [\mathrm{Pb}^{2+}][\mathrm{SO_4^{2-}}] = [\mathrm{Pb}^{2+}]^2$

or $[\mathrm{Pb}^{2+}] = \sqrt{K_{sp}} = \sqrt{2.43\times 10^{-8}}$

For $\mathrm{Hg_2SO_4} \rightleftharpoons \mathrm{Hg_2^{2+}} + \mathrm{SO_4^{2-}}$

$$[\mathrm{Hg_2^{2+}}] = \sqrt{K_{sp}} = \sqrt{1.46\times 10^{-6}}$$

$$\therefore E_{cell} = 0.126 + 0.789 + \frac{0.059}{2}\log\frac{\sqrt{1.46\times 10^{-6}}}{\sqrt{2.43\times 10^{-8}}} = \mathbf{0.941\ V}$$

93. $\because$ $E_{\mathrm{Ag^+/Ag}} = E^\circ_{\mathrm{Ag^+/Ag}} + \frac{0.059}{1}\log_{10}[\mathrm{Ag}^+]$ ...(1)

Also, $K_{sp_{\mathrm{AgI}}} = [\mathrm{Ag}^+][\mathrm{I}^-]$

$\because$ $[\mathrm{Ag}^+] = [\mathrm{I}^-]$ (for a saturated solution)

$\therefore$ $[\mathrm{Ag}^+] = \sqrt{K_{sp_{\mathrm{AgI}}}} = \sqrt{8.7\times 10^{-17}} = 9.32\times 10^{-9}$ ...(2)

$\therefore$ By Eq. (1), $E_{\mathrm{Ag^+/Ag}} = 0.799 + \frac{0.059}{1}\log_{10}(9.32\times 10^{-9})$

$$= 0.799 - 0.474 = \mathbf{0.32\ V}$$

Also, $\mathrm{Ag} \longrightarrow \mathrm{Ag}^+ + e;$ $E^\circ_{OP} = -0.799\ \mathrm{V}$

$$\underline{\mathrm{AgI}(s) + e \longrightarrow \mathrm{Ag} + \mathrm{I}^-}$$
$$\mathrm{AgI} \rightleftharpoons \mathrm{Ag}^+ + \mathrm{I}^-$$

$$\therefore E_{cell} = E^\circ_{OP_{\mathrm{Ag/Ag^+}}} - \frac{0.059}{1}\log[\mathrm{Ag}^+] + E^\circ_{RP_{\mathrm{I^-/AgI/Ag}}} + \frac{0.059}{1}\log\frac{1}{[\mathrm{I}^-]} \quad ...(3)$$

$\because$ $E_{cell} = 0$ at equilibrium, thus, from Eq. (3)

$$E^\circ_{OP_{\mathrm{Ag/Ag^+}}} + E^\circ_{RP_{\mathrm{I^-/AgI/Ag}}} = \frac{0.059}{1}\log[\mathrm{Ag}^+][\mathrm{I}^-]$$
$$= \frac{0.059}{1}\log K_{sp_{\mathrm{AgI}}}$$
$$-0.799 + E^\circ_{RP_{\mathrm{I^-/AgI/Ag}}} = \frac{0.059}{1}\log 8.7\times 10^{-17}$$

or $E^\circ_{RP_{\mathrm{I^-/AgI/Ag}}} = -0.948 + 0.799 = \mathbf{-0.149\ V}$

94. $\mathrm{Ag}(s) + \frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{AgCl}(s);$ $\Delta G^\circ_1 = -109\ \mathrm{kJ}$ ...(1)

$\mathrm{Ag}(s) \longrightarrow \mathrm{Ag}^+(aq.) + e;$ $\Delta G^\circ_2 = +77\ \mathrm{kJ}$ ...(2)

$\frac{1}{2}\mathrm{Cl_2}(g) + e \longrightarrow \mathrm{Cl}^-(aq.);$ $\Delta G^\circ_3 = -129\ \mathrm{kJ}$ ...(3)

By Eqs. (1) – (2) – (3),

$Ag^+(aq.) + Cl^-(aq.) \longrightarrow AgCl\,(s);$

$$\Delta G_4^\circ = -109 - 77 + 129 = -57\text{ kJ}$$

$\because$ $$-\Delta G^\circ = nE^\circ F$$

$\therefore$ $$57 \times 10^3 = 1 \times E^\circ \times 96500 \quad \therefore \quad E_{cell}^\circ = 0.59\text{ V}$$

The cell is $\underset{\textbf{(Anode)}}{\textbf{Ag}}\;\mathbf{|AgCl(s)||Cl^-(aq.)||Ag^+(aq.)|}\underset{\textbf{(Cathode)}}{\textbf{Ag}}$

Also, $$E_{cell} = E_{OP_{Ag/AgCl/Cl^-}}^\circ - 0.059\log\frac{1}{[Cl^-]} + E_{RP_{Ag^+/Ag}}^\circ + 0.059\log[Ag^+]$$

At equilibrium $E_{cell} = 0$, thus,

$$E_{Ag/AgCl/Cl^-}^\circ + E_{RP_{Ag^+/Ag}}^\circ = -0.059\log[Ag^+][Cl^-]$$

$$E_{cell}^\circ = -0.059\log K_{sp\,AgCl}$$

$\therefore$ $$0.59 = -0.059\log K_{sp\,AgCl}$$

or $$\mathbf{K_{sp\,AgCl} = 1 \times 10^{-10}\ M^2}$$

Let solubility of AgCl be S, then

$$S = \sqrt{K_{sp}} = \sqrt{10^{-10}} = 10^{-5}\text{ M}$$

Mole of AgCl in its 100 mL saturated solution

$$= 10^{-5} \times \frac{100}{1000} = 10^{-6}$$

Mole of Zn added in it $= \dfrac{6.539 \times 10^{-2}}{65.39} = 10^{-3}$

For $$Ag \longrightarrow Ag^+ + e; \quad \Delta G^\circ = 77\text{ kJ}$$

$\therefore$ $$-\Delta G^\circ = nE^\circ F$$

or $$E_{Ag/Ag^+}^\circ = \frac{-77 \times 10^3}{1 \times 96500} = -0.80\text{ V}$$

For the redox change on addition of Zn to AgCl saturated solution

$$\begin{array}{ll} Zn \longrightarrow Zn^{2+} + 2e & E_{OP}^\circ = +0.76\text{ V} \\ 2Ag^+ + 2e \longrightarrow 2Ag & E_{RP}^\circ = +0.80\text{ V} \\ \hline Zn + 2Ag^+ \longrightarrow Zn^{2+} + 2Ag & E_{cell}^\circ = 1.56\text{ V} \end{array}$$

Also, $$E_{cell} = E_{cell}^\circ + \frac{0.059}{2}\log\frac{[Ag^+]^2}{[Zn^{2+}]}$$

At equilibrium, $E_{cell} = 0$

$\therefore$ $$E_{cell}^\circ = \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Ag^+]^2}$$

$\therefore$ $$\log\frac{[Zn^{2+}]}{[Ag^+]^2} = \frac{1.56 \times 2}{0.059} = \mathbf{52.88}$$

and $$K_C = \frac{[Zn^{2+}]}{[Ag^+]^2} = 7.61 \times 10^{52}$$

Since, K_C is appreciably high, thus, nearly whole of Ag^+ is converted to Ag. Thus, mole of Ag formed = mole of Ag^+ in 100 mL solution $= 10^{-6}$. Note that Zn is in excess.

95. $Pt_{H_2}(g)|HCl(aq.)||AgCl(s)|Ag(s)$

(i)
$$\begin{array}{ll} \frac{1}{2}H_2 \longrightarrow H^+ + e & \text{(Anode)} \\ AgCl + e \longrightarrow Ag + Cl^- & \text{(Cathode)} \\ \hline \frac{1}{2}H_2 + AgCl \longrightarrow H^+ + Ag + Cl^- & \end{array}$$

(ii) $-\Delta G^\circ = nE^\circ F = 1 \times 0.23 \times 96500 = 22195\text{ J (at 15° C)}$

$-\Delta G^\circ = nE^\circ F = 1 \times 0.21 \times 96500 = 20265\text{ J (at 35° C)}$

Also, $$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$\therefore$
$$\begin{array}{c} -22195 = \Delta H^\circ - 288 \times \Delta S^\circ \\ -20265 = \Delta H^\circ - 308 \times \Delta S^\circ \\ +\qquad\quad -\qquad + \\ \hline \end{array}$$

$\therefore$ $$\Delta S^\circ = -96.50\text{ J}$$

Also, $$-22195 = \Delta H^\circ - 288 \times (-96.5) = -49987\text{ J}$$

$\therefore$ $$\Delta H^\circ = -49.987\text{ kJ}$$

(iii) Consider the following reaction at $AgCl(s)Cl^-/Ag$ electrodes

$$E_{cell} = 0\text{ at equilibrium}$$

Also, $$E_{RP_{Cl^-/AgCl/Ag}}^\circ + E_{OP_H}^\circ = 0.22\text{ at 25° C}$$

$\therefore$ $$E_{RP_{Cl^-/AgCl/Ag}}^\circ = 0.22\text{ at 25° C}$$

Also, $$E_{Cl^-/AgCl/Ag}^\circ = E_{Ag^+/Ag}^\circ + 0.059\log K_{sp_{AgCl}}$$

or $$0.22 = 0.80 + 0.059\log K_{sp\,AgCl}$$

$\therefore$ $$K_{sp_{AgCl}} = 1.47 \times 10^{-10}$$

$\therefore$ Solubility of AgCl $= \sqrt{K_{sp}} = \sqrt{1.47 \times 10^{-10}}$

$$\mathbf{= 1.21 \times 10^{-5}\ mol\ litre^{-1}}$$

96. When two half reactions are added to give an overall reaction, the no. of mole of electrons involved in each half reaction and overall reaction are necessarily the same, *e.g.*,

$$\begin{array}{ll} M_1 \longrightarrow M_1^{n_1+} + n_1e; & -\Delta G_1^\circ = n_1E_1^\circ F \\ M_2^{n_2+} + n_2e \longrightarrow M_2; & -\Delta G_2^\circ = n_2E_2^\circ F \\ \hline M_1 + M_2^{n_2+} \longrightarrow M_1^{n_1+} + M_2; & -\Delta G_3^\circ = n_3E_3^\circ F \\ \hline \end{array}$$

$\therefore$ $$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

$$n_3E_3^\circ F = n_1E_1^\circ F + n_2E_2^\circ F$$

or $$E_3^\circ = \frac{n_1E_1^\circ + n_2E_2^\circ}{n_3}$$

Since, $$n_1 = n_2 = n_3$$

$\therefore$ $$E_3^\circ = E_1^\circ + E_2^\circ$$

Also, when two half reactions are added to give a third reaction then $n_1 \neq n_2 \neq n_3$, *e.g.*,

$$\begin{array}{ll} M_1 \longrightarrow M_1^{n_1+} + n_1e & -\Delta G_1^\circ = n_1E_1^\circ F \\ M_1^{n_1+} \longrightarrow M_1^{n_2+} + (n_2 - n_1)e & -\Delta G_2^\circ = (n_2 - n_1)E_2^\circ F \\ \hline M_1 \longrightarrow M_1^{n_2+} + n_2e & -\Delta G_3^\circ = n_2E_3^\circ F \end{array}$$

$\therefore$ $$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

$$n_2E_3^\circ F = n_1E_1^\circ F + (n_2 - n_1)E_2^\circ F$$

$\therefore$ $$E_3^\circ = \frac{\mathbf{n_1E_1^\circ + n_2E_2^\circ - n_1E_2^\circ}}{\mathbf{n_2}}$$

97. $MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O;\ E_1^\circ = 1.51\,V$ ...(1)

$\therefore \quad \Delta G_1^\circ = -5 \times 1.51 \times F = -7.55\,F$

$MnO_2 + 4H^+ + 2e \longrightarrow Mn^{2+} + 2H_2O;\ E_2^\circ = 1.23\,V$ ...(2)

$\therefore \quad \Delta G_2^\circ = -2 \times 1.23 \times F = -2.46\,F$

Subtracting Eqs. (2) from (1),

$MnO_4^- + 4H^+ + 3e \longrightarrow 2H_2O + MnO_2;\quad E_3^\circ = ?$

or $\quad \Delta G_3^\circ = -n_3 E_3^\circ F$

$\therefore \quad \Delta G_3^\circ = \Delta G_1^\circ - \Delta G_2^\circ$

$-3E_3^\circ F = -7.55F + 2.46F$

$\therefore \quad E_3^\circ = \frac{-5.09}{-3} = \mathbf{1.70\ volt}$

98. Given,

$$Cu^{2+} + e \longrightarrow Cu^+;\quad E_1^\circ = 0.15\,V;\quad \Delta G_1^\circ \quad ...(1)$$
$$Cu^+ + e \longrightarrow Cu;\quad E_2^\circ = 0.5\,V;\quad \Delta G_2^\circ \quad ...(2)$$
$$Cu^{2+} + 2e \longrightarrow Cu;\quad E_3^\circ = ?;\quad \Delta G_3^\circ \quad ...(3)$$

For Eq. (1), $+\Delta G_1^\circ = -nE_1^\circ F = -1 \times 0.15 \times F = -0.15F$

For Eq. (2), $+\Delta G_2^\circ = -nE_2^\circ F = -1 \times 0.5 \times F = -0.5F$

$\therefore$ Adding $\quad \Delta G_1^\circ + \Delta G_2^\circ = \Delta G_3^\circ$

$-0.15F + (-0.5F) = \Delta G_3^\circ$

$\Delta G_3^\circ = -0.65F$

$\therefore \quad -nE_3^\circ F = -0.65F$

or $\quad E_3^\circ = \frac{-0.65F}{-2F} = 0.325\ \text{volt}$

$\therefore \quad X = \mathbf{+0.325\ volt}$

Now for disproportionation,

$$\begin{array}{ll} Cu^+ \longrightarrow Cu^{2+} + e; & E_{OP}^\circ \\ \underline{Cu^+ + e \longrightarrow Cu} & \underline{;\quad E_{RP}^\circ} \\ 2Cu^+ \longrightarrow Cu^{2+} + Cu & \end{array} \quad ...(4)$$

$\therefore \quad E_{cell}^\circ = E_{OP_{Cu^+/Cu^{2+}}}^\circ + E_{RP_{Cu^+/Cu}}^\circ$

$= -0.15 + 0.5 = \mathbf{+0.35\ V}$

Since, E° of Eq. (4) is +ve and thus the reaction is feasible. In other words disproportionation of Cu^+ takes place, *i.e.*, Cu^+ acts as reductant and oxidant both.

99.

$$Fe \longrightarrow Fe^{2+} + 2e;\quad -\Delta G_1^\circ = 2E_1^\circ F \quad ...(1)$$
$$Fe^{2+} \longrightarrow Fe^{3+} + e,\quad -\Delta G_2^\circ = E_2^\circ F \quad ...(2)$$
$$Fe \longrightarrow Fe^{3+} + 3e;\quad -\Delta G_3^\circ = 3E_3^\circ F \quad ...(3)$$

Subtracting Eqs. (1) from (3),

$$\begin{array}{ll} Fe \longrightarrow Fe^{3+} + 3e; & -\Delta G_3^\circ = 3E_3^\circ F \\ Fe \longrightarrow Fe^{2+} + 2e; & -\Delta G_1^\circ = 2E_1^\circ F \\ -\qquad\quad -\quad - & \quad + \qquad\quad - \\ \hline Fe^{2+} \longrightarrow Fe^{3+} + e, & -\Delta G_3^\circ + \Delta G_1^\circ = 3E_3^\circ F - 2E_1^\circ F \end{array}$$

...(4)

Comparing Eqs. (2) and (4),

$-\Delta G_2^\circ = -\Delta G_3^\circ + \Delta G_1^\circ = 3E_3^\circ F - 2E_1^\circ F$

$+E_2^\circ F = 3E_3^\circ F - 2E_1^\circ F$

$\therefore \quad E_3^\circ \frac{\mathbf{2E_1^\circ + E_2^\circ}}{\mathbf{3}}$ or $\mathbf{3E_3^\circ = 2E_1^\circ + E_2^\circ}$

100. During electrolysis some Zn^{2+} will discharge and some Cu^{2+} will pass in solution

Thus, $\quad \frac{w}{E} = \frac{0.48 \times 10 \times 60 \times 60}{96500} = 0.18$

or Mole of Cu^{2+} formed = Mole of Zn^{2+} deposited = 0.09

or m mole of Cu^{2+} formed = m mole of Zn^{2+} deposited = 90

$\therefore \quad m$ mole of Zn^{2+} left $= 100 \times 1 - 90 = 10$

m mole of Cu^{2+} left $= 100 \times 1 + 90 = 190$

Both are present in 100 mL solution of each

Now

$$E_{cell} = E_{OP_{Zn/Zn^{2+}}}^\circ + E_{RP_{Cu^{2+}/Cu}}^\circ + \frac{0.059}{2}\log_{10}\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$= 0.76 + 0.34 + \frac{0.059}{2}\log_{10}\frac{190}{10}$$

$E_{cell} = \mathbf{1.137\ V}$

101. Note that given cell will not work as electrochemical cell since $E_{OP_{Cu}}^\circ > E_{OP_{Ag}}^\circ$. The equation for electrochemical cell will be:

$$Cu \longrightarrow Cu^{2+} + 2e$$
$$2Ag^+ + 2e \longrightarrow 2Ag$$

Thus, emf of cell $Cu|Cu^{2+}||Ag^+|Ag$ will be

$$E_{cell} = E_{OP_{Cu}}^\circ + E_{RP_{Ag}}^\circ + \frac{0.059}{2}\log_{10}\frac{[Ag^+]^2}{[Cu^{2+}]}$$

$\because \quad [Ag^+] = 1M$ and $[Cu^{2+}] = 1M$

$\therefore \quad E_{cell} = E_{cell}^\circ + \frac{0.059}{2}\log_{10}\frac{1}{1}$

$E_{cell} = E_{cell}^\circ$ (where $E_{cell}^\circ = E_{OP_{Cu}}^\circ + E_{RP_{Ag}}^\circ$)

After the passage of 9.65 ampere for 1 hr, *i.e.*, 9.65 × 60 × 60 coulomb charge, during which the cell reaction is reversed thus, Cu^{2+} are discharged from solution and Ag metal passes to ionic state. The reaction during passage of current are:

$$Cu^{2+} + 2e \longrightarrow Cu$$
$$2Ag \longrightarrow 2Ag^+ + 2e$$

Ag^+ ions formed $= \frac{9.65 \times 60 \times 60}{96500}\,eq = 0.36\,eq = 0.36\,mol$

Cu^{2+} ions discharged $= \frac{9.65 \times 60 \times 60}{96500}\,eq$

$= 0.36\,eq = 0.18\,mol$

Thus, $\quad [Ag^+]_{left} = 1 + 0.36 = 1.36\,M$

$[Cu^{2+}]_{left} = 1 - 0.18 = 0.82\,M$

Thus, $\quad$ new cell is $Cu\left|\begin{array}{c} Cu^{2+} \\ 0.82\,M \end{array}\right|\left|\begin{array}{c} Ag^+ \\ 1.36\,M \end{array}\right| Ag$

Thus, $\quad E_{cell} = E_{cell}^\circ + \frac{0.059}{2}\log_{10}\frac{(1.36)^2}{(0.82)}$

$= E_{cell}^\circ + 0.010\ \text{volt}$

Thus, E_{cell} increases by **0.010 V**

102. $$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

$$\therefore \quad K_f = 1\times 10^{12} = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4} = \frac{1.0}{x(2.0)^4}$$

$$\therefore \quad x = 6.25\times 10^{-14}\text{ M}$$

Note that due to high value of K_f almost all of the Cu^{2+} ions are converted to $Cu(NH_3)_4^{2+}$ ion

Now

$$E_{cell} = E^\circ_{OP_{Zn/Zn^{2+}}} + E^\circ_{RP_{Cu^{2+}/Cu}} + \frac{0.059}{2}\log_{10}\frac{Cu^{2+}}{Zn^{2+}}$$

$$= 0.76 + 0.34 + \frac{0.059}{2}\log_{10}\left[\frac{6.25\times 10^{-14}}{1}\right]$$

$$E_{cell} = \mathbf{0.71\ V}$$

103. For I cell, half reactions are;

$$V^{2+} \longrightarrow V^{3+} + e$$

$$e + V^{4+} \longrightarrow V^{3+}$$

$$V^{2+} + V^{4+} \longrightarrow 2V^{3+} \quad \text{...(A)}$$

$$\therefore \quad E^\circ_{cell} = E^\circ_{V^{2+}/V^{3+}_{OP}} + E_{V^{4+}/V^{3+}_{RP}} \quad \text{...(1)}$$

For II cell, half reactions are;

$$V^{3+} \longrightarrow V^{4+} + e$$

$$Ag^+ + e \longrightarrow Ag(s)$$

$$V^{3+} + Ag^+ \longrightarrow V^{4+} + Ag(s) \quad \text{...(B)}$$

$$\therefore \quad E^\circ_{cell} = E^\circ_{V^{3+}/V^{4+}_{OP}} + E^\circ_{Ag^+/Ag_{RP}} \quad \text{...(2)}$$

$$\therefore \quad 0.439 = E^\circ_{V^{3+}/V^{4+}_{OP}} + 0.799$$

or $E^\circ_{V^{3+}/V^{4+}_{OP}} = -0.360\text{ V}$ or $E^\circ_{V^{4+}/V^{3+}_{RP}} = +0.360\text{ V}$

On substituting this value in Eq. (1),

$$E^\circ_{cell} = E_{V^{2+}/V^{3+}_{OP}} + 0.360$$

$$\because \quad E^\circ_{cell} = 0.616\text{ V}$$

$$\because \quad 0.616 = E_{V^{2+}/V^{3+}_{OP}} + 0.360$$

or $E^\circ_{V^{2+}/V^{3+}_{OP}} = \mathbf{0.256\ V}$ or $E_{V^{3+}/V^{2+}_{RP}} = \mathbf{-0.256}$

104. According to Gibbs-Helmholtz equation, heat of reaction ΔH, given as,

$$\Delta H = nF\left[T\left(\frac{\delta E}{\delta T}\right)_P - E\right]$$

$T = 273 + 25 = 298\text{ K}, n = 2, F = 96500\text{ C}, E = +0.03\text{ V}$

and $\left(\frac{\delta E}{\delta T}\right)_P = -1.4\times 10^{-4}\text{ V/K}$

$$\therefore \Delta H = 2\times 96500[298\times(-1.4\times 10^{-4}) - 0.03]$$

$$= -13842\text{ joule} = \mathbf{-13.842\ kJ\ mol^{-1}}$$

105. For $H_2(g) + 2AgCl(s) + 2H_2O(l) \longrightarrow 2Ag(s) + 2H_3O^+(aq.) + 2Cl^-(aq.)$

$$\Delta G^\circ_{Reaction} = G^\circ_{Products} - G^\circ_{Reactants}$$

$$= 2G^\circ_{Ag}(s) + 2G^\circ_{(H_3O^+ + Cl^-)} - G^\circ_{H_2} - 2G^\circ_{AgCl}(s) - 2G^\circ_{H_2O}$$

$$= 0 + 2\times(-368.4) - 0 - 2\times(-109.7) - 2\times(-237.2)$$

$$= -43.0\text{ kJ}$$

($\therefore$ G° of pure element $= 0$, *i.e.*, $G^\circ_{Ag} = 0$ and $G^\circ_{H_2} = 0$)

Now $\Delta G^\circ = -nE^\circ F$

$$-43\times 10^3 = -2\times E^\circ\times 96500$$

$$E^\circ = 0.2228\text{ volt}$$

Further $E = E^\circ + \frac{0.059}{2}\log_{10}\frac{[AgCl(s)]^2 P_{H_2}}{[Ag(s)]^2[H_3O^+]^2[Cl^-]^2}$

$\because$ [Solid] = 1

$$\therefore \quad E = E^\circ + \frac{0.059}{2}\log_{10}\frac{P_{H_2}}{[H_3O^+]^2[Cl^-]^2}$$

$$= 0.2228 + \frac{0.059}{2}\log_{10}\frac{1}{(0.01)^2(0.01)^2}$$

$$= \mathbf{0.458\ volt}$$

106. For given cell reaction,

$$\Delta G^\circ = -nE^\circ F$$

$$\therefore \quad \Delta G^\circ = -12\times 2.73\times 96500\text{ J}$$

$$= -3.1613\times 10^3\text{ kJ}$$

$$\begin{bmatrix} n = 12 \because 4Al^\circ \longrightarrow 4Al^{3+} + 12e \\ 3O_2^\circ + 12e \longrightarrow 6O^{2-} \end{bmatrix}$$

Now for given reaction,

$$\Delta G^\circ = 4\times G^\circ_f[Al(OH)_4]^- - 6\times G^\circ_f[H_2O] - 4\times G^\circ_f[OH^-]$$

(Also note that G°_f for elements is zero)

$$-3.1613\times 10^3 = 4\times G^\circ_f[Al(OH)_4]^- - 6\times(-237.2) - 4\times(-157)$$

$$\therefore \quad G^\circ_f[Al(OH)_4]^- = \mathbf{1303\ kJ\ mol^{-1}}$$

107. At L.H.S.:

From $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$[H^+] = C\times\alpha = C\sqrt{\left(\frac{K_a}{C}\right)} = \sqrt{(K_a\cdot C)}$$

$$= \sqrt{(1.8\times 10^{-5}\times 0.1)} = 1.342\times 10^{-3}\text{ mol litre}^{-1}$$

At R.H.S.: From $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$[OH^-] = C\times\alpha = C\sqrt{\left(\frac{K_b}{C}\right)}$$

$$= \sqrt{(K_b\cdot C)} = \sqrt{(1.8\times 10^{-5}\times 0.01)}$$

$$= 0.424\times 10^{-3}\text{ mol litre}^{-1}$$

$$\therefore \quad [H^+] = \frac{10^{-14}}{0.424\times 10^{-3}} = 2.359\times 10^{-11}\text{ mol litre}^{-1}$$

Note : See chapter 13 of ionic equilibria for dissociation of weak acids and weak bases.

Now for cell $\frac{1}{2}H_2 \longrightarrow H^+ + e$ At anode, *i.e.*, L.H.S.

$H^+ + e \longrightarrow \frac{1}{2}H_2$ At cathode, *i.e.*, R.H.S.

$$E_{cell} = E_{OP_{\mathrm{H/H^+}}} + E_{RP_{\mathrm{H^+/H}}}$$

$$= E^\circ_{OP_{\mathrm{H/H^+}}} - \frac{0.059}{1}\log_{10}\frac{[\mathrm{H^+}]_{\mathrm{L.H.S.}}}{[P_{\mathrm{H_2}}]^{1/2}} + E^\circ_{RP_{\mathrm{H^+/H}}} + \frac{0.059}{1}\log_{10}\frac{[\mathrm{H^+}]_{\mathrm{R.H.S.}}}{[P_{\mathrm{H_2}}]^{1/2}}$$

$$= \frac{0.059}{1}\log_{10}\frac{[\mathrm{H^+}]_{\mathrm{R.H.S.}}}{[\mathrm{H^+}]_{\mathrm{L.H.S.}}} \quad (\because P_{\mathrm{H_2}} = 1\,\text{atm on both sides})$$

$$= \frac{0.059}{1}\log_{10}\frac{2.359\times10^{-11}}{1.342\times10^{-3}} = \mathbf{-0.4575\ volt}$$

108. The cell is demonstrated as,

$$\mathrm{Pt\ H_2\ (1atm)\,|\,H}A_2\,||\,\mathrm{H}A_1\,|\mathrm{(H_2)(1atm)\ Pt}$$

At L.H.S. : $E_{\mathrm{H/H^+}} = E^\circ_{OP_{\mathrm{H/H^+}}} - \frac{0.059}{1}\log_{10}[\mathrm{H^+}]_2$

$\because$ $-\log \mathrm{H^+} = \mathrm{pH}$

$\therefore$ $E_{\mathrm{H/H^+}} = E^\circ_{OP_{\mathrm{H/H^+}}} + 0.059\,(\mathrm{pH})_2$

At R.H.S.: $E_{\mathrm{H^+/H}} = E^\circ_{RP_{\mathrm{H^+/H}}} + \frac{0.059}{1}\log_{10}[\mathrm{H^+}]_1$

$\therefore$ $E_{\mathrm{H^+/H}} = E^\circ_{RP_{\mathrm{H^+/H}}} - 0.059\,(\mathrm{pH})_1$

For Acid $\mathrm{H}A_1$, $\mathrm{H}A_1 \rightleftharpoons \mathrm{H^+} + A_1^-$

$$[\mathrm{H^+}] = C\cdot\alpha = \sqrt{K_a\cdot C}$$

$\therefore$ $(\mathrm{pH})_1 = \frac{1}{2}\mathrm{p}K_{a_1} - \frac{1}{2}\log_{10}C$

Similarly, $(\mathrm{pH})_2 = \frac{1}{2}\mathrm{p}K_{a_2} - \frac{1}{2}\log_{10}C$ $(\because C$ are same$)$

$\therefore$ $E_{cell} = E_{OP_{\mathrm{H/H^+}\ \text{for II}}} + E_{RP_{\mathrm{H^+/H}\ \text{for I}}}$

$$= 0.059\left[\frac{1}{2}\mathrm{p}K_{a_2} - \frac{1}{2}\mathrm{p}K_{a_1}\right]$$

$$= \frac{0.059}{2}[5-3] = \mathbf{+0.059\ V}$$

109. Use $\mathrm{Ag} \longrightarrow \mathrm{Ag^+} + e;$ $E^\circ_{OP} = -0.799\ \mathrm{V}$

$\underline{\mathrm{Ag(NH_3)_2^+} + e \longrightarrow \mathrm{Ag} + 2\mathrm{NH_3};}$ $E^\circ_{RP} = ?$

$\therefore$ $\mathrm{Ag(NH_3)_2^+} \rightleftharpoons \mathrm{Ag^+} + 2\mathrm{NH_3}$

and $E_{cell} = E^\circ_{cell} + \frac{0.059}{1}\log_{10}\frac{[\mathrm{Ag(NH_3)_2^+}]}{[\mathrm{Ag^+}][\mathrm{NH_3}]^2}$

Also, $E_{cell} = 0$

and $E^\circ_{cell} = E^\circ_{OP_{\mathrm{Ag/Ag^+}}} + E^\circ_{RP_{\mathrm{Ag(NH_3)_2^+/Ag}}}$

$\therefore$ $E^\circ_{cell} = \frac{0.059}{1}\log_{10}K_C$

$$= \frac{0.059}{1}\log_{10}6\times10^{-14} = -0.780\ \mathrm{V}$$

$\therefore$ $E^\circ_{\mathrm{Ag(NH_3)_2^+/Ag}} = -0.780 + 0.799 = \mathbf{+0.019\ V}$

110. Use $\mathrm{Co(CN)_6^{4-}} \longrightarrow \mathrm{Co(CN)_6^{3-}} + e,$ $E^\circ_{OP} = +0.83\,V$

$\underline{Co^{3+} + e \longrightarrow Co^{2+};\quad E^\circ_{RP} = 1.82\,V}$

$$\mathrm{Co(CN)_6^{4-}} + \mathrm{Co^{3+}} \rightleftharpoons \mathrm{Co^{2+}} + \mathrm{Co(CN)_6^{3-}}$$

and $E_{cell} = E^\circ_{cell} + \frac{0.059}{1}\log_{10}\frac{[\mathrm{Co^{3+}}][\mathrm{Co(CN)_6^{4-}}]}{[\mathrm{Co^{2+}}][\mathrm{Co(CN)_6^{3-}}]}$

or $E_{cell} = E^\circ_{cell} + \frac{0.059}{1}\log_{10}\frac{[\mathrm{Co^{3+}}][\mathrm{Co(CN)_6^{4-}}][\mathrm{CN^-}]^6}{[\mathrm{Co^{2+}}][\mathrm{Co(CN)_6^{3-}}][\mathrm{CN^-}]^6}$

Also, $6\mathrm{CN^-} + \mathrm{Co^{2+}} \rightleftharpoons \mathrm{Co(CN)_6^{4-}}$

and $K_{f_1} = \frac{[\mathrm{Co(CN)_6^{4-}}]}{[\mathrm{Co^{2+}}][\mathrm{CN^-}]^6}$

and $6\mathrm{CN^-} + \mathrm{Co^{3+}} \rightleftharpoons \mathrm{Co(CN)_6^{3-}}$

and $K_{f_2} = \frac{[\mathrm{Co(CN)_6^{3-}}]}{[\mathrm{Co^{3+}}][\mathrm{CN^-}]^6}$

$\therefore$ $E_{cell} = E^\circ_{cell} + \frac{0.059}{1}\log_{10}\frac{K_{f_1}}{K_{f_2}}$

$$0 = 0.83 + 1.82 + \frac{0.059}{1}\log_{10}\frac{10^{19}}{K_{f_2}}\ (\text{At equilibrium } E_{cell} = 0)$$

$\therefore$ $\frac{K_{f_2}}{10^{19}} = 8.23\times10^{44}$ $\therefore$ $K_{f_2} = \mathbf{8.23\times10^{63}}$

111. $\mathrm{Zn} \longrightarrow \mathrm{Zn^{2+}} + 2e$

$$\mathrm{Zn^{2+}} + 2e \longrightarrow \mathrm{Zn}$$

$\therefore$ $E_{cell} = E^\circ_{OP_{\mathrm{Zn}}} - \frac{0.059}{2}\log[\mathrm{Zn^{2+}}]_{\mathrm{L.H.S.}} + E^\circ_{RP_{\mathrm{Zn}}} + \frac{0.059}{2}\log[\mathrm{Zn^{2+}}]_{\mathrm{R.H.S.}}$

$$0.099 = \frac{0.059}{2}\log\frac{3.84\times10^{-4}}{[\mathrm{Zn^{2+}}]_{\mathrm{L.H.S.}}}$$

Also, $[\mathrm{Zn^{2+}}]_{\mathrm{L.H.S.}} = 1.69\times10^{-7}$

$$K_{\text{inst.}} = \frac{[\mathrm{Zn^{2+}}][\mathrm{CN^-}]^4}{[\mathrm{Zn(CN)_4}]^{2-}}$$

for $[\mathrm{Zn(CN)_4}]^{2-} \rightleftharpoons \mathrm{Zn^{2+}} + 4\mathrm{CN^-}$

$$= \frac{\mathbf{1.69\times10^{-7}\times(2.65\times10^{-3})^4}}{\mathbf{0.45}}$$

$$K_{\text{inst.}} = \mathbf{1.85\times10^{-17}}$$

112. $\mathrm{N^{3+}} \longrightarrow \mathrm{N^{5+}} + 2e;$ $E^\circ = -0.94\ \mathrm{V}$

$2\mathrm{N^{3+}} + 2e \longrightarrow 2\mathrm{N^{2+}};$ $E^\circ = 0.99\ \mathrm{V}$

or $3\mathrm{N^{3+}} \longrightarrow 2\mathrm{N^{2+}} + \mathrm{N^{5+}}$

$\therefore$ $E^\circ_{cell} = E^\circ_{OP_{\mathrm{HNO_2/NO_3^-}}} + E^\circ_{RP_{\mathrm{HNO_2/NO}}}$

$$E^\circ_{cell} = -0.94 + 0.99 = 0.05$$

Also, $E^\circ_{cell} = \frac{0.059}{2}\log K_c$

$$0.05 = \frac{0.059}{2}\log K_c$$

$\therefore$ $K_c = \mathbf{49.53}$

113. Given, $\mathrm{Au^{3+}}(aq.) + 3e \longrightarrow \mathrm{Au}(s);$

$E^\circ_{RP} = 1.42\ \mathrm{V}$ and $E^\circ_{OP} = -1.42\ \mathrm{V}$

$$\mathrm{H^+} + e \longrightarrow \frac{1}{2}\mathrm{H_2};$$

$E^\circ_{RP} = 0.0\ \mathrm{V}$ and $E^\circ_{OP} = 0$

More is $\overset{\circ}{E}_{OP}$ more is the tendency for oxidation, thus in case of above two half reactions.

$$\frac{3}{2}\mathrm{H_2} \longrightarrow 3\mathrm{H^+} + 3e$$

$$\mathrm{Au^{3+}} + 3e \longrightarrow \mathrm{Au}$$

$$\frac{3}{2}\mathrm{H_2} + \mathrm{Au^{3+}} \longrightarrow \mathrm{Au} + 3\mathrm{H^+}$$

$$E^\circ = \overset{\circ}{E}_{OP_\mathrm{H}} + \overset{\circ}{E}_{RP_\mathrm{Au}} = \mathbf{1.42\ V}$$

Thus H_2 will reduce Au^{3+} to Au ($\overset{\circ}{E}_{cell} = +$ ve) but HCl will not dissolve Au ($\overset{\circ}{E}_{cell} = -$ve for reverse reaction).

114. Cathode : $\mathrm{Hg_2Br_2}(s) + 2e \longrightarrow 2\mathrm{Hg}(l) + 2\mathrm{Br^-}(aq.)$

Anode : $2\mathrm{Ag}(s) + 2\mathrm{Br^-} \longrightarrow 2\mathrm{AgBr}(s) + 2e$

Cell reaction: $\mathrm{Hg_2Br_2}(s) + 2\mathrm{Ag}(s) \longrightarrow 2\mathrm{Hg}(l) + 2\mathrm{AgBr}(s)$

Also, $$\left(\frac{\partial E}{\partial T}\right)_P = \frac{0.070 - 0.066}{10} = 0.0004$$

$$\Delta G = -nFE = -2 \times 96500 \times 0.068$$
$$= \mathbf{-13124\ J = -13.124\ kJ}$$

$$\Delta H = -nF\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right]$$
$$= -2 \times 96500\,[0.068 - 298 \times 0.0004]$$
$$= \mathbf{9881.6\ J = 9.882\ kJ}$$

Also, $$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P = 2 \times 96500 \times 0.0004 = \mathbf{77.2\ J}$$

115. $$\frac{1}{2}\mathrm{H_2} \longrightarrow \mathrm{H^+} + e$$

$$\mathrm{H^+} + e \longrightarrow \frac{1}{2}\mathrm{H_2}$$

$$\therefore\ E_{cell} = E_{OP_{\mathrm{H_2/H^+}}} - \frac{0.059}{1}\log[\mathrm{H^+}] + \overset{\circ}{E}_{RP_{\mathrm{H^+/H_2}}} + \frac{0.059}{1}\log[\mathrm{H^+}]$$

$$-0.188 = 0 + 0 + \frac{0.059}{1}\log[\mathrm{H^+}]$$

$$\therefore\ [\mathrm{H^+}] = 6.51 \times 10^{-4}\ M$$

Now $$\mathrm{C_6H_4NH_3^+} + \mathrm{H_2O} \rightleftharpoons \mathrm{C_6H_5NH_2} + \mathrm{H_3O^+}$$

$$\therefore\ [\mathrm{H^+}] = c \cdot h \quad \text{or} \quad 6.51 \times 10^{-4} = \frac{1}{32} \times h$$

$$\therefore\ h = 2.08 \times 10^{-2}$$

Also, $$K_\mathrm{H} = ch^2$$

$$K_\mathrm{H} = \frac{1}{32} \times (2.08 \times 10^{-2})^2 = \mathbf{1.352 \times 10^{-5}}$$

116. The net reaction for given change will be

$$4\mathrm{SO_4^{2-}} + \mathrm{O_2} + 4\mathrm{H^+} \longrightarrow 2\mathrm{H_2O} + \mathrm{S_2O_8^{2-}}$$

$$\overset{\circ}{E}_{cell} = \overset{\circ}{E}_{OP_{\mathrm{SO_4^{2-}/S_2O_8^{2-}}}} + \overset{\circ}{E}_{RP_{\mathrm{O_2/H_2O}}}$$

$$\overset{\circ}{E}_{cell} = -2.01 + 1.23 = -0.78\ \mathrm{V}$$

Since, $\overset{\circ}{E}_{cell}$ is negative and thus oxygen will not oxidise SO_4^{2-} to $S_2O_8^{2-}$.

117. (a) More or +ve is the $\overset{\circ}{E}_{OP}$ more is the tendency for oxidation. Therefore, since, maximum $\overset{\circ}{E}_{OP}$ stands for :

$$\mathrm{Sn^{2+}} \longrightarrow \mathrm{Sn^{4+}} + 2e; \qquad \overset{\circ}{E}_{OP} = -0.1\ \mathrm{V}$$

∴ Strongest reductant: $\mathbf{Sn^{2+}}$

and Weakest oxidant: $\mathbf{Sn^{4+}}$

(b) More or +ve is $\overset{\circ}{E}_{RP}$, more is the tendency for reduction. Therefore, since maximum $\overset{\circ}{E}_{RP}$ stands for:

$$\mathrm{MnO_4^-} + 8\mathrm{H^+} + 5e \longrightarrow \mathrm{Mn^{2+}} + 4\mathrm{H_2O};$$
$$\overset{\circ}{E}_{RP} = +1.52\ \mathrm{V}$$

∴ Strongest oxidant: $\mathbf{MnO_4^-}$

and Weakest reductant: $\mathbf{Mn^{2+}}$

Note : Stronger is oxidant, weaker is its conjugate reductant and *vice-versa*.

(c) For (i)

$$\overset{\circ}{E}_{cell} = \overset{\circ}{E}_{OP_{\mathrm{Fe^{2+}/Fe^{3+}}}} + \overset{\circ}{E}_{RP_{\mathrm{Sn^{2+}/Sn^{3+}}}} = -0.77 + 0.1$$

∵ Fe^{2+} oxidises and Sn^{4+} reduces in change.

$$\overset{\circ}{E}_{cell} = -0.67\ \mathrm{V}$$

$\overset{\circ}{E}_{cell}$ is negative.

(i) Is non-spontaneous change.

For (ii) $$\overset{\circ}{E}_{cell} = \overset{\circ}{E}_{OP_{\mathrm{Fe^{2+}/Fe^{3+}}}} + \overset{\circ}{E}_{RP_{\mathrm{I_2/I^-}}}$$
$$= -0.77 + 0.54 = \mathbf{-0.23\ V}$$

(ii) Is non-spontaneous change.

For (iii) $$\overset{\circ}{E}_{cell} = \overset{\circ}{E}_{OP_{\mathrm{I^-/I_2}}} + \overset{\circ}{E}_{RP_{\mathrm{Sn^{4+}/Sn^{2+}}}}$$
$$= -0.54 + 0.1 = \mathbf{-0.44\ V}$$

(iii) Is non-spontaneous change.

For (iv) $$\overset{\circ}{E}_{cell} = \overset{\circ}{E}_{OP_{\mathrm{Sn^{2+}/Sn^{4+}}}} + \overset{\circ}{E}_{RP_{\mathrm{I_2/I^-}}}$$
$$= -0.1 + 0.54 = \mathbf{+0.44\ V}$$

(iv) Is spontaneous change.

118. Given,

For A $\quad A^{n+} + ne \longrightarrow A$	$\overset{\circ}{E}_{RP} = -0.76\ \mathrm{V}$
For B $\quad B^{n+} + ne \longrightarrow B$	$\overset{\circ}{E}_{RP} = +0.80\ \mathrm{V}$
We have,	
For H $\quad \mathrm{H^+} + e \longrightarrow \frac{1}{2}\mathrm{H_2}$	$\overset{\circ}{E}_{RP} = 0$

Now coupling A with H_2SO_4:

$$2A + n\mathrm{H_2SO_4} \longrightarrow A_2(\mathrm{SO_4})_n + n\mathrm{H_2}$$
$$\overset{\circ}{E}_{cell} = \overset{\circ}{E}_{OP_A} + \overset{\circ}{E}_{RP_H} = +0.76 + 0.0 = +0.76\ \mathrm{V}$$

Since, E° is +ve;

∴ Reaction $2A + nH_2SO_4 \longrightarrow A_2(SO_4)_n + nH_2$ is spontaneous, *i.e.*, ***A* will liberate H_2 from H_2SO_4.**

Now coupling B with H_2SO_4:

$$2B + n\mathrm{H_2SO_4} \longrightarrow B_2(\mathrm{SO_4})_n + n\mathrm{H_2}$$
$$\overset{\circ}{E}_{cell} = \overset{\circ}{E}_{OP_B} + \overset{\circ}{E}_{RP_\mathrm{H}} = -0.80 + 0 = -0.80$$

Since, E° is −ve;

∴ Reaction $2B + nH_2SO_4 \longrightarrow B_2(SO_4)_n + nH_2$ will not occur, *i.e.*, ***B* will not liberate H_2 from H_2SO_4.**

• SINGLE INTEGER ANSWER PROBLEMS •

1. The quantity of charge (in Faraday) required to electrolyse 54 g H_2O is ......
2. The quantity of charge (in Faraday) required to reduce 96 g Mg from molten solution of $MgCl_2$.
3. The quantity of charge (in Faraday) required to liberate 33.6 litre Cl_2 from molten NaCl.
4. On electrolysing the solution of $CH_3COONa(aq.)$ the volume ratio of gases formed at anode and cathode is ......
5. On electrolysing the solution of sodium butyrate the mole ratio of gases formed at anode and cathode is ......
6. In rusting of iron, iron is oxidised and O_2 is reduced. The no. of electrons used during reduction of O_2 are ......
7. $E°$ (in volt) of cell $A + B^{+n} \longrightarrow A^{+n} + B$ if $E^{\circ}_{A^{n+}/A} = -2.5$ V and $E_{B^{n+}/B} = +0.5$ V.
8. 9650 charge is passed through an aqueous solution of metal nitrate $M(NO_3)_x$ to obtain 2 g metal (atomic mass 80). The valence of metal is ......
9. If $-\Delta G°$ is zero for a cell, the equilibrium constant for cell reaction is ......
10. If E_1°, E_2° and E_3° are standard oxidation potentials for $Fe|Fe^{2+}$, $Fe^{2+}|Fe^{3+}$ and $Fe|Fe^{3+}$, then $E_3^{\circ} = \dfrac{E_2^{\circ} + 2E_1^{\circ}}{n}$. The value of n is ......
11. The no. of cells which may be constructed with different E^0_{cell} values for the reaction : $Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+}$.
12. The concentration (in molarity) of $Ni(NO_3)_2$ left after passing 965 ampere current for one second through 2 M $Ni(NO_3)_2$ solution using Ni electrode.
13. The equivalent of metal discharged when 482.5 ampere is passed through its aqueous salt solution for 800 seconds.
14. $E°$ for a cell having 2 electrons involved in redox change is 0.2655 V. The equilibrium constant for the redox change is 10^a. The value of a is ......
15. The standard oxidation potential of Ni/Ni^{2+} $(Ni^{2+} = 1M)$ electrode is 0.236 V. If this is combined with a hydrogen electrode ($P_{H_2} = 1$ atm) in acid solution, at what pH of the solution will the measured e.m.f. be zero at 25°C?
16. How much of the following element will not discharge at cathode during electrolysis of their salts in aqueous medium Al, Na, Ba, Cu, Ag, Ni, Cr?
17. Number of Faraday required to show the conversion of one mole of $Fe_2(SO_4)_3$ to $FeSO_4$.
18. The potential for the reaction : $\underset{1\text{ atm}}{O_2(g)_2} + 4H^+ + 4e \longrightarrow 2H_2O$ is 1.23 V in 0.1 N strong acid solution. If potential measured in an aqueous solution is 0.994 V, the pH of solution is....
19. K_{sp} of $Cu(OH)_2$ is 1×10^{-19}. If reduction potential of Cu^{2+}/Cu couple is 0.1335 V in a solution and $E°$ for Cu^{2+}/Cu is 0.34V, the pH of solution is....
20. A solution of metal salt MA_n was electrolysed with a current of 9.65 ampere for 100 minutes. The deposition of metal was 18g at cathode. If the atomic mass of metal is 120, the value of n is.....
21. Current is passed through a cathode where the reaction is :

    $5e + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$

    All the permanganate ions present in 100 mL has been reduced after a current of 15 A is passed for 96.5 sec. The original millimoles of $KMnO_4$ in 100 mL solution were....
22. A current of 4.825 amperes is passed through Hg_2Cl_2 solution (Atomic mass of $Hg_2Cl_2 = 471$) for 1000 second to reduce it completely into Hg. The total mass of Hg deposited in g is....
23. An impure silver anode of 20 g and 50.8% purity made anode in refining of silver by electrolytic method. If a current of 193 ampere is passed for 10 sec, the mass of pure Ag (atomic mass 108) left at anode is....
24. The mole ratio of gases evolved at cathode and anode during electrolysis of H_2SO_4 using Pt electrodes is....
25. 3 ampere current was passed through an aqueous solution of an unknown salt AX_n for an hour. 2.977 g of A was deposited at cathode. If the atomic mass of A is 106.4, what is the value of n?
26. A cell was prepared by using of aM $ZnSO_4$ and bM $CuSO_4$. Another cell was prepared with aM $ZnSO_4$ and 0.5 M $CuSO_4$ and this time emf of this cell was lower than 0.03V than the previous one. The value of b is....
27. The standard oxidation potential of Ni/Ni^{2+} electrode is 0.236 V. If this is connected with a hydrogen electrode in acid solution, at what pH of the solution will the measured emf be zero at 25°C. Assume $[Ni^{2+}] = 1M$ and $P_{H_2} = 1$ atm
28. For a redox cell Hg (l) |Solution A| |Solution B| Hgl. The solution A contains 0.263g/ litre mercury (I) nitrate and solution B contains 2.63 g/litre mercury (I) nitrate. If the measured emf is 0.0289 V at 18°C, what is the value of n?
29. How many faraday of charge is required to completely oxidise one mole of $Fe_2(C_2O_4)_3$?

30. E_{RP} for $M^{(x+n)+} + ne \longrightarrow M^{x+}$ are 0.115 V and 0.101 V respectively, when percentage of reduced form is 25 and 50 respectively. What is the value of n ?

31. Total charge (in coulomb) required for the oxidation of $\frac{1}{2}$ mole of Mn_3O_4 into MnO_4^{2-}.

32. A molten salt of $InCl_x$ on electrolysis using 3.20 A current for a period of 40 minute leads to the formation of 3.05 g In. If atomic mass of In is 114.8, the value of x is ....

33. A cell having two H-electrodes. The negative electrode present in acid solutions is in contact with H^+ ion having pH = 6. What should be the pH of other electrode so that cell may deliver an emf of 0.118 V at 25°C.

34. A source of light of 100 V will produce 6 kJ energy if 10 ampere current is passed for t sec. The value of t is ....

35. 4 M solution of $AgNO_3$ is electrolysed using Ag electrode. A current of 3 ampere is passed for 9.65×10^3 sec. The molarity of solution after electrolysis is ....

36. 4 M $NiSO_4$ solution is electrolysed by passing 3 ampere current for 9.65×10^3 sec using Pt electrodes. The equivalent of gas formed at anode are ....

37. An electrolysis of oxytungsten complex ion using 1.10 A for 40 minute produces 0.838 g tungsten. If atomic mass of tungsten is 184, the charge on tungsten in complex is ....

38. The charge required to deposites all Al from the electrolysis of 1 mol molten Al_2O_3.

39. The oxidation potential of a hydrogen electrode is 0.531 V. If $P_{H_2} = 1$ atm, the pH of solution will be ....

40. The emf of cell

$$\text{Pt} \mid Q, H_2 \mid Q, H^+ \parallel 1\,\text{M HCl} \mid Hg_2Cl_2(s) \mid Hg(l)\ \text{Pt}$$

is –0.065 V. If E^0_{RP} of Quinhydrone electrode and standard calomel electrode are 0.699 and 0.280 V respectively, the pH of left hand compartment is ....

41. A current of 2 A is passed for 5 hour through a molten metal salt, deposits 22.2 g of metal having atomic mass 177. The oxidation state of metal in salt is ....

ANSWERS

1. Six	**2.** Eight	**3.** Three	**4.** Three	**5.** Two	**6.** Four	**7.** Three	**8.** Four	**9.** One	**10.** Three	**11.** Three	**12.** Two
13. Four	**14.** Nine	**15.** Four	**16.** Three	**17.** Two	**18.** Five	**19.** Eight	**20.** Four	**21.** Three	**22.** Five	**23.** Eight	**24.** Two
25. Four	**26.** Five	**27.** Four	**28.** Two	**29.** Six	**30.** Two	**31.** Five	**32.** Three	**33.** Four	**34.** Six	**35.** Four	**36.** Three
37. Six	**38.** Six	**39.** Nine	**40.** Six	**41.** Three							

OBJECTIVE PROBLEMS (One Answer Correct)

1. $E°$ for $Cr^{3+} + 3e \longrightarrow Cr$ and $Cr^{3+} + e \longrightarrow Cr^{2+}$ are -0.74 V and -0.40 V respectively. $E°$ for $Cr^{2+} + 2e \longrightarrow Cr$ is :

−0.74
+0.6

(a) -0.91 V (b) $+0.91$ V
(c) -1.14 V (d) $+0.34$ V

2. A cell is to be constructed to show a redox change : $Cr + 2Cr^{3+} \rightleftharpoons 3Cr^{2+}$. The number of cells with different $E°$ and 'n' but same value of $\Delta G°$ can be made: (Given, $E^{\circ}_{Cr^{3+}/Cr^{2+}} = -0.40$ V, $E^{\circ}_{Cr^{3+}/Cr} = -0.74$ V and $E^{\circ}_{Cr^{2+}/Cr} = -0.91$ V)

(a) 1 (b) 2
(c) 3 (d) 4

3. The solubility product of $Pb_3(AsO_4)_2$ is 4.1×10^{-36}. The $E°$ for the reaction :

$$Pb_3(AsO_4)_{2(s)} + 6e \rightleftharpoons 3Pbs_{(s)} + 2AsO_4^{2-} \text{ if}$$

$E^{\circ}_{Pb^{2+}/Pb} = -0.13$ V

(a) $+0.478$ V (b) -0.13 V
(c) -0.478 V (d) $+0.13$ V

4. Calculate the $E°$ for the reaction $ZnY^{2-} + 2e \rightleftharpoons Zn_{(s)} + Y^{4-}$, where Y^{4-} is the completely deprotonated anion of EDTA. The formation constant for ZnY^{2-} is : 3.2×10^{16} and $E°$ for $Zn \longrightarrow Zn^{2+} + 2e$ is 0.76 V

(a) -1.25 V (b) 0.48 V
(c) $+0.68$ V (d) -0.27 V

5. If $Fe^{3+} + Y^{4-} \rightleftharpoons FeY^{-}$; $K_f = 1.3 \times 10^{25}$

$Fe^{2+} + Y^{4-} \rightleftharpoons FeY^{2-}$; $K_f = 2.1 \times 10^{14}$

and $Fe^{3+} + e \longrightarrow Fe^{2+}$; $E° = +0.77$ V

The $E°$ for $FeY^{-} + e^{-} \longrightarrow FeY^{2-}$

(a) 0.13 V (b) -0.636 V
(c) $+0.636$ V (d) 1.41 V

6. A constant current was passed through a solution of $AuCl_4^-$ ion between gold electrodes. After a period of 10.0 minute the increase in mass of cathode was 1.314g. The total charged passed through solution is : (atomic mass of $AuCl_4^- = 339$)

(a) 1.16×10^{-2} F (b) 3.5×10^{-2} F
(c) 2×10^{-2} F (d) 4×10^{-3} F

7. Efficiency of a fuel cell is 80% and the standard heat of reaction is -300 kJ. The reaction involves two electrons in redox change. The $E°$ for the cell is :

(a) 1.24 V (b) 2.48 V
(c) 0 V (d) 0.62 V

8. The E_{cell} for a given cell is 1.2346 and 1.2340 V at 300 and 310 K respectively. Calculate the change in entropy during the cell reaction if the redox change involves three electrons:

(a) $-17.37\ JK^{-1}$ (b) $+17.37\ JK^{-1}$
(c) $173.7\ JK^{-1}$ (d) $5.79\ JK^{-1}$

9. A current of 3 ampere was passed for 1 hour through an electrolyte solution of A_xB_y in water. If 2.977 g of A (atomic mass 106.4) was deposited at cathode and B was a monovalent ion, the formula of electrolyte was :

(a) AB_2 (b) AB
(c) AB_3 (d) AB_4

10. The $E°$ for Cu^{2+}/Cu^{+}; Cu^{+}/Cu, Cu^{2+}/Cu are 0.15 V, 0.50 V and 0.325 V respectively. The redox cell showing redox reaction $2Cu^{+} \longrightarrow Cu^{2+} + Cu$ is made. The $E°$ of this cell reaction and $\Delta G°$ may be :

(a) $E° = 0.175$ V or $E° = 0.350$ V
(b) $n = 2$ or 1 respectively
(c) $\Delta G° = -33.775$ kJ
(d) all of the above

11. Total charge required to convert three mole of Mn_3O_4 to MnO_4^- in presence of alkaline medium :

(a) 10 F (b) 20 F
(c) 30 F (d) 40 F

12. A current of 965 ampere is passed for 1 sec through 1 litre solution of 0.02 N $NiSO_4$ using Ni electrodes. What is the new concentration of $NiSO_4$?

(a) 0.01 N (b) 0.01 M
(c) 0.002 M (d) 0.02 M

13. For the given cell $Pt_{D_2/D^+} || H^+ | Pt_{H_2}$ if $E^{\circ}_{D_2/D^+} = 0.003$ V, what will be ratio of D^+ and H^+ at 25°C when the reaction : $D_2 + 2H^+ \longrightarrow 2D^+ + H_2$ attains equilibrium :

(a) 1.34 (b) 1.24
(c) 1.124 (d) 1.45

14. What is E°_{RP} for the reaction : $Cu^{2+} + 2e \longrightarrow Cu$ in the half cell $Pt_{S^{2-}/CuS/Cu}$ if $E^{\circ}_{Cu^{2+}/Cu}$ is 0.34 V and K_{sp} of $CuS = 10^{-35}$?

(a) 0.34 V (b) -0.6925 V
(c) $+0.6925$ V (d) -0.66 V

15. The combustion of butane in O_2 at 1 bar and 298 K shows a decrease in free energy equal to 2.75×10^3 kJ mol^{-1} in a fuel cell. K and $E°$ of fuel cell are :

(a) 9.55×10^{482}, 1.096 V (b) 9.55, 1.096 V
(c) 1.023×10^{966}, 2.85 V (d) 5.5×10^{484}, 0.55 V

16. A half cell reaction : $Ag_2S_{(s)} + 2e \longrightarrow 2Ag_{(s)} + S^{2-}$ is carried out in a half cell $Pt_{Ag_2S/Ag,\ \underset{0.1\,M}{H_2S}}$, at $[H^+] = 10^{-3}$.

The emf of a half cell is :

[if $E^{\circ}_{Ag^+/Ag} = 0.80\ V$, $K_{a\,H_2S} = 10^{-21}$ and K_{sp} of $Ag_2S = 10^{-49}$]

(a) -0.1735 V (b) -0.19 V
(c) $+0.1735$ (d) $+0.19$ V

17. Which one is not correct if electrolysis of $CH_3COONa\ (aq.)$ is made using Pt electrodes ?

(a) pH of solution increases
(b) Molar ratio of gases at anode and cathode is 3 : 1
(c) $[CH_3COO^-]$ in solution decreases
(d) The molar ratio of gases at anode and cathode is 2 : 1

18. The calomel electrode and Quinhydrone electrodes are reversible with respect to which ions respectively :

(a) Cl^-, H^+ (b) H^+, Cl^-
(c) Hg_2^{2+}, OH^- (d) Hg_2^{2+}, OH^+

19. EMF of Ni-Cad battery is dependent of :

(a) $Cd\ (OH)_2$ (b) $Ni\ (OH)_2$
(c) OH^- (d) none of these

20. The electrode with reaction :

$$Cr_2O_{7\,(aq.)}^{2-} + 14H^+_{(aq.)} + 6e \longrightarrow 2Cr^{3+}_{(aq.)} + 7H_2O;$$

can be represented as :

(a) $Pt \mid H^+_{(aq.)}, Cr_2O^{2-}_{7\,(aq.)}$
(b) $Pt \mid H^+_{(aq.)}, Cr_2O^{2-}_{7\,(aq.)}, Cr^{3+}_{(aq.)}$
(c) $Pt_{H_2} \mid H^+_{(aq.)}, Cr_2O_7^{2-}$
(d) $Pt_{H_2} \mid H^+_{(aq.)}, Cr_2O^{2-}_{7\,(aq.)}, Cr^{3+}_{(aq.)}$

21. For a given reaction : $M^{(X+n)} + ne \longrightarrow M^{X+}, E^{\circ}_{RP}$ is known along with M^{X+n} and M^{X+} ion concentrations, then:

(a) n can be evaluated
(b) X can be evaluated
(c) $(X+n)$ can be evaluated
(d) $n, X, (X+n)$ can be evaluated

22. A dilute aqueous solution of Na_2SO_4 is electrolyzed using platinum electrodes. The products at the anode and cathode are :

(a) O_2, H_2 (b) $S_2O_8^{2-}$, Na
(c) O_2, Na (d) $S_2O_8^{2-}, H_2$

23. A standard hydrogen electrode has zero electrode potential because :

(a) hydrogen is easiest to oxidise
(b) this electrode potential is assumed to be zero
(c) hydrogen atom has only one electron
(d) hydrogen is the lightest element

24. The standard reduction potentials of Cu^{2+}/Cu and Cu^{2+}/Cu^+ are 0.339 V and 0.153 V respectively. The standard electrode potential of Cu^+/Cu half cell is :

(a) 0.525 V (b) 0.827 V
(c) 0.184 V (d) 0.490 V

25. The standard reduction potential values of three metalic cations of X, Y and Z are 0.52, -3.03 and -1.18 V respectively. The order of reducing power of the corresponding metals is:

(a) $Y > Z > X$ (b) $X > Y > Z$
(c) $Z > Y > X$ (d) $Z > X > Y$

26. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 MY^- and 1 MZ^- at 25°C. If the reduction potential of $Z > Y > X$, then :

(a) Y will oxidise X and not Z
(b) Y will oxidise Z and not X
(c) Y will oxidise both X and Z
(d) Y will reduce both X and Z

27. Select the incorrect statement :

(a) The electrolysis of molten CaH_2 liberates H_2 at cathode.
(b) During discharge of lead storage battery, sulphuric acid is consumed.
(c) Sulphur acts as polymerising agent in vulcanisation of rubber.
(d) Galvanisation of iron denotes coating with Zn.

28. Select the correct statement :

(a) Faraday represents 96500 coulomb per sec.
(b) Coulomb represents one ampere for 1/2 sec.
(c) Coulomb represents 1/2 ampere for 1 sec.
(d) Coulomb represents charge of one mole electron.

29. E^0_{RP} for the reaction,

$$\underset{1M}{TeO_3^{2-}}\,(aq) + 3H_2O\,(l) + 4e \longrightarrow Te\,(s) + 6OH^-\,(aq)$$

is -0.57 V. Calculate the potential of pH = 12.

(a) -0.17 V (b) -0.21 V
(c) -0.39 V (d) -0.747 V

30. Calculate E_{cell} for $Cr \mid \underset{0.04M}{Cr^{3+}} \parallel \underset{1M}{Cr^{3+}} \mid Cr$:

(a) 0.028 V (b) 0.083 V
(c) 0 V (d) 0.125 V

31. Given that K_{sp} of $CuS = 10^{-35}$ and $E^0_{Cu/Cu^{2+}} = -034\ V$. The standard oxidation potential of $Cu \mid CuS \mid S^{2-}$ half cell is ....

(a) 1.0 V (b) 0.693 V
(c) -0.690 V (d) -1.0 V

32. The temperature coefficient of a given cell, $\left(\frac{\partial E}{\partial T}\right)_P$ is $1.5 \times 10^{-4}\ V\,K^{-1}$ at 300 K. The change in entropy of cell during the course of reaction,

$$Pb(s) + HgCl_2(aq) \longrightarrow PbCl_2(aq) + Hg(l)$$

(a) 28.95 J/K (b) 14.47 J/K
(c) 57.9 J/K (d) 21.70 J/K

33. If $E^0_{ClO_3^-/ClO_4^-} = -0.36$ V and $E^0_{ClO_3^-/ClO_2^-} = 0.33$ V at 300 K. The equilibrium concentration of perchlorate ion (ClO_4^-) which was initially 1.0 M in ClO_3^- when the reaction starts to attain the equilibrium,

$$2ClO_3^- \rightleftharpoons ClO_2^- + ClO_4^-$$

(a) 0.0236 M (b) 0.0190 M
(c) 0.123 M (d) 0.40 M

34. The reduction of NO_3^- occurs as

$$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O;\ E° = 0.96\text{ V}$$

The electrons are provided by Cd till that the solution originally having 0.1 M NO_3^- and 0.4 M H^+ shows that 80% of NO_3^- ions are converted to NO showing 1 bar pressure. The reduction potential of remaining solution.

(a) 0.84 V (b) 1.36 V
(c) 1.08 V (d) 1.56 V

35. 108 g solution of $AgNO_3$ is electrolysed using Pt electrodes by passing a charge of 0.1 F. The mass of resultant solution left is :

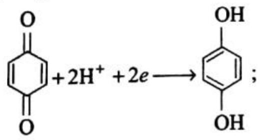
(a) 98 g (b) 107.2 g
(c) 11.6 g (d) 96.4 g

36. On the basis of reaction, $4Al + 3O_2 \longrightarrow 2Al_2O_3$; $\Delta G = -827$ kJ mol^{-1} of O_2 the minimum emf required to carry out an electrolysis of Al_2O_3 :

(a) 8.5 V (b) 2.14 V
(c) 2.83 V (d) 1.42 V

37. A Quinhydrone electrode in contact of H^+ ion is coupled with standard calomel electrode. The $E°$ of both electrodes are given as :

$Pt \mid Q, QH_2 \mid H^+ \parallel 1M KCl \mid Hg_2Cl_2(s) \mid Hg(l) \mid Pt$



$$E^0_{Q|QH_2|H^+|Pt} = +0.699\text{ V}$$

$$\frac{1}{2}Hg_2Cl_2(s) + e \rightarrow Hg(l) + Cl^-;$$

$$E^0_{Cl^-|Hg_2Cl_2|Hg} = +0.280\text{ V}$$

If emf of cell so obtained is – 0.124, then pH is :

(a) 5 (b) 6
(c) 7 (d) 8

38. The standard reduction potentials at 298 K for the following half reactions are given against each

$$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s) - 0.762$$

$$Cr^{+3}(aq) + 2e \rightleftharpoons Cr(s) - 0.740$$

$$2H^+(aq) + 2e \rightleftharpoons H_2(g)\ 0.000$$

$$Fe^{3+}(aq) + 2e \rightleftharpoons Fe^{2+}(aq)\ 0.770$$

which is the strongst reducing agent?

(a) Zn (s) (b) Cr (s)
(c) $H_2(g)$ (d) $Fe^{2+}(aq)$

39. Faraday's laws of electrolysis are related to the :

(a) atomic number of the reactants
(b) atomic number of the anion
(c) equivalent mass of the electrolyte
(d) speed of the cation

40. A solution containing one mole per litre of each $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$ is being electrolysed by using inert electrode. The values of standard electrode potential in volts reduction potential are :

$Ag \mid Ag^+ = +0.80$, $2Hg \mid Hg_2^{++} = -0.79$
$Cu \mid Cu^{++} = +0.34$, $Mg \mid Mg^{++} = -2.37$

With increasing voltage, the sequence of deposition of metals on the cathode will be :

(a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag
(c) Ag, Hg, Cu (d) Cu, Hg, Ag

41. The electric charge for electrode deposition of one gram equivalent of a substance is :

(a) one ampere per second
(b) 96.500 coloumbs per second
(c) one ampere for one hour
(d) charge on one mole of electrons

42. The reaction,

$$\frac{1}{2}H_2(g) + AgCl(s) \longrightarrow H^+(aq) + Cl^-(aq) + Ag(s)$$

occurs in the galvanic cell :

(a) $Ag \mid AgCl(s) \mid KCl\,(soln.) \mid AgNO_3\,(soln.) \mid Ag$
(b) $Pt \mid H_2(g) \mid HCl\,(soln.) \mid AgNO_3\,(soln.) \mid Ag$
(c) $Pt \mid H_2(g) \mid HCl(soln.) \mid AgCl(s) \mid Ag$
(d) $Pt \mid H_2(g) \mid KCl(soln.) \mid AgCl(s) \mid Ag$

43. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively :

(a) H_2, O_2 (b) O_2, H_2
(c) O_2, Na (d) O_2, SO_2

44. When a lead storage battery is discharged :

(a) SO_2 is evolved (b) Lead is formed
(c) $PbSO_4$ is consumed (d) H_2SO_4 is consumed

45. The standard oxidation potentials, $E°$, for the half reactions are as follows :

$$Zn \longrightarrow Zn^{2+} + 2e^-;\ E° = +0.76\text{ V}$$

$$Fe \longrightarrow Fe^{2+} + 2e^-;\ E° = +0.41\text{ V}$$

The EMF for the cell reaction,

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

(a) – 0.35 V (b) + 0.35 V
(c) + 1.17 V (d) – 1.17 V

46. If $E^{\circ}_{Cu^{2+}|Cu} = 0.34$ V and $E^{\circ}_{Cu^{2+}|Cu^{+}} = 0.15$ V than the value for disproportionation for Cu^+ is :

(a) -0.19 V
(b) -0.38 V
(c) 0.94 V
(d) 0.38 V

47. For the electrochemical cell, $M \mid M^+ \parallel X^- \mid X$ $E^{\circ}_{(M^+/M)} = 0.44$ V and $E^{\circ}_{(X/X^-)} = 0.33$ V. From this data one can deduce that : **(IIT 2000)**

(a) $M + X \longrightarrow M^+ + X^-$ is the spontaneous reaction
(b) $M^+ + X^- \longrightarrow M + X$ is the spontaneous reaction
(c) $E_{cell} = 0.77$ V
(d) $E_{cell} = -0.77$ V

48. The correct relationship between Gibb's energy change in a reaction and the corresponding equilibrium constant K_c is :

(a) $\Delta G^{\circ} = RT \ln K_c$
(b) $-\Delta G^{\circ} = RT \ln K_c$
(c) $\Delta G = RT \ln K_c$
(b) $-\Delta G = RT \ln K_c$

49. Saturated solution of KNO_3 is used to make salt bridge because : **(IIT 2001)**

(a) velocity of K^+ is greater than that of NO_3^-
(b) velocity of NO_3^- is greater than that of K^+
(c) velocity of both K^+ and NO_3^- are nearly the same
(d) KNO_3 is highly soluble in water

50. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is : **(IIT 2001)**

(a) LiCl > NaCl > KCl
(b) KCl > NaCl > LiCl
(c) NaCl > KCl > LiCl
(d) LiCl > KCl > NaCl

51. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below :

$$MnO^-_{4(aq.)} + 8H^+_{(aq.)} + 5e \longrightarrow Mn^{2+}_{(aq.)} + 4H_2O_{(l)};$$

$E^{\circ} = 1.51$ V

$$Cr_2O_7^{2-}{}_{(aq.)} + 14H^+_{(aq.)} + 6e \longrightarrow 2Cr^{3+}_{(aq.)} + 7H_2O_{(l)};$$

$E^{\circ} = 1.38$ V

$$Fe^{3+}_{(aq.)} + e^- \longrightarrow Fe^{2+}_{(aq.)}; E^{\circ} = 0.77 \text{ V}$$

$$Cl_{2(g)} + 2e^- \longrightarrow 2Cl^-_{(aq.)}; E^{\circ} = 1.40 \text{ V}$$

Identify the only incorrect statement regarding the quantitative estimation of aqueous $Fe(NO_3)_2$: (IIT 2002)

(a) MnO_4^- can be used in aqueous HCl
(b) $Cr_2O_7^{2-}$ can be used in aqueous HCl
(c) MnO_4^- can be used in aqueous H_2SO_4
(d) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

52. In the electrolytic cell, flow of electrons is from : **(IIT 2003)**

(a) cathode to anode in solution
(b) anode to cathode through external supply
(c) cathode to anode through internal supply
(d) anode to cathode through internal supply

53. The emf of the cell $Zn \mid \underset{(0.01\,M)}{Zn^{2+}} \parallel \underset{(0.001\,M)}{Fe^{2+}} \mid Fe$ at 298 K is 0.2905, then the value of equilibrium constant for the cell reaction is : **(IIT 2004)**

(a) $e^{0.32/0.0295}$
(b) $10^{0.32/0.0295}$
(c) $10^{0.26/0.0295}$
(d) $10^{0.32/0.0591}$

54. The rusting of iron takes place as follows :

$$2H^+ + 2e + 1/2O_2 \longrightarrow H_2O_{(l)}; E^{\circ} = +1.23 \text{ V}$$

$$Fe^{2+} + 2e \longrightarrow Fe_{(s)}; \quad E^{\circ} = -0.44 \text{ V}$$

The ΔG° for the net process is : **(IIT 2005)**

(a) -322 kJ mol^{-1}
(b) -161 kJ mol^{-1}
(c) -152 kJ mol^{-1}
(d) -76 kJ mol^{-1}

55. Electrolysis of dilute NaCl solution was carried out by passing 10 mA current. The time required to liberate 0.01 mol. of H_2 gas at the cathode is : **(IIT 2008)**

(a) 9.65×10^4 sec
(b) 19.3×10^4 sec
(c) 28.95×10^4 sec
(d) 38.6×10^4 sec

56. Consider the following cell reaction :

$$2Fe(s) + O_2(g) + 4H^+ \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

$E^{\circ} = 1.67$V

At $[Fe^{2+}] = 10^{3-}$ M, $P(O_2) = 0.1$ atm and pH = 3, the cell potential at 25°C is : **(IIT 2011)**

(a) 1.47 V
(b) 1.77 V
(c) 1.87 V
(d) 1.57 V

57. Given

$$E^{\circ}_{Cr^{3+}/Cr} = -0.74 \text{ V}; E^{\circ}_{MnO_4^-/Mn^{2+}} = 1.51 \text{ V}$$

$$E^{\circ}_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33 \text{ V}; E^{\circ}_{Cl/Cl^-} = 1.36 \text{ V}$$

Based on the data given above, the strongest oxidising agent will be : **[JEE (Main) 2013]**

(a) Mn^{2+}
(b) MnO_4^-
(c) Cl^-
(d) Cr^{3+}

58. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E^0_{M^{3+}/M^{2+}}$ value ? **[JEE (Main) 2013]**

(a) Fe(Z=26)
(b) Co(Z=27)
(c) Cr(Z=24)
(d) Mn(Z=25)

SOLUTIONS (One Answer Correct)

1. (a) $\mathrm{Cr}^{3+} + 3e \longrightarrow \mathrm{Cr}; \qquad -\Delta G_1^\circ = 3\times 0.74\times F$

$$\underline{\underset{-}{\mathrm{Cr}^{3+}} + e \longrightarrow \underset{-}{\mathrm{Cr}^{2+}}; \quad \underset{+}{-\Delta G_2^\circ} = 1\times 0.40\times F}$$

$$\mathrm{Cr}^{2+} + 2e \longrightarrow \mathrm{Cr}; \qquad -\Delta G_3^\circ = 2\times E^\circ \times F$$

$$= (3\times 0.74 - 1\times 0.40)F = 1.82\,F$$

$\therefore \quad E^\circ = 0.91\,\mathrm{V}$

2. (c) $\underset{\mathrm{I}}{\mathrm{Cr}|\mathrm{Cr}^{3+}||\mathrm{Cr}^{3+},\mathrm{Cr}^{2+}|\mathrm{Pt}}; \quad \underset{\mathrm{II}}{\mathrm{Cr}|\mathrm{Cr}^{2+}||\mathrm{Cr}^{3+}|\mathrm{Cr}};$

$\underset{\mathrm{III}}{\mathrm{Cr}|\mathrm{Cr}^{2+}||\mathrm{Cr}^{3+},\mathrm{Cr}^{2+}|\mathrm{Pt}}$

(I) $\mathrm{Cr} \longrightarrow \mathrm{Cr}^{3+} + 3e; \qquad E^\circ = +0.74\ \mathrm{V}$

$\underline{3\mathrm{Cr}^{3+} + 3e \longrightarrow 3\mathrm{Cr}^{2+}; \quad E^\circ = -0.4\ \mathrm{V}}$

$\mathrm{Cr} + 2\mathrm{Cr}^{3+} \longrightarrow 3\mathrm{Cr}^{2+}\ (n = 3)$

(II) $3\mathrm{Cr} \longrightarrow 3\mathrm{Cr}^{2+} + 6e; \quad E^\circ = 0.91\,\mathrm{V}$

$\underline{2\mathrm{Cr}^{3+} + 6e \longrightarrow 2\mathrm{Cr}; \quad E^\circ = -0.74\ \mathrm{V}}$

$\mathrm{Cr} + 2\mathrm{Cr}^{3+} \longrightarrow 3\mathrm{Cr}^{2+}\ (n = 6)$

(III) $\mathrm{Cr} \longrightarrow \mathrm{Cr}^{2+} + 2e; \qquad E^\circ = 0.91\,\mathrm{V}$

$\underline{2\mathrm{Cr}^{3+} + 2e \longrightarrow 2\mathrm{Cr}^{2+}; \quad E^\circ = -0.40\ \mathrm{V}}$

$\mathrm{Cr} + 2\mathrm{Cr}^{3+} \longrightarrow 3\mathrm{Cr}^{2+}\ (n = 2)$

$$E^\circ = 0.74 - 0.4 = 0.34\ \mathrm{V}$$
$$-\Delta G^\circ = 3\times 0.34\times F$$
$$= 1.02\,F$$
$$E^\circ = 0.91 - 0.74 = 0.17\,\mathrm{V}$$
$$-\Delta G^\circ = 0.17\times 6\times F$$
$$= 1.02\,F$$
$$E^\circ = 0.91 - 0.40 = 0.51\,\mathrm{V}$$
$$-\Delta G^\circ = 2\times 0.51\times F$$
$$= 1.02\,F$$

3. (c) $E^\circ_{\mathrm{AsO_4^{2-}}|\mathrm{Pb_3(AsO_4)_2}|\mathrm{Pb}} = E^\circ_{\mathrm{Pb^{2+}/Pb}} + \frac{0.059}{6}\log K_{sp}$

$$= -0.13 + \frac{0.059}{6}\log 4.1\times 10^{-36}$$

$$= -0.13 - 0.348 = -0.478\ \mathrm{V}$$

4. (a) $E^\circ_{\mathrm{Zn^{2+}}/\mathrm{Zn}Y^{2-}/Y^{4-}} = E^\circ_{\mathrm{Zn^{2+}/Zn}} + \frac{0.059}{2}\log K$

$$K_f = \frac{[\mathrm{Zn}Y^{2-}]}{[Y^{4-}]} \qquad \therefore\ K = \frac{1}{K_f}$$

$\therefore \quad E^\circ_{\mathrm{Zn^{2+}}/\mathrm{Zn}Y^{2-}/Y^{4-}} = -0.76 + \frac{0.059}{2}\log\frac{1}{3.2\times 10^{16}}$

$$= -1.25\ \mathrm{V}$$

5. (a) For $\mathrm{Fe}Y^- + e \longrightarrow \mathrm{Fe}Y^{2-}$ the change is

$$\mathrm{Fe}^{3+} + e \longrightarrow \mathrm{Fe}^{2+}$$

$\therefore \quad E^\circ_{\mathrm{Fe^{3+}}/\mathrm{Fe}Y^{2-}/\mathrm{Fe}Y^-} = E^\circ_{\mathrm{Fe^{3+}/Fe^{2+}}} +$

$$\frac{0.059}{1}\log\frac{[\mathrm{Fe}Y^{2-}][\mathrm{Fe}^{3+}]}{[\mathrm{Fe}Y^-][\mathrm{Fe}^{2+}]}$$

$$= 0.77 + \frac{0.059}{1}\log\frac{2.1\times 10^{14}}{1.3\times 10^{25}} = 0.77 - 0.64 = +0.13\mathrm{V}$$

6. (c) $\mathrm{Au}^{3+} + 3e \longrightarrow \mathrm{Au}$

$\therefore \quad \frac{w}{197/3} = \frac{\text{Charge}}{96500}$

$\therefore$ Charge $= \frac{1.314\times 3\times \mathrm{F}}{197} = 0.02F$

7. (a) Efficiency $= \frac{\Delta G^\circ}{\Delta H^\circ} = -\frac{nE^\circ F}{\Delta H} = 80$

$\therefore \quad E^\circ = -\frac{80\times(-300)\times 10^3}{2\times 96500\times 100} = 1.24\ \mathrm{V}$

8. (a) By $\Delta S = \frac{\Delta H - \Delta G}{T}$;

$\Delta H = -nF\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right]$ and $\Delta G = -nEF$

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P = 3\times 96500\times\left(-\frac{0.0006}{10}\right)$$

$$= -17.37\ \mathrm{JK^{-1}}$$

9. (d) $\frac{w}{E} = \frac{i\cdot t}{96500} \qquad A^{Y^+} + Ye \longrightarrow A$

$$\frac{2.977}{\frac{106.4}{Y}} = \frac{3\times 1\times 60\times 60}{96500}$$

$\therefore\ Y = 4\ \ \therefore$ electrolyte is AB_4.

10. (d) $2\mathrm{Cu}^+ \longrightarrow \mathrm{Cu}^{2+} + \mathrm{Cu}$;

Cell I :	**Cell II :**
$\mathrm{Cu}^+ \longrightarrow \mathrm{Cu}^{2+} + e$	$\mathrm{Cu} \longrightarrow \mathrm{Cu}^{2+} + 2e$
$\underline{\mathrm{Cu}^+ + e \longrightarrow \mathrm{Cu}}$	$\underline{2\mathrm{Cu}^+ + 2e \longrightarrow 2\mathrm{Cu}}$
$2\mathrm{Cu}^+ \longrightarrow \mathrm{Cu}^{2+} + \mathrm{Cu}$	$2\mathrm{Cu}^+ \longrightarrow \mathrm{Cu}^{2+} + \mathrm{Cu}$
$E^\circ = -0.15 + 0.50$	$E^\circ = -0.325 + 0.50$
$= +0.35\ \mathrm{V}$	$= +0.175\ \mathrm{V}$
$n = 1$	$n = 2$

11. (c) $(\mathrm{Mn}^{+8/3})_3 \longrightarrow 3\mathrm{Mn}^{6+} + 10e$

$\therefore$ 10 Faraday charge is required for conversion of 1 mole of $\mathrm{Mn_3O_4}$ to $\mathrm{MnO_4^{2-}}$.

12. (b) $\frac{w}{E} = \frac{965\times 1}{96500} = 0.01$

Equivalent of $\mathrm{NiSO_4}$ present initially $= 1\times 0.02 = 0.02$
If Ni electrodes are used no change in conc. of $\mathrm{NiSO_4}$, *i.e.*, 0.02 N or 0.01 M.

If Pt electrodes are used then eq. of $\mathrm{NiSO_4}$ left $= 0.01$

13. (c) $E_{\text{cell}} = E_{OP_{D_2}} = E_{RP_{\mathrm{H_2}}}$

$$= E^\circ_{OP_{D_2/D^+}} - \frac{0.059}{2}\log[D^+]^2 + E^\circ_{RP_{\mathrm{H^+/H_2}}} +$$

$$0.059\log[\mathrm{H}^+]^2$$

$$0 = 0.003 - \frac{0.059}{2}\log\frac{[D^+]^2}{[\mathrm{H}^+]^2} \qquad (E^\circ_{RP_{\mathrm{H^+/H_2}}}) = 0$$

$$\therefore \quad \frac{[D^+]}{[\mathrm{H}^+]} = 1.124$$

14. (b) $E_{\mathrm{S^{2-}/CuS/Cu}} = E^\circ_{\mathrm{Cu^{2+}/Cu}} + \frac{0.059}{2}\log K_{sp}\ \mathrm{CuS}$

$$= 0.34 + \frac{0.059}{2}\log^{10^{-35}} = -0.6925\ \mathrm{V}$$

15. (a) $-\Delta G = -\Delta G^\circ = 2.75\times 10^6\ \mathrm{J\ mol^{-1}}$

(as $P = 1\mathrm{bar}$ and $T = 298\ \mathrm{K}$)

$$-\Delta G^\circ = nE^\circ F$$

$$\therefore \quad E^\circ = \frac{2.75\times 10^6}{26\times 96500}$$

$$\left[\begin{array}{r} \mathrm{C_4H_{10}} + \frac{13}{2}\mathrm{O_2} \longrightarrow 4\mathrm{CO_2} + 5\mathrm{H_2O} \\ (\mathrm{C}^{-5/2})_4 \longrightarrow 4\mathrm{C}^{4+} + 26e \end{array}\right]$$

$E^\circ = 1.096\ \mathrm{V}$, Also, $E^\circ = \frac{0.059}{n}\log K_p$

$$1.096 = \frac{0.059}{26}\log K_p \quad K = 9.55\times 10^{482}$$

16. (a) $\mathrm{H_2S} \rightleftharpoons 2\mathrm{H}^+ + \mathrm{S}^{2-}$

$$\therefore \quad K_a = \frac{[\mathrm{H}^+]^2[\mathrm{S}^{2-}]}{[\mathrm{H_2S}]} = \frac{(10^{-3})^2\times[\mathrm{S}^{2-}]}{0.1}$$

$$\therefore \quad [\mathrm{S}^{2-}] = \frac{10^{-21}\times 0.1}{10^{-6}} = 10^{-16},$$

Since, $\because\ [\mathrm{Ag}^+]^2[\mathrm{S}^{2-}] = K_{sp}$

$$\therefore \quad [\mathrm{Ag}^+] = \sqrt{\frac{K_{sp}}{[\mathrm{S}^{2-}]}} = \sqrt{\frac{10^{-49}}{10^{-16}}} = \sqrt{10^{-33}}$$

$$2\mathrm{Ag}^{2+} + e \longrightarrow 2\mathrm{Ag}$$

$$E_{\mathrm{S^{2-}/Ag_2S/Ag}} = E_{\mathrm{Ag^+/Ag}}$$

$$E_{\mathrm{S^{2-}/Ag_2S/Ag}} = E^\circ_{\mathrm{Ag^+/Ag}} + \frac{0.059}{2}\log[\mathrm{Ag}^+]^2$$

$$= 0.80 + \frac{0.059}{2}\log 10^{-33} = -0.1735\ \mathrm{V}$$

17. (d) Anode : $2\mathrm{CH_3COO^-} \longrightarrow \mathrm{C_2H_6} + 2\mathrm{CO_2} + 2e$

Cathode : $2\mathrm{H}^+ + 2e \longrightarrow \mathrm{H_2}$

18. (a) Follow text.

19. (d) The net redox change :

$$\mathrm{NiO}_{2(s)} + \mathrm{Cd} + 2\mathrm{H_2O} \longrightarrow \mathrm{Ni\,(OH)}_{2(s)} + \mathrm{Cd\,(OH)}_{2(s)}$$

20. (d) Follow text.

21. (a) $E_{RP} = E^\circ_{RP} + \frac{0.059}{n}\log\frac{[M^{x+n}]}{[M^{x+}]}$

22. (a) Anode : $2\mathrm{OH}^- \longrightarrow \mathrm{H_2O} + \frac{1}{2}\mathrm{O_2} + 2e$

Cathode : $2\mathrm{H}^- + 2e \longrightarrow \mathrm{H_2}$

23. (b) It is a fact.

24. (a)

$$\begin{array}{l} \mathrm{Cu}^{2+} + 2e \longrightarrow \mathrm{Cu}; \quad -\Delta G_1^\circ \\ \mathrm{Cu}^{2+} + e \longrightarrow \mathrm{Cu}^+; \quad -\Delta G_2^\circ \\ \underline{\ \ -\qquad -\qquad\qquad -\qquad\quad +\ \ } \end{array}$$

$$\therefore \quad \mathrm{Cu}^+ + e \longrightarrow \mathrm{Cu}; -\Delta G_3^\circ = -\Delta G_1^\circ + \Delta G_2^\circ$$

or $\quad n\times E_3^\circ F = n_1E_1^\circ F - n_2E_2^\circ F$

$$E_3^\circ = \frac{n_1E_1^\circ F - n_2E_2^\circ F}{nF} = \frac{0.339\times 2 - 1\times 0.153}{1} = 0.525\ \mathrm{V}$$

25. (a) More is E°_{RP}, more is the tendency to get reduced or more is the oxidizing power or lesser is reducing power. Thus, oxidizing power = $X^+ > Z^+ > Y^+$
reducing power = $Y > Z > X$

26. (a) $E^\circ_{RPZ/Z^-} > E^\circ_{RPY/Y^-} > E^\circ_{RPX/X^-}$.

Thus, order of oxidizing power will be $Z > Y > X$

27. (a) $2\mathrm{H}^- \longrightarrow \mathrm{H_2} + 2e$; H is –ve in ionic hydrides.

28. (d) $F = N\times e, \qquad 96500 = 6.023\times 10^{23}\times e$

$$\therefore \quad e = 1.602\times 10^{-19}$$

29. (c) $E_{RP} = E^\circ_{RP} + \frac{0.059}{4}\log\frac{[\mathrm{TeO_3^{2-}}]}{[\mathrm{OH^-}]^6}$

$[\mathrm{Te}^{4+} + 4e \rightarrow \mathrm{Te}$; Also $\mathrm{pH} = 12\ \therefore\ [\mathrm{OH}^-] = 10^{-2}]$

$$\therefore \quad E_{RP} = -0.57 + \frac{0.059}{4}\log\frac{1}{(10^{-2})^6} = -0.393\ \mathrm{V}$$

30. (a) $E = \frac{0.059}{3}\log\frac{[\mathrm{Cr}^{3+}]_{\mathrm{R.H.S.}}}{[\mathrm{Cr}^{3+}]_{\mathrm{L.H.S.}}}$

$$= \frac{0.059}{3}\log\frac{1}{[0.04]} = 0.028\ \mathrm{V}$$

31. (b)

$$\begin{array}{r} \mathrm{Cu}^{2+}(aq) + 2e \longrightarrow \mathrm{Cu}\,(s) \\ \underline{\mathrm{Cu}\,(s) + \mathrm{S}^{2-}(aq) \longrightarrow \mathrm{CuS}\,(s) + 2e} \\ \mathrm{Cu}^{2+}(aq) + \mathrm{S}^{2-}(aq) \longrightarrow \mathrm{CuS}\qquad \end{array}$$

$$E_{\mathrm{Cu|CuS|S^{2-}}} = E_{\mathrm{Cu|Cu^{2+}}} - \frac{0.059}{2}\log K_{SP}$$

$$= -0.34 - \frac{0.059}{2}\log 10^{-35}$$

$$= -0.34 + 1.0325 = 0.693\ \mathrm{V}$$

32. (a) $\left(\frac{\partial E}{\partial T}\right)_P = \frac{\Delta S}{nF}$

$$\Delta S = 1.5\times 10^{-4}\times 2\times 96500 = 28.95\ \mathrm{J}$$

33. (d) $E_{\mathrm{cell}} = E^\circ_{OP} + E^\circ_{RP}$

$$= E^\circ_{\mathrm{ClO_3^-|ClO_4^-}} - \frac{0.059}{2}\log\frac{[\mathrm{ClO_4^-}]}{[\mathrm{ClO_3^-}]}$$

$$+ E^\circ_{\mathrm{ClO_3^-|ClO_2^-}} + \frac{0.059}{2}\log\frac{[\mathrm{ClO_3^-}]}{[\mathrm{ClO_2^-}]}$$

$$\mathrm{Cl}^{5+} \longrightarrow \mathrm{Cl}^{7+} + 2e$$

$$2e + \mathrm{Cl}^{5+} \longrightarrow \mathrm{Cl}^{3+}$$

$E_{\mathrm{cell}} = 0$ at equilibrium. Also

$$\underset{\substack{1\\(1-2x)}}{2\mathrm{ClO_3^-}} \rightleftharpoons \underset{\substack{0\\x}}{\mathrm{ClO_4^-}} + \underset{\substack{0\\x}}{\mathrm{ClO_2^-}}$$

$$E_{\mathrm{cell}} = E^\circ_{\mathrm{ClO_3^-|ClO_4^-}} + E^\circ_{\mathrm{ClO_3^-|ClO_2^-}}$$

$$+ \frac{0.059}{2}\log\frac{[\mathrm{ClO_3^-}]^2}{[\mathrm{ClO_4^-}][\mathrm{ClO_2^-}]}$$

$$0 = -0.36 + 0.33 + \frac{0.059}{2}\log\frac{[1-2x]^2}{x^2}$$

$$0 = -0.03 + 0.059\log\frac{1-2x}{x}$$

$$\text{or } \log\frac{1-2x}{x} = \frac{0.03}{0.059}$$

$$\therefore \quad \frac{1-2x}{x} = 0.509$$

$$\therefore \quad x = \frac{1}{2.509} = 0.40\text{ M}$$

34. (a) $$\underset{\substack{0.1\\(0.1-x)}}{NO_3^-} + \underset{\substack{0.4\\(0.4-0.4x)}}{4H^+} + 3e \longrightarrow \underset{\substack{0\\-}}{NO} + \underset{\substack{0\\-}}{2H_2O}$$

$$x = \frac{80}{100} \times 0.1 = 0.08$$

After reduction,

$$[NO_3^-] = 0.1 - 0.08 = 0.02$$

$$[H^+] = 0.4 - 0.32 = 0.08$$

$$\therefore \quad E_{RP} = E^\circ_{RP} + \frac{0.059}{3}\log\frac{[NO_3^-][H^+]^4}{[P_{NO}]}$$

$$= 0.96 + \frac{0.059}{3}\log\frac{0.02 \times (0.08)^4}{1}$$

$$= 0.96 - 0.12 = 0.84\text{ V}$$

35. (d) $Ag^+ + e \longrightarrow Ag$

$$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$$

$\therefore$ Eq. of Ag^+ lost $= 0.1 =$ Eq. of O_2 formed and escaped

$\therefore$ Total mass loss $= 0.1 \times 108 + \frac{0.1 \times 32}{4} = 11.6$

$\therefore$ Mass of solution $= 108 - 11.6 = 96.47$

36. (b) $\frac{4}{3}Al + O_2 \longrightarrow \frac{2}{3}Al_2O_3;\ \Delta G = -827\text{ kJ}$ (Given per mole of O_2)

$\because \quad 2Al^\circ \longrightarrow (Al^{3+})_2 + 6e$

1 Al gives $3e$

$$\therefore \quad \frac{4}{3}Al = 4e$$

Now $\quad \Delta G = -nEF$

$$-827 \times 10^3 = -4 \times E \times 96500$$

$$\therefore \quad E = 2.14\text{ V}$$

37. (a) $$E_{cell} = E_{OP_{QH}} + E_{RP_{calomel}}$$

$$= E^\circ_{OP_{QH}} - \frac{0.059}{2}\log[H^+]^2 + E^\circ_{RP_{cal}}$$

($\because E^\circ_{RP} = E_{RP}$ for calomel)

$$= -0.699 + 0.059\text{ pH} + 0.280$$

$$E_{cell} = -0.419 + 0.059\text{ pH}$$

$$-0.124 = -0.419 + 0.059\text{ pH}$$

$$\text{pH} = 5$$

38. (a) E°_{OP} for Zn $= +0.762$ V (maximum in given values). More positive is E°_{OP}, more is the tendency to get itself oxidised or strong reducing agent.

39. (c) $\frac{w}{E} = \frac{i \cdot t}{96500}$ (Ist Law)

40. (c) E°_{RP} for Ag, Hg and Cu are -0.80, -0.79, -0.34. Mg^{2+} is not discharged in aqueous solution.

41. (d) 1 Faraday $= N \times e$

42. (d) None of the other cell contains salt bridge involving this reaction.

43. (a) Cathode : $2H^+ + 2e \longrightarrow H_2$

Anode : $\quad 2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$

44. (d) $PbO_2 + Pb + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$

(Discharging reaction)

45. (b) $E^\circ_{cell} = E^\circ_{OP_{Zn}} + E^\circ_{RP_{Fe}} = 0.76 - 0.41 = 0.35\text{ V}$

46. (d)

$$\begin{array}{ll} 2e + Cu^{2+} \longrightarrow Cu; & \Delta G_1^\circ = -2 \times 0.34 \times F \\ \quad Cu^+ \longrightarrow Cu^{2+} + e; & \Delta G_2^\circ = -1 \times (-0.15) \times F \\ \quad + \qquad\quad + & \quad + \qquad\qquad + \\ \hline e + Cu^+ \longrightarrow Cu; & \Delta G_3^\circ = -1 \times E_3^\circ \times F \end{array}$$

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ = -0.68F + 0.15 \times F$$

$$\therefore \quad E_3^\circ = +0.53\text{ V}$$

Now, for $2Cu^+ \longrightarrow Cu + Cu^{2+}$

$$E^\circ = E^\circ_{OP_{Cu^+|Cu^{2+}}} + E^\circ_{RP_{Cu^+|Cu}}$$

$$= -0.15 + 0.53 = +0.38\text{ V}$$

47. (b) $E_{cell} = \overset{\circ}{E}_{OPM/M^+} + \overset{\circ}{E}_{RPX/X^-} = -0.44 + 0.33 = -0.11\text{ V}$ for $M + X \longrightarrow M^+ + X^-$. Thus reaction is non-spontaneous. The spontaneous reaction in $M^+ + X^- \longrightarrow M + X; E^\circ = 0.11\text{ V}$

48. (b) $\Delta G = \Delta G^\circ + RT\ln Q$, at eq. $\Delta G = 0$ and $Q = K_c$

$$\therefore \quad -\Delta G^\circ = RT\ln K_c$$

49. (c) The salt bridge possesses the electrolyte having nearly same ionic mobilities of its cation and anion.

50. (b) Ionic mobilities depends upon size of ion. The ionic size in case of hydrated cation is $K^+_{(aq.)} < Na^+_{(aq.)} < Li^+_{(aq.)}$. Smaller is ion more is hydration and larger in size of hydrated ion.

51. (a) MnO_4^- will oxidise Cl^- ion according to equation.

$$Mn^{7+} + 5e \longrightarrow Mn^{2+}$$

$$2Cl^- \longrightarrow Cl_2 + 2e$$

$$\text{Thus,} \quad \overset{\circ}{E}_{cell} = \overset{\circ}{E}_{OPCl^-/Cl_2} + \overset{\circ}{E}_{RPMn^{7+}/Mn^{2+}}$$

$$= -1.40 + 1.51 = 0.11\text{ V}$$

or reaction is feasible.

MnO_4^- will oxidise Fe^{2+} to Fe^{3+}

$$Mn^{7+} + 5e \longrightarrow Mn^{2+}$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$

$$E^\circ_{cell} = E^\circ_{OP\,Fe^{2+}/Fe^{3+}} + E^\circ_{RP\,Mn^{7+}/Mn^{2+}}$$

$$= -0.77 + 1.51 = 0.74 \text{ V}$$

or reaction is feasible.

Thus, MnO_4^- will not oxidise only Fe^{2+} to Fe^{3+} in aqueous HCl but it will also oxidise Cl^- to Cl_2. Suitable oxidant should not oxidise Cl^- to Cl_2 and should oxidise only Fe^{2+} to Fe^{3+} in redox titration.

52. (b) Current flows from anode to cathode in external circuit of electrolytic cell and thus electrons flow from anode to cathode through external wires.

53. (b) $Zn + Fe^{2+} \longrightarrow Fe + Zn^{2+}$

$$E_{cell} = E^\circ_{cell} + \frac{0.059}{2}\log\frac{[Fe^{2+}]}{[Zn^{2+}]}$$

$$0.2905 = E^\circ_{cell} + \frac{0.059}{2}\log\frac{0.001}{0.01}$$

$$\therefore \quad E^\circ_{cell} = 0.2905 + 0.0295 = 0.32 \text{ V}$$

$$\text{Now} \quad E^\circ_{cell} = \frac{0.059}{2}\log_{10} K_c$$

$$0.32 = \frac{0.059}{2}\log_{10} K_c$$

$$\therefore \quad K_c = 10^{0.32/0.0295}$$

54. (a) $E^\circ_{cell} = E^\circ_{OP\,Fe} + E^\circ_{RP\,H_2O} = 0.44 + 1.23 = 1.67 \text{ V}$

$$\therefore \quad \Delta G^\circ = -nE^\circ F = -2 \times 1.67 \times 96500 \text{ J}$$

$$= -322.31 \text{ kJ mol}^{-1}$$

55. (b)

$$\frac{w}{E} = \frac{i \cdot t}{96500}$$

$$0.01 \times 2 = \frac{10 \times 10^{-3} \times t}{96500},$$

$$t = 19.3 \times 10^4 \text{ sec}$$

56. (d) In the given reaction Fe is oxidised and O_2 is reduced.

$$2Fe \longrightarrow 2Fe^{2+} + 4e$$

$$4e + O_2 + 4H^+ \longrightarrow 2H_2O$$

$$\therefore E_{cell} = E^\circ_{OPFe} - \frac{0.059}{4}\log[Fe^{2+}]^2$$

$$+ E^\circ_{RPO_2} + \frac{0.059}{4}\log P_{O_2} \times [H^+]^4$$

$$= E^\circ_{cell} + \frac{0.059}{4}\log\frac{P_{O_2} \times [H^+]^4}{[Fe^{2+}]^2}$$

$$= 1.67 + \frac{0.059}{4}\log\frac{0.1 \times (10^{-3})^4}{(10^{-3})^2}$$

$$= 1.67 + \frac{0.059}{4}\log 10^{-7}$$

$$= 1.67 + \frac{0.059 \times (-7)}{4}$$

$$= 1.67 - 0.103 = 1.57 \text{ V}$$

57. (b) E^0_{RP} of MnO_4^- / Mn^{2+} is highest and thus MnO_4^- is easily reduced and is the strongest oxidising agent.

$$Mn^{7+} + 5e \longrightarrow Mn^{2+}$$

$$\text{or} \quad MnO_4^- + 5e + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

58. (b) $E^\circ_{Mn^{3+}/Mn^{2+}} = 1.57 \text{ V}$

$$E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77 \text{ V}$$

$$E^\circ_{Co^{3+}/Co^{2+}} = 1.97 \text{ V}$$

$$E^\circ_{Cr^{3+}/Cr^{2+}} = -0.41 \text{V}$$

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. In the atmosphere of industrial smog, copper corrodes to form:
(a) basic copper carbonate
(b) copper sulphide
(c) basic copper sulphate
(d) copper oxide

2. The tarnishing of silver ornaments in atmosphere is due to :
(a) Ag_2O (b) Ag_2S
(c) Ag_2CO_3 (d) Ag_2SO_4

3. If, : $A + B \rightleftharpoons C + D; K_C = K_1$ and $E° = a$ V
$2A + 2B \rightleftharpoons 2C + 2D; K_C = K_2$ and $E° = b$ V
then,
(a) $a = b$ (b) $K_2 = K_1^2$
(c) $a = 2b$ (d) $b = a^2$

4. Rusting of iron is catalysed by :
(a) H^+ (b) dissolved CO_2 in water
(c) O_2 (d) impurities present in Fe

5. Select the wrong relations :
(a) $\Delta S = \left(\frac{\partial E}{\partial T}\right)_P \times nF$ (b) $-\Delta S = \left(\frac{\partial E}{\partial T}\right)_P \times nF$
(c) $\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial \Delta S}{\partial T}\right)$ (d) $\left(\frac{\partial E}{\partial T}\right)_P = \frac{\Delta H + nEF}{T}$

6. Select the correct statements about NHE :
(a) $E°$ of NHE has arbitrarily assumed to be zero
(b) $E°$ of NHE is equal to zero
(c) NHE refers as $\underset{1\text{ bar}}{Pt_{H_2g}} \Big| \underset{a=1}{H^+_{aq}}$ at 25°C
(d) NHE is very susceptible to dissolved O_2, H_2S and all other reducing agents

7. In which of the following salt bridge is not needed ?
(a) $Pb | PbSO_{4(s)} | H_2SO_4 | PbO_{2(s)} | Pb$
(b) $Cd | CdO_{(s)} | KOH_{aq} | NiO_{2(s)} | Ni$
(c) $Fe_{(s)} | FeO_{(s)} | KOH_{aq}, Ni_2O_{3(s)} | Ni$
(d) $Zn | ZnSO_4 | CuSO_4 | Cu$

8. Select the correct statements if 9.65 ampere current is passed for 1 hour through the cell $Ag | \underset{1M}{Ag^+} || \underset{1M}{Cu^{2+}} | Cu$:
(a) Ag will oxidise to Ag^+ and new $[Ag^+] = 1.36\ M$
(b) Ag^+ will reduce to Ag and new $[Ag^+] = 0.64\ M$
(c) Cu^{2+} will reduce to Cu and new $[Cu^{2+}] = 0.82\ M$
(d) Cu will oxidise to Cu^{2+} and new $[Cu^{2+}] = 0.82\ M$

9. Which of the following metals can not be obtained by the electrolysis of an aqueous solution of their salt :
(a) Ag (b) Mg
(c) Cu (d) Cr
(e) Al

10. The standard reduction potential values of three metallic cations, X, Y and Z are 0.52, – 3.03 and – 1.18 V respectively. The order of reducing power of the corresponding metals is :
(a) $Y > Z > X$ (b) $X > Y > Z$
(c) $Z > Y > X$ (d) $Z > X > Y$

11. The function of salt bridge is :
(a) to maintain electrical neutrality of two half cell solution
(b) to eliminate liquid junction potential
(c) to complete the circuit
(d) to produce current

12. In a cell $Zn | Zn^{2+} || H^+ | H_2Pt$, the addition of H_2SO_4 to cathode compartment :
(a) decreases EMF
(b) increases EMF
(c) shift equilibrium to right
(d) shifts equilibrium to left

13. For the reduction of NO_3^- ion in aqueous solution, $E°$ is +0.96 V. Values of $E°$ for some metals are given below :
$V^{2+}(aq.) + 2e \longrightarrow V$; $E° = -1.19$ V
$Fe^{3+}(aq.) + 3e \longrightarrow Fe$; $E° = -0.04$ V
$Au^{3+}(aq.) + 3e \longrightarrow Au$; $E° = +1.40$ V
$Hg^{2+}(aq.) + 2e \longrightarrow Hg$; $E° = +0.86$ V
The pairs of metal that is (are) oxidised by NO_3^- in aqueous solution is (are) : **(IIT 2009)**
(a) V and Hg (b) Hg and Fe
(c) Fe and Cu (d) Fe and V

SOLUTIONS (More Than One Answer Correct)

1. (a, c) $8Cu + 6H_2O + 2SO_2 + 5O_2 \longrightarrow 2[CuSO_4 \cdot 3Cu(OH)_2]$

$2Cu + H_2O + CO_2 + O_2 \longrightarrow [CuCO_3 \cdot Cu(OH)_2]$

2. (a, b) $2Ag + \frac{1}{2}O_2 \longrightarrow Ag_2O$

$2Ag + H_2S \longrightarrow Ag_2S + H_2$

3. (a, b) $K_1 = \frac{[C][D]}{[A][B]}$ and $K_2 = \frac{[C]^2[D]^2}{[A][B]}$

Also, $E°$ is independent of stoichiometry.

4. (a,b,c,d) Follow text.

5. (a,d) $\Delta G = \Delta H - T\Delta S$ and $\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$

$$\therefore \quad \left(\partial \frac{\Delta G}{\partial T}\right)_P = \frac{\Delta G - \Delta H}{T} = -\frac{T\Delta S}{T} = -\Delta S$$

$$\therefore \quad \Delta S = +nF\left(\frac{\partial E}{\partial T}\right)_P$$

Also, $-nEF = \Delta H + T \times (-nF)\left(\frac{\partial E}{\partial T}\right)_P$

$$\therefore \quad \left(\frac{\partial E}{\partial T}\right)_P = \frac{\Delta H + nEF}{T}$$

6. (a,c,d) Follow text.

7. (a,b,c) Salt bridge is used to eliminate liquid junction potential arised due to different speed of ions present in cathodic and anodic compartments.

8. (a,c) $\frac{w}{E} = \frac{it}{96500} = \frac{9.65 \times 3600}{96500} = 0.36\,eq.$

of $Ag^+ = 0.36\,eq.$ of Cu^{2+}

$= 0.36$ mole of $Ag^+ = 0.18$ mole of Cu^{2+}

Now, Ag will oxidise to Ag^+ and Cu^{2+} will reduce to Cu.

9. (b,e) Strong electropositive metals cannot be reduced in presence of H_2O.

10. (a) Lower is E°_{RP}, more is E°_{OP}, more is the tendency to get itself oxidised and thus more is reducing power E°_{OP} order in $Y > Z > X$.

11. (a,b,c)

12. (b,c) $E = E^\circ_{cell} + \frac{0.059}{2}\log\frac{[H^+]^2}{[Zn^{2+}]}$

$$\begin{array}{ll} \text{Anode :} & Zn \longrightarrow Zn^{2+} + 2e \\ \text{Cathode:} & \underline{2H^+ + 2e \longrightarrow H_2} \\ & Zn + 2H^+ \longrightarrow Zn^{2+} + H_2 \end{array}$$

On addition of H_2SO_4 to cathode compartment, $[H^+]$ increases and reaction will shift towards right.

13. (a,b,d) The oxidation of Au is not possible as E°_{cell} is –ve.

(a) $E° = E^\circ_{OP_V} + E^\circ_{RP_{NO_3^-}} = +1.19 + 0.96 = 2.15\text{ V}$

(b) $E° = E^\circ_{OP_{Fe}} + E^\circ_{RP_{NO_3^-}} = +0.04 + 0.96 = 1.0\text{ V}$

(c) $E° = E^\circ_{OP_{Au}} + E^\circ_{RP_{NO_3^-}} = -1.40 + 0.96 = -0.44\text{ V}$

(d) $E° = E^\circ_{OP_{Hg}} + E^\circ_{RP_{NO_3^-}} = -0.86 + 0.96 = +0.10\text{ V}$

COMPREHENSION BASED PROBLEMS

Comprehension 1 : A current of 15 ampere is used to plate Ni from $NiSO_4$ bath. Both H_2 and Ni are formed at cathode. The current efficiency of Ni formation is 60%.

(atomic mass of Ni = 58.71)

[1] Mass of Ni is plated per hr?

(a) 9.85 g (b) 0.5596 g
(c) 16.42 g (d) 12.82 g

465.00
193

[2] The thickness of plating if the cathode consists of a sheet of $4\,cm^2$ which is coated on both sides : (The density of Ni is $8.9\,g\,mL^{-1}$)

(a) 0.276 cm (b) 0.272 cm
(c) 0.316 cm (d) 0.138 cm

[3] The volume of H_2 is formed per hr at STP:

(a) 6.62 litre (b) 6.26 litre
(c) 2.51 litre (d) 5.02 litre

[4] The volume of O_2 is formed per hr at STP:

(a) 6.26 litre (b) 3.13 litre
(c) 9.39 litre (d) 2.51 litre

Comprehension 2: $E°$ values for $Fe \longrightarrow Fe^{2+} + 2e$ and $Fe \longrightarrow Fe^{3+} + 3e$ are 0.440 V and 0.036 V respectively.

[1] The number of cells showing the overall cell reaction $Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+}$:

(a) 1 (b) 2
(c) 3 (d) 4

[2] $\Delta G°$ for each cell for given overall reaction in (J) is:

(a) +2.424 F (b) −2.424 F
(c) +1.616 F (d) −1.616 F

[3] $E°$ for $Fe^{3+} + e \longrightarrow Fe^{2+}$ is:

(a) +0.672 V (b) +0.772 V
(c) −0.040 (d) +0.040 V

[4] The $E°$ for $Fe \mid Fe^{2+} \parallel Fe^{3+}, Fe^{2+} \mid Pt$ is:

(a) 1.212 V (b) 0.404 V
(c) 0.808 V (d) − 0.404 V

[5] Select the correct statements:

(a) The overall reaction and $\Delta G°$ for each cell is same
(b) The E°_{cell} and '*n*' values are different for each cell
(c) The $\Delta G°$ depends upon the cell reaction where as E°_{cell} depends upon the make-up of cell
(d) All of the above

Comprehension 3 : Numerical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept. A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (atomic mass : Na = 23, Hg = 200; 1 Faraday = 96500 coulombs) **(IIT 2007)**

[1] The total number of mole of chlorine gas evolved is:

(a) 0.5 (b) 1.0
(c) 2.0 (d) 3.0

[2] If the cathode is a Hg electrode, the maximum mass (g) of amalgam formed from this solution is :

(a) 200 (b) 225
(c) 400 (d) 446

[3] The total charge (coulomb) required for complete electrolysis is :

(a) 24125 (b) 48250
(c) 96500 (d) 193000

Comprehension 4 : Redox reactions play a pivotal role in chemistry and biology. The values of standard redox potential ($E°$) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their $E°$ (V with respect to normal hydrogen electrode) values. Using this data obtain the correct explanations to questions given

$$I_2 + 2e^- \rightarrow 2I^- \qquad E° = 0.54$$
$$Cl_2 + 2e^- \rightarrow 2Cl^- \qquad E° = 1.36$$
$$Mn^{3+} + e^- \rightarrow Mn^{2+} \qquad E° = 1.50$$
$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E° = 0.77$$
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E° = 1.23$$

[IIT2007]

[1] Among the following, identify the correct statement :

(a) Chloride ion is oxidised by O_2
(b) Fe^{2+} is oxidised by iodine
(c) Iodide ion is oxidised by chlorine
(d) Mn^{2+} is oxidised by chlorine

[2] While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because :

(a) O_2 oxidises Mn^{2+} to Mn^{3+}
(b) O_2 oxidises both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
(c) Fe^{3+} oxidises H_2O to O_2
(d) Mn^{3+} oxidises H_2O to O_2

[3] Sodium fusion extract, obtained from aniline, on treatment with ion (II) sulphate and H_2SO_4 in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of:

(a) $Fe_4[Fe(CN)_6]_3$ (b) $Fe_3[Fe(CN)_6]_2$
(c) $Fe_4[Fe(CN)_6]_2$ (d) $Fe_3[Fe(CN)_6]_3$

Comprehension 5: The concentration of potassium ions inside a biological cell is atleast twenty times higher than the out side. The resulting potential difference across the cell is important in several processess such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is:

$$\mathrm{M}(s)\,|\,\mathrm{M}^+(aq), 0.05\,\mathrm{M}\,||\,M^+(aq), 1\,\mathrm{M}\,|\,\mathrm{M}(s)$$

For the above electrolytic cell, the magnitude of cell potential $|E_{\text{cell}}| = 70$ mV **(IIT 2010)**

[1] For the above cell :

(a) $E_{\text{cell}} < 0; \Delta G > 0$ (b) $E_{\text{cell}} > 0; \Delta G < 0$

(c) $E_{\text{cell}} < 0; \Delta G^\circ > 0$ (d) $E_{\text{cell}} > 0; \Delta G^\circ < 0$

[2] If the 0.05 M solution of M^+ is replaced by a 0.0025 M solution M^+, then the magnitude of cell potential will be:

(a) 35 mV (b) 70 mV

(c) 140 mV (d) 700 mV

Comprehension 6: The electrochemical cell shown below is a concentration cell.

$$M\,|\,M^{2+\text{(saturated solution of a}}_{\text{sparingly soluble salt)}}\; MX_2)\,||\,M^{2+}_{(0.001\ \text{mol dm}^{-3})}\,|\,M$$

The emf of the cell depends on the difference in concentrations of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059 V. **(IIT 2012)**

[1] The value of ΔG (kJ mol^{-1}) for the given cell is (take 1F = 96500 C mol^{-1}) :

(a) -5.7 (b) 5.7

(c) 11.4 (d) -11.4

[2] The solubility product (K_{sp}; mol^3 dm^{-9}) of MX_2 at 298 K based on the information available for the given concentration cell is (take $2.303 \times R \times 298/\mathrm{F} = 0.059$ V):

(a) 1×10^{-15} (b) 4×10^{-15}

(c) 1×10^{-12} (d) 4×10^{-12}

SOLUTIONS

Comprehension 1

At cathode two reductions occur, *i.e.*, of Ni^{2+} and H^+. Since, current efficiency of Ni^{2+} is 60%.

$\therefore$ Current efficiency for H^+ is 40%.

$$\text{Anode}: \quad 2OH^- \longrightarrow H_2O + 1/2O_2$$

$$\text{Cathode}: \quad Ni^{2+} + 2e \longrightarrow Ni$$

$$2H^+ + 2e \longrightarrow H_2$$

[1] (a) At cathode $\left(\frac{w}{E}\right) = \frac{i \cdot t}{96500} = \frac{15 \times 60 \times 60}{96500} = 0.5596$

or

At anode

At cathode Ni and H_2 both are formed and thus

$$w_{Ni} = \frac{0.5596 \times 60}{100} \times \frac{58.71}{2} = \mathbf{9.856\ g}$$

$$w_{H_2} = \frac{0.5596 \times 40}{100} \times \frac{2}{2} = \mathbf{0.2238\ g}$$

$$\therefore V_{H_2} \text{ at NTP} = \frac{0.2238 \times 22.4}{2} = \mathbf{2.51\ litre}$$

[2] (d) Volume on which Ni coated $= 4 \times 2 \times \text{thickness} = \frac{w}{d}$

$$\therefore \quad \text{Thickness} = \frac{w}{d \times 8} = \frac{9.856}{8.9 \times 8} = 0.138\,\text{cm}$$

$\therefore$ Thickness $(d) = \mathbf{0.138\ cm}$

[3] (c)

$$w_{H_2} = 0.2238\,\text{g}$$

$$V_{H_2} = \frac{0.2238 \times 22.4}{2} = \mathbf{2.51\ litre}$$

[4] (b) $w_{O_2} = 0.5596 \times 8 = 4.4768\,\text{g}$

$$\therefore \quad V_{O_2} = \frac{4.4768 \times 22.4}{32} = \mathbf{3.13\ litre}$$

Comprehension 2

[1] (c) **[2]** (b), **[3]** (b), **[4]** (a) **[5]** (d)

$Fe \longrightarrow Fe^{2+} + 2e;\ E^\circ_{OP} = +0.440\,V;$

$$-\Delta G^\circ_1 = 2 \times 0.440 \times F$$

$Fe^{3+} + 3e \longrightarrow Fe;\ E^\circ_{RP} = -0.036\,V;$

$$-\Delta G^\circ_2 = 3 \times (-0.036) \times F$$

$\therefore Fe^{3+} + e \longrightarrow Fe^{2+}; -1 \times E^\circ F$

$$= 2 \times 0.440 \times F - 3 \times 0.036 \times F$$

$$= +0.772\,F$$

$$\therefore \quad E^\circ = +\mathbf{0.772\ V}$$

Cell No. 1 : The cell is $Fe|Fe^{2+}||Fe^{3+}|Fe$

$3Fe \longrightarrow 3Fe^{2+} + 6e;$

$E^\circ_{OP} = +0.440\,V$

$$\begin{array}{ll} 2Fe^{3+} + 6e \longrightarrow 2Fe; & E^\circ_{RP} = -0.036\,V \\ \hline Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+}; & E^\circ_{cell} = \mathbf{0.404\ V} \end{array}$$

$+\Delta G^\circ = -nE^\circ F = -6 \times 0.404\,F = -\mathbf{2.424}\,\boldsymbol{F}$

Cell No. 2 : The cell is $Fe|Fe^{2+}||Fe^{3+}, Fe^{2+}|Pt$

$$\begin{array}{ll} Fe \longrightarrow Fe^{2+} + 2e; & E^\circ_{OP} = +0.440\,V \\ 2Fe^{3+} + 2e \longrightarrow 2Fe^{2+}; & E^\circ_{RP} = +0.772\,V \\ \hline Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+}; & E^\circ_{cell} = \mathbf{1.212\ V} \end{array}$$

$\therefore \quad \Delta G^\circ = -2 \times 1.212 \times F = -2.424\,F$

Cell No. 3 : The cell is $Fe|Fe^{3+}||Fe^{3+}, Fe^{2+}|Pt$

$$\begin{array}{ll} Fe \longrightarrow Fe^{3+} + 3e; & E^\circ = +0.036\,V \\ 3Fe^{3+} + 3e \longrightarrow 3Fe^{2+}; & E^\circ = 0.772\,V \\ \hline Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+}; & E^\circ = 0.808\,V \end{array}$$

$\Delta G^\circ = -3 \times 0.808 \times F = -\mathbf{2.424}\,\boldsymbol{F}$

Comprehension 3

[1] (b) Meq. of $Cl^- = 4 \times 500 = 2000$

$\therefore$ Eq. of $Cl^- = 2 =$ Eq. of Cl_2

$\therefore$ Mole of $Cl_2 = \mathbf{1}$ $\qquad [\because 2Cl^- \rightarrow Cl_2 + 2e]$

[2] (d) Eq. of Na $= \frac{4 \times 500}{1000} = 2$

mass of 2 [NaHg] = 2 [23 + 200] = **446 g**

[3] (d) $\frac{w}{E} = \frac{Q}{9.6500}$ $\qquad \left(\frac{w}{E} = 2\right)$

$\therefore$ Q = 2 × 96500 = 193000

Comprehension 4

[1] (c) $2I^- + Cl_2 \longrightarrow I_2 + 2Cl^-$

$\therefore E_{redox} = E^\circ_{RP_{Cl_2}} + E^\circ_{OP_{I_2}}$

$= 1.36 - 0.54 = \mathbf{0.82\ V}$

[2] (d) $4Mn^{3+} + 2H_2O \longrightarrow 4Mn^{2+} + O_2 + 4OH^-$

$E_{redox} = E^\circ_{RP_{Mn}} + E^\circ_{OP_{H_2O}}$

$= 1.50 - 1.23 = 0.27\,V$

$\therefore$ Reaction is possible

whereas for Fe^{3+} and H_2O

$E_{redox} = E^\circ_{RP_{Fe}} + E^\circ_{OP_{H_2O}}$

$= 0.77 - 1.23 = -0.46\,V$

Thus Fe^{3+} is not reduced by H_2O.

[3] (a)

Comprehension 5

The given cell is not electrolytic cell as reported. It is cencentration cell (a type of electrochemical cell). Also E° or E may be > 0 or < 0 but ΔG is either +ve or −ve and not > 0 or < 0.

As given $|E_{cell}| = 70$ mV means + ve or − ve value

Now $\quad E_{cell} = \underset{\text{R.H.S.}}{E_{OP}} + \underset{\text{L.H.S.}}{E_{RP}}$

$$= E^{\circ}_{OP_{M/M^+}} - \frac{0.059}{1}\log[M^+]_{\text{L.H.S.}} + E^{\circ}_{RP^{\circ}_{M^+/M}} + \frac{0.059}{1}\log[M^+]_{\text{R.H.S.}}$$

$$= 0.059\log\frac{[M^+]_{\text{R.H.S.}}}{[M^+]_{\text{L.H.S.}}}$$

$$= 0.059\log\frac{1}{0.05} = 0.059\times 1.30 = 0.076\,\text{V} = 76\,\text{mV} \simeq 70\,\text{mV}$$

[1] (b) $E_{\text{cell}} = +ve$ and $\Delta G = -\text{ve}$

[2] (c) $E_{\text{cell}} = 0.059\log\frac{1}{0.0025} = 0.059\log\frac{1}{(0.05)^2}$

$$= 0.059\times 2\times 0.76 = 0.146\,\text{V} \simeq 140\,\text{mV}$$

Comprehension 6

[1] (d) At anode : $M(s) \longrightarrow M^{2+}(aq.) + 2e^-$

At cathode : $M^{2+}(aq.) + 2e^- \longrightarrow M(s)$

n-factor of the cell reaction is 2.

$$\Delta G = -nFE_{cell} = -2\times 96500\times 0.059 = -113873\ \text{kJ/mole}$$
$$= -11.387\ \text{kJ/mole} = -11.4\ \text{kJ/mol}$$

[2] (b) $M\,|\,M^{2+}$ (saturated solution of salt MX_2) $||$ $M^{2+}(0.001M)$ emf of concentration cell,

$$E_{cell} = \frac{0.059}{n}\log\frac{[M^{2+}]_{\text{R.H.S.}}}{[M^{2+}]_{\text{L.H.S.}}}$$

$$0.059 = \frac{0.059}{2}\log\frac{[0.001]}{[M^{2+}]_{\text{L.H.S.}}}$$

$$\therefore [M^{2+}]_{\text{L.H.S.}} = 10^{-5}\,M$$

Let solubility of salt be S mol/litre

thus $\underset{(S)}{MX_2} \longrightarrow \underset{S}{M^{2+}} + \underset{2S}{2X^-}$

$$\therefore K_{sp} = 4s^3 = 4\times(10^{-5})^3 = 4\times 10^{-15}$$

STATEMENT-EXPLANATION PROBLEMS

In each sub question given below a statement (**S**) and explanation (**E**); Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) **S** is correct but **E** is wrong

(b) **S** is wrong but **E** is correct

(c) Both **S** and **E** are corect and **E** is correct explanation of **S**

(d) Both **S** and **E** are correct but **E** is not correct explanation of **S**

1. S : Anode is the electrode at which oxidation occurs and cathode is the electrode at which reduction occurs.

E : Anode and cathode in electrochemical cells and electrolyte cells have opposite polarity.

2. S : An irreversible cell is $Zn | H_2SO_4 | Ag$ showing redox change :

$$\begin{array}{l} Zn \longrightarrow Zn^{2+} + 2e \\ 2H^+ + 2e \longrightarrow H_2 \\ \hline Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2 \end{array}$$

E : The cell on connecting through another cell having its potential slightly greater than test cell, the redox reaction becomes:

$$\begin{array}{l} 2Ag \longrightarrow 2Ag^+ + 2e \\ 2H^+ + 2e \longrightarrow H_2 \\ \hline 2Ag + H_2SO_4 \longrightarrow Ag_2SO_4 + H_2 \end{array}$$

3. S : E°_{cell} is an intensive property.

E : $\frac{\Delta G^\circ}{n}$ is also an intensive property.

4. S : H_2S reacts with oxygen under standard conditions in acid medium to give H_2O and sulphur.

E : $E^\circ_{H^+/O_2/Pt} > E^\circ_{H^+/H_2S/S}$

5. S : The standard reduction potential of M^{n+}/M electrode increases with increase in activity of M^{n+} ion.

E : The standard reduction potential is given by :

$$E_{RP} = E^\circ_{RP} + \frac{0.059}{n}\log[M^{n+}]$$

6. S : The concentration cell $\underset{P_1}{PtH_2}\Big| HCl \Big| \underset{P_2}{H_2Pt}$ would show spontaneous flow of current only when $P_1 > P_2$ whereas the concentration cell $PtH_2 \Big| \underset{C_1}{HCl} \Big\| \underset{C_2}{HCl} \Big| H_2Pt$ show spontaneous flow of current only when $C_2 > C_1$.

E : Case I : $E_{cell} = \frac{0.059}{2}\log\frac{P_2}{P_1}$

Case II : $E_{cell} = \frac{0.059}{1}\log\frac{C_1}{C_2}$

7. S : The reference electrode of silver-silver chloride is used as secondary reference electrode.

E : The electrode is reversible with respect to Cl^- ions.

8. S : Passage of charge through $CuSO_4$ (aq) solution in presence of Pt electrode increases its pH.

E : Concentration of $[OH^-]$ in solution decreases.

9. S : If two half reaction with electrode potential E°_1 and E°_2 gives a third half reaction, then

$$\Delta G^\circ_3 = \Delta G^\circ_1 + \Delta G^\circ_2$$

E : $E^\circ_3 = E^\circ_1 + E^\circ_2$

10. S : 1 Faraday is the charge that liberates 1 eq. of metal at cathode.

E : Passage of 1 Faraday charge through *aq.* $MgCl_2$ liberates 12 g Mg at cathode.

11. S : Electrolysis involves electronation or de-electronation as a result of passage of current.

E : The species undergoes electronation at anode and other show de-electronation at cathode.

12. S : Very pure form of iron does not show rusting.

E : Rusting is catalysed by impurities present in iron and H^+ ions.

13. S : The cathode of electrolytic cell during electrolysis of NaCl (aq) on addition of little litmus shows a blue colour.

E : At cathode : $2H^+ + 2e \longrightarrow H_2$. The reaction at cathode give rise to an increase in pH ranging in alkaline medium and litmus shows blue colour.

14. S : In concentration cell neither electronation occurs at cathode nor de-electronation at anode.

E : The electrical energy is produced due to decrease in free energy during the transfer of concentration for high to low region.

15. S : In case of H^+ and Na^+ present in a solution discharge of H^+ is preferred at cathode.

E : The higher is discharge potential of ion, lesser is its tendency to get discharged.

16. S : Milliequivalent of a metal discharged at cathode during electrolysis $= \frac{i \cdot t}{96.5}$

E : This is faradays I law of electrolysis.

17. S : Pt H_2/HCl at 25°C $E^\circ_H = 0$.

E : For primary reference electrode $E^\circ_{H/H^+} = 0$.

18. S : $\left(\frac{\partial E}{\partial T}\right)_P$ is called temperature coefficient of e.m.f.

E : $\left(\frac{\partial E}{\partial T}\right)_P$ may be +ve, –ve and depends upon heat of reaction.

19. S : Liquid junction potential can be eliminated by putting a salt bridge of KCl.

E : The function of salt bridge is to remove liquid junction potential because the salt used has same speed of cations and anions.

20. S : The electrolytic cells involve conversion of electrical energy into chemical energy.

E : An increase in free energy is responsible for the flow of current.

21. S : During electrolysis of CH_3COONa the molar ratio of gases formed at anode and cathode is 2 : 1.

E : Anode : $2CH_3COO^- \longrightarrow C_2H_6 + 2CO_2 + 2e$

Cathode : $2H^+ + 2e \longrightarrow H_2$

22. S : Electrolysis of $CuCl_2$ (*aq*) gives 1 mole of Cu and 1 mole of Cl_2 by the passage of suitable charge.

E : Equal equivalents of Cu and Cl_2 are formed during the passage of same charge.

23. S : A copper rod turns colourless solution of $ZnSO_4$ to light blue.

E : Zn reduces Cu^{2+} to Cu.

24. S : Anode possesses negative polarity in electrochemical cell.

E : Anode is the electrode which show liberation of electrons and thus electrode acquires negative charge because electrons are left on electrode.

25. S : Zinc protects the iron better than tin even after it cracks.

E : $E^\circ_{OP_{Zn}} < E^\circ_{OP_{Fe}}$ but $E^\circ_{OP_{Sn}} > E^\circ_{OP_{Fe}}$

26. S : A dry cell becomes dead after a long time, even if it has not been used.

E : Reaction of NH_4Cl and Zn is spontaneous one.

27. S : The anode of Daniell cell possesses negative polarity.

E : The zinc electrode shows oxidation and thus becomes –vely charged with respect to surrounding solution.

28. S : Rusting of iron is favoured by moist air, CO_2 and O_2.

E : Purest form of metal is not corroded.

29. S : Discharge potential of Na^+ is more than H^+.

E : E°_{Na/Na^+} is lesser than E°_{H/H^+}.

30. S : Discharge potential of Cl^- is lesser than OH^-.

E : $E^\circ_{Cl/Cl^-} < E^\circ_{H_2O/OH^-}$.

ANSWERS (Statement Explanation Problems)

1. (d) Both are facts.

2. (c) In reversible cell, redox change is reversed if it is connected with another cell of slightly higher e.m.f. but in test cell it is not so in this cell.

3. (c) $-\Delta G^\circ = nE^\circ F \quad \therefore \; E^\circ = \frac{-\Delta G^\circ}{nF}$. Since, ΔG is intensive property and then E° is also intensive property.

4. (c) The half cell reactions gives a redox change with +ve value of $\overset{\circ}{E}_{\text{cell}}$

$$\begin{array}{ll} 2H^+ + \frac{1}{2}O_2 + 2e \longrightarrow H_2O & \overset{\circ}{E}_{RP} = A \\ \underline{H_2S \longrightarrow 2H^+ + S + 2e} & \overset{\circ}{E}_{OP} = B \\ H_2S + \frac{1}{2}O_2 \longrightarrow H_2O + S & \end{array}$$

$$\overset{\circ}{E}_{\text{cell}} = \overset{\circ}{E}_{OP_{H_2S/H^+/S}} + \overset{\circ}{E}_{RP_{H^+/O_2/Pt}}$$

$$\overset{\circ}{E}_{\text{cell}} = +\text{ve} \qquad (\text{Given } \overset{\circ}{E}_{RP_{H^+/O_2/Pt}} > \overset{\circ}{E}_{RP_{H^+/H_2S/S}})$$

5. (c) Explanation is correct reason for statement.

6. (a)

$$\begin{array}{c|c|c} H_2 & HCl & H_2 \\ P_1 & & P_2 \end{array} \qquad H_2 \left| \begin{array}{c} HCl \\ C_1 \end{array} \right\| \begin{array}{c} HCl \\ C_2 \end{array} \Big| H_2$$

$$\begin{array}{ll} H_2(P_1) \longrightarrow 2H^+ + 2e & H_2 \longrightarrow 2H^+(C_1) + 2e \\ \underline{2H^+ + 2e \longrightarrow H_2(P_2)} & \underline{2H^+_{C_2} + 2e \longrightarrow H_2} \\ H_2(P_1) \longrightarrow H_2(P_2) & H^+_{C_2} \longrightarrow H^+_{C_1} \end{array}$$

$$\therefore \; E_{\text{cell}} = \frac{0.059}{2}\log\frac{P_1}{P_2} \qquad E_{\text{cell}} = \frac{0.059}{2}\log\frac{C_2}{C_1}$$

if $P_1 > P_2$ $E_{\text{cell}} = +\text{ve}$ if $C_2 > C_1$ $E_{\text{cell}} = +\text{ve}$

7. (d) Both are facts.

8. (c) Anode : $2H_2O \longrightarrow 4H^+ + O_2 + 4e$

or $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$

Cathode : $Cu^{2+} + 2e \longrightarrow Cu$.

9. (a) In such case E° are not additive.

10. (a) $MgCl_2(aq)$ shows discharge of H^+ and not of Mg^{2+}.

11. (a) Electronation (reduction) occurs at cathode and de-electronation (oxidation) occurs at anode.

12. (d) Both are facts and true.

13. (c) Explanation is correct reason for statement.

14. (b) In concentration cells no doubt oxidation occurs at anode and reduction at cathode but net redox change is zero.

15. (c) Explanation is correct reason for statement.

16. (c) Explanation is correct reason for statement.

17. (b) Primary reference electrode is $\underset{1\text{ atm}}{PtH_2} \mid \underset{1M}{HCl}$ at 25°C its

$E^\circ_H = 0$.

18. (d) $\Delta H = nF\left[T\left(\frac{\partial E}{\partial T}\right)_P - E\right]$; where $\left(\frac{\partial E}{\partial T}\right)_P$ is temperature coefficient.

19. (c) Explanation is correct reason for statement.

20. (a) In electrolytic cell, electrical energy is given to produce chemical changes.

21. (b) The molar ratio of gases at anode and cathode is 3 : 1.

22. (c) Anode : $2Cl^- \longrightarrow Cl_2 + 2e$

Cathode : $Cu^{2+} + 2e \longrightarrow Cu$

23. (b) $Zn + Cu^{2+} \longrightarrow \underset{\text{Colourless}}{Zn^{2+}} + Cu$. $CuSO_4$ solution turns light blue on addition of Zn.

24. (c) Explanation is correct reason for statement.

25. (a) $\overset{\circ}{E}_{OP_{Zn}} > \overset{\circ}{E}_{OP_{Fe}}; \overset{\circ}{E}_{OP_{Sn}} < \overset{\circ}{E}_{OP_{Fe}}$

26. (c) Explanation is correct reason for statement.

27. (c) $\underset{\text{Electrode}}{Zn} \longrightarrow \underset{\text{Solution}}{Zn^{2+}} + 2e$;

The electrons remaining on Zn electrode develops negative polarity.

28. (d) Both are correct.

29. (a) Higher is discharge potential, lesser is tendency to get discharged. In case of cation discharge potential refers for $\overset{\circ}{E}_{OP}$.

$$\overset{\circ}{E}_{OP\,Na/Na^+} < \overset{\circ}{E}_{OP\,H/H^+}$$

30. (b) In case of anion discharge potential refers for $\overset{\circ}{E}_{RP}$ and therefore $\overset{\circ}{E}_{OP\,Cl^-/Cl} > \overset{\circ}{E}_{OP\,OH^-/H_2O}$.

MATCHING TYPE PROBLEMS

Type I : Only One Match Is Possible

1. For a given reaction:

$$Fe + 2Fe^{2+} \longrightarrow 3Fe^{2+}$$

(3) (A) $E_1^\circ = E^\circ_{Fe/Fe^{2+}} + E^\circ_{Fe^{3+}/Fe}$	(i) $n=2$
(1) (B) $E_2^\circ = E^\circ_{Fe/Fe^{2+}} + E^\circ_{Fe^{3+}/Fe^{2+}}$	(ii) $n=3$
(2) (C) $E_3^\circ = E^\circ_{Fe/Fe^{3+}} + E^\circ_{Fe^{3+}/Fe^{2+}}$	(iii) $n=6$

Type II : More Than One Match Are Possible

12345 **2.**

(A) Corrosion	(i) Brown deposits on Fe
45 (B) Rusting	(ii) Green deposits on Cu
(C) Electrolysis 458	(iii) Blackening of Ag coins
67 (D) Faraday	(iv) Electronation
	(v) De electronation
	(vi) Charge on one mole electron
	(vii) 96500 C
	(viii) Electroplating

(145) **3.**

(A) Calomel electrode	1. Reversible with respect to Cl^-
(15) (B) Ag-AgCl(s) electrode	2. Reversible with respect to H^+
(236) (C) N.H. Electrode	3. $E° = 0$
(2) (D) $\underset{2\text{ atm}}{PtH_2}$ $\underset{1\,M}{H^+}$	4. $E°$ varies with KCl molarity
	5. Secondary reference electrodes
	6. Primary reference electrode

1356 **4.**

(A) $Zn \mid Zn^{2+} \mid\mid Cu^{2+} \mid Cu$	1. Reversible cell
456 (B) $Ag \mid Ag^+ \mid\mid H^+ \mid H_2$	2. Irreversible cell
4567 (C) Lead storage Battery	3. $E^\circ_{cell} = +ve$
1234567 (D) $Cd \mid CdO(s)\ KOH(aq) \mid\mid NiO_2(s) \mid Ni$	4. $E^\circ_{cell} = -ve$
	5. Redox cells
	6. $n=2$
	7. No liquid junction potential

Type III : One Match From Each List

5.

List A	List B	List C
(a i) 1. Coulometry	a. Electro deposition	(i) Analysis of a gas sample
(b i) 2. Eudiometry	b. Combustion in oxygen	(ii) Copper voltameter
(c 5) 3. Potentiometry	c. Titration	(iii) Optical rotation
(D4) 4. Conductometry	d. Micellisation study	(iv) Migration of ions
3 e 5. Polarimetry	e. Optical activity	(v) Glass electrode

6. The standard reduction potential data at 25°C is given below : **[JEE (Advanced) II 2013]**

$E°$ $(Fe^{3+}, Fe^{2+}) = +0.77\ V$;

$E°$ $(Fe^{2+}, Fe) = -0.44\ V$

$E°$ $(Cu^{2+}, Cu) = +0.34\ V$;

$E°$ $(Cu^{+}, Cu) = +0.52\ V$

$E°$ $(O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O] = +1.23\ V$;

$E°$ $(O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-] = +0.40\ V$

$E°$ $(Cr^{3+}, Cr) = -0.74\ V$;

$E°$ $(Cr^{2+}, Cr) = -0.91\ V$;

Match $E°$ of the redox pair in List I with the values given in List II and select the correct answer using the code given below the lists :

List I	List II
(P) $E°$ (Fe^{3+}, Fe)	(1) – 0.18 V
(Q) $E°$ $(4H_2O \rightleftharpoons 4H^+ + 4OH^-)$	(2) –0.4 V
(R) $E°$ $(Cu^{2+} + Cu \rightarrow 2Cu^+)$	(3) – 0.04 V
(S) $E°$ (Cr^{3+}, Cr^{2+})	(4) – 0.83 V

Codes:

	P	*Q*	*R*	*S*
(a)	4	1	2	3
(b)	2	3	4	1
(c)	1	2	3	4
(d)	3	4	1	2

ANSWERS

1. A—iii; B—i; C—ii

2. A—i, ii, iii, iv, v; B—i, iv, v; C—iv, v, viii; D—vi, vii

3. A—1, 4, 5; B—1, 5; C—2, 3, 6; D—2

4. A—1, 3, 5, 6; B—2, 4, 5, 6; C—1, 3, 5, 6, 7; D—1, 3, 5, 6, 7

5. 1-a-ii; 2-b-i; 3-c-v; 4-d-iv; 5-e-iii

6. (d)

$3e + Fe^{3+} \longrightarrow Fe$; $\quad \Delta G_1^\circ = -3 \times E_1^\circ \times F$

Given

$e + Fe^{3+} \longrightarrow Fe^{2+}$; $\quad 0\Delta G_2^\circ = -1 \times 0.77 \times F$

$2e + Fe^{2+} \longrightarrow Fe$; $\quad \Delta G_3^\circ = -2 \times (-0.44) \times F$

On adding last two

$Fe^{3+} + 3e \longrightarrow Fe$; $\Delta G_1^\circ = \Delta G_2^\circ + \Delta G_3^\circ$

$\therefore \quad \Delta G_1^\circ = -0.77F + 0.88F = +0.11F$

$\therefore -3E_1^\circ \times F = +0.11F$

$\therefore E_1^\circ = -0.04$

Thus *P* is (3)

$Cr^{3+} + e \longrightarrow Cr^{2+}$; $\quad \Delta G_1^\circ = -1 \times E_1^\circ \times F$

Given

$Cr^{3+} + 3e \longrightarrow Cr$; $\quad \Delta G_2^\circ = -3 \times (-0.74) \times F \ldots$ (i)

$Cr^{2+} + 2e \longrightarrow Cr$; $\quad \Delta G_3^\circ = -2 \times (-0.91) \times F \ldots$ (ii)

On substracting (ii) from (i)

$Cr^{3+} + e \longrightarrow Cr^{2+}$; $\quad \Delta G_1^\circ = \Delta G_2^\circ - \Delta G_3^\circ$

$\Delta G_1^\circ = +2.22F - 1.82F$

$\therefore -1 \times E_1^\circ F = -0.4F$

$E_1^\circ = -0.4V$

Thus *S* is (2)

8

Redox Titrations

1. The most important fact for solving the problems of redox changes is to evaluate equivalent mass of redox correctly using the formula:

$$\text{Eq. mass of reductant or oxidant} = \frac{\text{Molar mass of reductant or oxidant}}{\text{No. of electrons lost or gained by one molecule of reductant or oxidant respectively}}$$

2. $$\text{Valence factor} = \frac{\text{Molar mass}}{\text{Equivalent mass}}$$

or No. of electrons lost or gained by one molecule of reductant or oxidant.

3. Calculate the Meq. of desired substance and then calculate its mass by:

$$\begin{aligned}\text{Meq.} &= N \times V_{\text{in mL}}\\ &= M \times \text{Valence factor} \times V_{\text{in mL}}\end{aligned}$$

$$\text{Meq.} = \frac{\text{Mass}}{\text{Eq. mass}} \times 1000$$

This equation gives mass of substance whose Eq. mass is substituted.

4. Be careful in deciding equivalent mass. First write redox change for each and then derive no. of electron lost or gained by one molecule of reductant or oxidant.

5. In case balanced equation is given, it is always advised to proceed with mole concept to avoid complications in equivalent mass determination.

6. Method to calculate equivalent mass of an oxidant/ reductant in :

(a) Intermolecular redox :

$$HNO_3 \longrightarrow N_2O$$
$$8e + 2N^{5+} \longrightarrow (N^+)_2$$

$$\therefore \quad E_{HNO_3} = \frac{M_{HNO_3}}{4}$$

$$\text{and} \quad E_{N_2O} = \frac{M_{N_2O}}{8}$$

(b) Intramolecular redox :

$$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$$
$$(N^{3-})_2 \longrightarrow (N^0)_2 + 6e$$
$$6e + (Cr^{6+})_2 \longrightarrow (Cr^{3+})_2$$
$$\overline{(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O}$$

$$\because \quad 1 \text{ mole } (NH_4)_2Cr_2O_7 = 1 \text{ mole } N_2$$
$$= 1 \times 6 \text{ eq. } N_2\left(E_{N_2} = \frac{M}{6}\right)$$
$$= 1 \times 6 \text{ eq. } (NH_4)_2Cr_2O_7$$

$\therefore$ 'n' factor for $(NH_4)_2Cr_2O_7 = 6$

$$\therefore \quad E_{(NH_4)_2Cr_2O_7} = \frac{M}{6}$$

or 1 mole $(NH_4)_2Cr_2O_7 = 1$ mole Cr_2O_3

$$= 1 \times 6 \text{ eq. } Cr_2O_3\left(E_{Cr_2O_3} = \frac{M}{6}\right)$$
$$= 6 \text{ eq. } (NH_4)_2Cr_2O_7$$

$\therefore$ 'n' factor for $(NH_4)_2Cr_2O_7 = 6$

$$\therefore \quad E_{(NH_4)_2Cr_2O_7} = \frac{M}{6}$$

(c) Disproprionation reaction :

$$H_3PO_2 \longrightarrow PH_3 + H_3PO_3$$
$$4e + P^+ \longrightarrow P^{3-}$$
$$[P^+ \longrightarrow P^{3+} + 2e] \times 2$$
$$\overline{3P^+ \longrightarrow P^{3-} + 2P^{3+}}$$

$$\text{or} \quad 3H_3PO_2 \longrightarrow PH_3 + 2H_3PO_3$$

$\therefore$ 3 mole $H_3PO_2 \equiv 1$ mole PH_3

$\therefore$ 1 mole $H_3PO_2 \equiv \frac{1}{3}$ mole PH_3

$$\equiv \frac{1}{3} \times 4 \text{ eq. } PH_3 \qquad \left(E_{PH_3} = \frac{M}{4}\right)$$
$$\equiv \frac{4}{3} \text{ eq. } H_3PO_2$$

$\therefore$ 'n' factor for $H_3PO_2 = \frac{4}{3}$

$$\therefore \quad E_{H_3PO_2} = \frac{M}{4/3} = \frac{3M}{4}$$

or $3 \text{ mole } H_3PO_2 \equiv 2 \text{ mole } H_3PO_3$

or $1 \text{ mole } H_3PO_2 \equiv \frac{2}{3} \text{ mole } H_3PO_3$

$$\equiv \frac{2}{3} \times 2 \text{ eq. } H_3PO_3 \quad \left(E_{H_3PO_3} = \frac{M}{2}\right)$$

$$\equiv \frac{4}{3} \text{eq. } H_3PO_2$$

$\therefore$ 'n' factor for $H_3PO_2 = \frac{4}{3}$

$$\therefore \quad E_{H_3PO_2} = \frac{M}{4/3} = \frac{3M}{4}$$

• NUMERICAL PROBLEMS •

1. Calculate the equivalent mass of each oxidant and reductant in:

(a) $FeSO_4 + KClO_3 \longrightarrow KCl + Fe_2(SO_4)_3$

(b) $Na_2SO_3 + Na_2CrO_4 \longrightarrow Na_2SO_4 + Cr(OH)_3$

(c) $Fe_3O_4 + KMnO_4 \longrightarrow Fe_2O_3 + MnO_2$

(d) $KI + K_2Cr_2O_7 \longrightarrow Cr^{3+} + 3I_2$

(e) $Mn^{4+} \longrightarrow Mn^{2+}$

(f) $NO_3^- \longrightarrow N_2$

(g) $N_2 \longrightarrow NH_3$

(h) $Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

(i) $FeC_2O_4 \longrightarrow Fe^{3+} + CO_2$

2. Calculate the equivalent mass of potassium permanganate ($KMnO_4$) in (i) neutral medium (ii) acidic medium (iii) alkaline medium, by oxidation number method. **(MLNR 1997)**

3. What is the mass of sodium bromate and molarity of solution to prepare 85.5 mL of 0.672N solution when half cell reactions are?

(i) $BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O.$

(ii) $2BrO_3^- + 12H^+ + 10e^- \longrightarrow Br_2 + 6H_2O$

(IIT 1987)

4. How many mL of 0.05M $KMnO_4$ (acidic) are required to oxidize 2.0 g of $FeSO_4$ in dilute solution?

5. Dichromate ion in acid solution oxidizes stannous ion as

$$3Sn^{2+} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$$

(a) If $SnCl_2$ is the source of Sn^{2+}, how many gram of $SnCl_2$ would be contained in 2 litre of 0.1N solution?

(b) If $K_2Cr_2O_7$ is the source of $Cr_2O_7^{2-}$, what is the normality of solution containing 4.9 g $K_2Cr_2O_7$ in 0.1 litre of solution? **(IIT 1987)**

6. 20 mL of 0.2M $MnSO_4$ are completely oxidized by 16 mL of $KMnO_4$ of unknown normality, each forming Mn^{4+} oxidation state. Find out the normality and molarity of $KMnO_4$ solution.

7. Metallic tin in the presence of HCl is oxidized by $K_2Cr_2O_7$ to stannic chloride. What volume of decinormal dichromate solution would be reduced by 1 g of tin? **(MLNR 1994)**

8. 5.5g of a mixture of $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ required 5.4 mL of 0.1N $KMnO_4$ solution for complete oxidation. Calculate mole of hydrated ferric sulphate in mixture. **(IIT 1989)**

9. 0.5 g sample containing MnO_2 is treated with HCl, liberating Cl_2. The Cl_2 is passed into a solution of KI and 30.0 cm^3 of 0.1M $Na_2S_2O_3$ are required to titrate the liberated iodine. Calculate the percentage of MnO_2 in sample. (Atomic mass of Mn = 55) **(Roorkee 1994)**

10. The equivalent mass of an element is 13.16. It forms an acidic oxide which with KOH forms a salt, isomorphous with K_2SO_4. Deduce Atomic mass of element.

11. In an ore, the only oxidizable material is Sn^{2+}. This ore is titrated with a dichromate solution containing 2.5 g of $K_2Cr_2O_7$ in 0.5 litre. A 0.40g sample of the ore required 10.0 cm^3 of titrant to reach equivalence point. Calculate the percentage of tin in ore. **(Roorkee 1993)**

12. 1g of H_2O_2 solution containing X% H_2O_2 by mass requires X mL of $KMnO_4$ for complete oxidation in acid medium. Calculate normality of $KMnO_4$ solution.

13. An element A in a compound ABD has an oxidation No. A^{n-}. It is oxidized by $Cr_2O_7^{2-}$ in acid medium. In an experiment 1.68×10^{-3} mole of $K_2Cr_2O_7$ was required for 3.26×10^{-3} mole of the compound ABD. Calculate new oxidation state of A.

14. 20 mL of a solution containing 0.2 g of impure sample of H_2O_2 reacts with 0.316 g of $KMnO_4$ (acidic). Calculate:

(a) Purity of H_2O_2

(b) Volume of dry O_2 evolved at 27°C and 750 mm P.

(IIT 1985)

15. Find out the % of oxalate ion in given sample of oxalate salt of which 0.3 g dissolved in 100 mL of water required 90 mL of $N/20$ $KMnO_4$ for complete oxidation.

16. 50 mL of an aqueous solution of H_2O_2 was treated with an excess of KI solution in dil. H_2SO_4, the liberated iodine required 20 mL of 0.1 N $Na_2S_2O_3$ solution for complete reaction. Calculate concentration of H_2O_2 in g/litre.

17. 1.2 g of a commercial sample of oxalic acid was dissolved in 200 mL of water. 10 mL of this sample required 8.5 mL of $N/10$ $KMnO_4$. Calculate % of purity of sample.

18. (a) 25 mL of H_2O_2 solution were added to excess of acidified solution of KI. The iodine so liberated required 20 mL of $0.1N$ $Na_2S_2O_3$ for titration. Calculate the strength of H_2O_2 in terms of normality, percentage and volume. **(MLNR 1996)**

(b) To a 25 mL H_2O_2 solution, excess of acidified solution of KI was added. The iodine liberated required 20 mL of 0.3 N sodium thiosulphate solution. Calculate the volume strength of H_2O_2 solution. **(IIT July 1997)**

19. Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of $KMnO_4$ (20 mL) acidified with dilute H_2SO_4. The same volume of the $KMnO_4$ solution is just decolourized by 10 mL of $MnSO_4$ in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO_2. The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute H_2SO_4. Write the balanced equations involved in the reactions and calculate the molarity of H_2O_2. **(IIT 2001)**

20. 0.56 g of limestone was treated with oxalic acid to give CaC_2O_4. The precipitate decolorized 45 mL of $0.2N$ $KMnO_4$ in acid medium. Calculate % of CaO in limestone. **(IIT 1988)**

21. 25 g of a sample of $FeSO_4$ was dissolved in water containing dil. H_2SO_4 and the volume made upto 1 litre. 25 mL of this solution required 20 mL of $N/10$ $KMnO_4$ for complete oxidation. Calculate % of $FeSO_4 \cdot 7H_2O$ in given sample.

22. $KMnO_4$ oxidizes X^{n+} ion to XO_3^-, itself changing to Mn^{2+} in acid solution. 2.68×10^{-3} mole of X^{n+} requires 1.61×10^{-3} mole of MnO_4^-. What is the value of n? Also calculate the atomic mass of X, if the mass of 1g-equivalent of XCl_n is 56.

23. 5.7 g of bleaching powder was suspended in 500 mL of water. 25 mL of this suspension on treatment with KI and HCl liberated iodine which reacted with 24.35 mL of $N/10$ $Na_2S_2O_3$. Calculate % of available Cl_2 in bleaching powder. **(Roorkee 1990)**

24. A solution of $0.1M$ $KMnO_4$ is used for the reaction:

$$S_2O_3^{2-} + 2MnO_4^- + H_2O \longrightarrow MnO_2 + SO_4^{2-} + OH^-$$

What volume of solution in mL will be required to react with 0.158 g of $Na_2S_2O_3$? **(MLNR 1991)**

25. A sample of $Fe_2(SO_4)_3$ and FeC_2O_4 was dissolved in dil. H_2SO_4. The complete oxidation of reaction mixture required 40 mL of $N/16$ $KMnO_4$. After the oxidation, the reaction mixture was reduced by Zn and dil. H_2SO_4. On again oxidation by same $KMnO_4$, 60 mL were required. Calculate the ratio of Meq. of $Fe_2(SO_4)_3$ and FeC_2O_4 in mixture.

26. A solution of 0.2 g of a compound containing Cu^{2+} and $C_2O_4^{2-}$ ions on titration with $0.02M$ $KMnO_4$ in presence of H_2SO_4 consumes 22.6 mL oxidant. The resulting solution is neutralized by Na_2CO_3, acidified with dilute CH_3COOH and titrated with excess of KI. The liberated I_2 required 11.3 mL of $0.05M$ $Na_2S_2O_3$ for complete reduction. Find out mole ratio of Cu^{2+} and $C_2O_4^{2-}$ in compound. **(IIT 1991)**

27. 1 g sample of $AgNO_3$ is dissolved in 50 mL of water. It is titrated with 50 mL of KI solution. The AgI precipitated is filtered off. Excess of KI in filtrate is titrated with $M/10$ KIO_3 in presence of $6M$ HCl till all I^- converted into ICl. It requires 50 mL of $M/10$ KIO_3 solution. 20 mL of the same stock solution of KI requires 30 mL of $M/10$ KIO_3 under similar conditions. Calculate % of $AgNO_3$ in sample. The reaction is:

$$KIO_3 + 2KI + 6HCl \longrightarrow 3ICl + 3KCl + 3H_2O$$

(IIT 1992)

28. 1.6 g of pyrolusite ore was treated with 50 cm^3 of 1.0 N oxalic acid and some sulphuric acid. The oxalic acid left undecomposed was raised to 250 cm^3 in a flask. 25 cm^3 of this solution when titrated with 0.1 N $KMnO_4$ required 32 cm^3 of the solution. Find out the percentage of pure MnO_2 in the sample and also the percentage of available oxygen. **(Roorkee 1996)**

29. An aqueous solution containing 0.10 g KIO_3 (formula mass = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated I_2 consumed 45 mL of thiosulphate solution to decolourize the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution. **(IIT 1998)**

30. 2.6 g sample of pyrolusite was boiled with 65 mL of N oxalic acid and excess of dil. H_2SO_4. The liquid was then filtered and the residue washed. The filtrate and the washing were mixed and made upto 500 mL. 100 mL of this solution required 50 mL of $N/10$ $KMnO_4$. Calculate % of MnO_2 in sample.

31. 25 mL of a solution containing Fe^{2+} and Fe^{3+} sulphate acidified with H_2SO_4 is reduced by 3 g of metallic zinc. The solution required 34.25 mL of $N/10$ solution of $K_2Cr_2O_7$ for oxidation. Before reduction with zinc, 25 mL of the same solution required 22.45 mL of same $K_2Cr_2O_7$ solution. Calculate the strength of $FeSO_4$ and $Fe_2(SO_4)_3$ in solution.

32. A sample of $MnSO_4 \cdot 4H_2O$ is strongly heated in air. The residue (Mn_3O_4) left was dissolved in 100 mL of

$0.1N$ $FeSO_4$ containing dil. H_2SO_4. This solution was completely reacted with 50 mL of $KMnO_4$ solution. 25 mL of this $KMnO_4$ solution was completely reduced by 30 mL of 0.1 N $FeSO_4$ solution. Calculate the amount of $MnSO_4 \cdot 4H_2O$ in sample. **(Roorkee 2001)**

33. A solution contains mixture of H_2SO_4 and $H_2C_2O_4$. 25 mL of this solution requires 35.5 mL of $N/10$ NaOH for neutralization and 23.45 mL of $N/10$ $KMnO_4$ for oxidation. Calculate:

(a) Normality of $H_2C_2O_4$ and H_2SO_4.

(b) Strength of $H_2C_2O_4$ and H_2SO_4.

Assume molar mass of $H_2C_2O_4 = 126$

34. Calculate the mass of MnO_2 and the volume of HCl of specific gravity $1.2\ g\ mL^{-1}$ and 4% nature by mass, needed to produce 1.78 litre of Cl_2 at STP by the reaction:

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

35. A sample of hydrazine sulphate ($N_2H_6SO_4$) was dissolved in 100 mL water. 10 mL of this solution was reacted with excess of $FeCl_3$ solution and warmed to complete the reaction. Ferrous ions formed were estimated and it required 20 mL of $M/50$ $KMnO_4$ solution. Estimate the mass of hydrazine sulphate in one litre of solution:

Given, $4Fe^{3+} + N_2H_4 \longrightarrow N_2 + 4Fe^{2+} + 4H^+$

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(IIT 1988; MLNR 1993, 96)

36. A 1 g sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made upto 100 mL. An aliquot of 25 mL of this solution requires 17 mL of $0.0167M$ solution of an oxidant for titration. Calculate no. of electrons taken up by oxidant in the above titration. **(IIT 1991)**

37. 0.5 g sample of iron containing mineral mainly in the form of $CuFeS_2$ was reduced suitably to convert all the ferric ions into ferrous ions ($Fe^{3+} \rightarrow Fe^{2+}$) and was obtained as solution. In the absence of any interferring radical, the solution required 42 mL of $0.01\ M\ K_2Cr_2O_7$ for titration. Calculate % of $CuFeS_2$ in sample.

38. A mixture of $H_2C_2O_4$ and $NaHC_2O_4$ weighing 2.02 g was dissolved in water and the solution made upto one litre. 10 mL of this solution required 3.0 mL of $0.1N$ NaOH solution for complete neutralization. In another experiment 10 mL of same solution in hot dilute H_2SO_4 medium required 4 mL of $0.1N$ $KMnO_4$ for complete neutralization. Calculate the mass of $H_2C_2O_4$ and $NaHC_2O_4$ in mixture. **(IIT 1990)**

39. An equal volume of reducing agent is titrated separately with $1M$ $KMnO_4$ in acid, neutral and alkaline medium. The volumes of $KMnO_4$ required are 20 mL, 33.3 mL and 100 mL in acid, neutral and alkaline medium respectively. Find out oxidation state of Mn in each reaction product. Give balance equation. Find the volume of $1\ M\ K_2Cr_2O_7$ consumed if same volume of reductant is titrated in acid medium. **(IIT 1989)**

40. 0.2828 g of iron wire was dissolved in excess dilute H_2SO_4 and the solution was made upto 100 mL. 20 mL of this solution required 30 mL of $N/30\ K_2Cr_2O_7$ solution for exact oxidation. Calculate % purity of Fe in wire.

41. The reaction $Cl_2(g) + S_2O_3^{2-} \rightarrow SO_4^{2-} + Cl^-$ is to be carried out in basic medium. Starting with 0.15 mole of Cl_2, 0.010 mole $S_2O_3^{2-}$ and 0.30 mole of OH^-, how many mole of OH^- will be left in solution after the reaction is complete? Assume no other reaction occurs.

42. Mg can reduce NO_3^- to NH_3 in basic solution:

$$NO_3^- + Mg(s) + H_2O \longrightarrow Mg(OH)_2(s) + OH^-(aq.) + NH_3(g)$$

A 25.0 mL sample of NO_3^- solution was treated with Mg. The $NH_3(g)$ was passed into 50 mL of $0.15\ N$ HCl. The excess HCl required 32.10 mL of $0.10\ M$ NaOH for its neutralization. What was the molarity of NO_3^- ions in the original sample?

43. A new developed method for water treatment uses chlorine dioxide, ClO_2 rather than Cl_2 itself. ClO_2 can be obtained by passing $Cl_2(g)$ into concentrated solution of sodium chlorite $NaClO_2 \cdot NaCl(aq.)$ is the other product. If this reaction has a 97% yield, how many mole of ClO_2 are produced per gallon of 2.0 M $NaClO_2(aq.)$? (1 gallon = 3.78 litre)

44. A sample of ferrous sulphate and ferrous oxalate was dissolved in dil. H_2SO_4. The complete oxidation of reaction mixture required 40 mL of $N/15$ $KMnO_4$. After the oxidation, the reaction mixture was reduced by Zn and H_2SO_4. On again oxidation by same $KMnO_4$, 25 mL were required. Calculate the ratio of Fe in ferrous sulphate and oxalate.

45. Calculate the % of Cr in a sample of dichromate ore if 0.5 g of the sample after fusion in regular way is treated with 50 mL of 0.12 N ferrous ammonium sulphate and the excess of Fe^{2+} requires 15.05 mL of $K_2Cr_2O_7$. (1 mL of $K_2Cr_2O_7 = 0.006$ g Fe). Also find % of Cr_2O_3 in sample.

46. Hydroxylamine reduces iron III according to the equation

$4Fe^{3+} + 2NH_2OH \rightarrow N_2O + H_2O + 4Fe^{2+} + 4H^+$. Iron II thus produced is estimated by titration with standard $KMnO_4$ solution. The reaction is

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O.$$

A 10 mL of hydroxylamine solution was diluted to one litre. 50 mL of this diluted solution was boiled with an excess of Fe^{3+} solution. The resulting solution required 12 mL of $0.02M$ $KMnO_4$ solution for complete oxidation of Fe^{2+}. Calculate the mass of NH_2OH in one litre of original solution.

47. Chile salt peter, a source of $NaNO_3$ also contains $NaIO_3$. The $NaIO_3$ can be used as a source of iodine, produced in the following reactions.

$$IO_3^- + 3HSO_3^- \longrightarrow I^- + 3H^+ + 3SO_4^{2-} \quad ...(1)$$

$$5I^- + IO_3^- + 6H^+ \longrightarrow 3I_2(s) + 3H_2O \quad ...(2)$$

One litre of chile salt peter solution containing 5.80g $NaIO_3$ is treated with stoichiometric quantity of $NaHSO_3$. Now an additional amount of same solution is added to reaction mixture to bring about the second reaction. How many grams of $NaHSO_3$ are required in step I and what additional volume of chile salt peter must be added in step II to bring in complete conversion of I^- to I_2 ?

48. 30 mL of a solution containing 9.15 g/litre of an oxalate $K_xH_y(C_2O_4)_z \cdot nH_2O$ are required for titrating 27 mL of $0.12N$ NaOH and 36 mL of 0.12 N $KMnO_4$ separately. Calculate X, Y, Z and n. Assume all H-atoms are replaceable and X, Y, Z are in the simple ratio of g-atoms.

49. A polyvalent metal weighing 0.1 g and having atomic mass 51.0 reacted with dil. H_2SO_4 to give 43.9 mL of H_2 at STP. The solution containing the metal in the lower oxidation state was found to require 58.8 mL of $0.1N$ $KMnO_4$ for complete oxidation. What are valencies of metal?

50. 25 mL of a solution of ferric alum $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$ containing 1.25 g of the salt was boiled with iron when the reaction $Fe + Fe_2(SO_4)_3 \rightarrow 3FeSO_4$ occurred. The unreacted iron was filtered off and solution treated with $0.107N$ $KMnO_4$ in acid medium. What is titre value? If Cu had been used in place of Fe, what would have been titre value?

51. A 3.0 g sample containing Fe_3O_4, Fe_2O_3 and an inert impure substance is treated with excess of KI solution in presence of dilute H_2SO_4. The entire iron is converted to Fe^{2+} along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of dilute solution requires 11.0 mL of 0.5 M $Na_2S_2O_3$ solution to reduce the iodine present. A 50 mL of the diluted solution, after complete extraction of iodine requires 12.80 mL of 0.25 M $KMnO_4$ solution in dilute H_2SO_4 medium for the oxidation of Fe^{2+}. Calculate the percentage of Fe_2O_3 and Fe_3O_4 in the original sample. **(IIT 1996)**

52. The calcium contained in a solution of 1.048 g of a substance being analysed was precipitated with 25 mL $H_2C_2O_4$. The excess of $C_2O_4^{2-}$ in one fourth of filtrate was back titrated with 5 mL of 0.1025 N $KMnO_4$. To determine the conc. of $H_2C_2O_4$ solution, it was diluted four folds and titration of 25 mL of dilute solution used up 24.1 mL of same $KMnO_4$ solution. Calculate % of Ca in substance.

53. 0.804 g sample of iron ore was dissolved in acid. Iron was oxidized to +2 state and it required 47.2 mL of 0.112 N $KMnO_4$ solution for titration. Calculate % of Fe and Fe_3O_4 in ore. **(Roorkee 1988)**

54. A solution is containing 2.52 g $litre^{-1}$ of a reductant. 25 mL of this solution required 20 mL of $0.01M$ $KMnO_4$ in acid medium for oxidation. Find the molar mass of reductant. Given that each of the two atoms which undergo oxidation per molecule of reductant, suffer an increase in oxidation state by one unit.

55. On ignition, Rochelle salt $NaKC_4H_4O_6 \cdot 4H_2O$ (molar mass 282) is converted into $NaKCO_3$ (molar mass 122). 0.9546 g sample of the Rochelle salt on ignition gives $NaKCO_3$ which is titrated with 41.72 mL H_2SO_4. From the following data, find the percentage purity of the Rochelle salt. The solution after neutralization requires 1.91 mL of 0.1297 N NaOH. The H_2SO_4 used for the neutralization requires its 10.27 mL against 10.35 mL of 0.1297 N NaOH.

56. A mixture of $KMnO_4$ and $K_2Cr_2O_7$ weighing 0.24 g on being treated with KI in acid solution liberates just sufficient I_2 to react with 60 mL of $0.1N$ hypo. Find out % of Cr and Mn in mixture.

57. 0.5 g mixture of $K_2Cr_2O_7$ and $KMnO_4$ was treated with excess of KI in acidic medium. Iodine liberated required $100\,cm^3$ of $0.15N$ sodium thiosulphate solution for titration. Find the mass per cent of each in the mixture. **(Roorkee 1995)**

58. A $5.0\,cm^3$ solution of H_2O_2 liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of H_2O_2 solution in terms of volume strength at STP. **(IIT 1995)**

59. A sample weighing 2.198 g containing a mixture of AO and A_2O_3 takes 0.015 mole of $K_2Cr_2O_7$ to oxidize the sample completely to form AO_4^- and Cr^{3+}. If 0.0187 mole of AO_4^- is formed, what is atomic mass of A? **(Roorkee 2001)**

60. Calculate the mass of SeO_3^{2-} in solution on the basis of following data. 20 mL of $M / 60$ solution of $KBrO_3$ was added to a definite volume of SeO_3^{2-} solution. The bromine evolved was removed by boiling and excess of $KBrO_3$ was back titrated with 5.1 mL of $M / 25$ solution of $NaAsO_2$. The reactions are given below:

(a) $SeO_3^{2-} + BrO_3^- + H^+ \longrightarrow SeO_4^{2-} + Br_2 + H_2O$

(b) $BrO_3^- + AsO_2^- + H_2O \longrightarrow Br^- + AsO_4^{3-} + H^+$

61. A mixture containing As_2O_3 and As_2O_5 required 20.10 mL of 0.05 *N* iodine for titration. The resulting solution is then acidified and excess of KI was added. The liberated iodine required 1.1113 g hypo ($Na_2S_2O_3 \cdot 5H_2O$) for complete reaction. Calculate mass of mixture. The reactions are:

$$As_2O_3 + 2I_2 + 2H_2O \longrightarrow As_2O_5 + 4H^+ + 4I^-$$

$$As_2O_5 + 4H^+ + 4I^- \longrightarrow As_2O_3 + 2I_2 + 2H_2O$$

62. 1.5 g of brass containing Cu and Zn reacts with 3*M* HNO_3 solution, the following reactions take place.

$$Cu + HNO_3 \longrightarrow Cu^{2+} + NO_2(g) + H_2O$$

$$Zn + H^+ + NO_3^- \longrightarrow NH_4^+ + Zn^{2+} + H_2O$$

The liberated $NO_2(g)$ was found to be 1.04 litre at 25°C and one atm.

(a) Calculate the percentage composition of brass.

(b) How many mL of 3*M* HNO_3 will be required for completely reacting 1 g of brass?

63. In a quality control analysis for sulphur impurity 5.6 g steel sample was burnt in a stream of oxygen and sulphur was converted into SO_2 gas. The SO_2 was then oxidized to sulphate by using H_2O_2 solution to which had been added 30 mL of 0.04*M* NaOH. The equation for reaction is:

$$SO_2(g) + H_2O_2(aq.) + 2OH^-(aq.) \longrightarrow SO_4^{2-}(aq.) + 2H_2O(l)$$

22.48 mL of 0.024*M* HCl was required to neutralize the base remaining after oxidation reaction. Calculate % of sulphur in given sample.

64. 0.108 g of finely divided copper was treated with an excess of ferric sulphate solution until copper was completely dissolved. The solution after the addition of excess dilute sulphuric acid required 33.7 mL of 0.1*N* $KMnO_4$ for complete oxidation. Find the equation which represents the reaction between metallic copper and ferric sulphate solution. Atomic mass of Cu = 63.6; Fe = 56.

65. For estimating ozone in the air, a certain volume of air is passed through an acidified or neutral KI solution when oxygen is evolved and iodide is oxidized to give iodine. When such a solution is acidified, free iodine is evolved which can be titrated with standard $Na_2S_2O_3$ solution. In an experiment 10 litre of air at 1 atm and 27°C were passed through an alkaline KI solution, at the end, the iodine entrapped in a solution on titration as above required 1.5 mL of 0.01*N* $Na_2S_2O_3$ solution. Calculate volume % of O_3 in sample.

66. One litre of a mixture of O_2 and O_3 at NTP was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 mL of *M* / 10 sodium thiosulphate solution for titration. What is the mass per cent of ozone in the mixture?

Ultraviolet radiation of wavelength 300 nm can decompose ozone. Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture?
(IIT May 1997)

67. A 10 g mixture of Cu_2S and CuS was treated with 200 mL of 0.75*M* MnO_4^- in acid solution producing SO_2, Cu^{2+} and Mn^{2+}. The SO_2 was boiled off and the excess of MnO_4^- was titrated with 175 mL of 1*M* Fe^{2+} solution. Calculate % of CuS in original mixture.

68. One *g* sample of NaCN was dissolved in 50 mL of 0.33*M* alkaline $KMnO_4$ and heated strongly to convert all the CN^- to OCN^-. No other species in NaCN sample undergoes oxidation. Now acidifying the resulting mixture with H_2SO_4, the resulting solution requires 0.5 litre of 0.06 *M* $FeSO_4$. Calculate the % purity of NaCN in sample.

69. 1.249 g of a sample of pure $BaCO_3$ and impure $CaCO_3$ containing some CaO was treated with dil. HCl and it evolved 168 mL of CO_2 at NTP. From this solution $BaCrO_4$ was precipitated, filtered and washed. The dry precipitate was dissolved in dilute H_2SO_4 and diluted to 100 mL. 10 mL of this solution when treated with KI solution liberated iodine which required exactly 20 mL of 0.05 *N* $Na_2S_2O_3$. Calculate percentage of CaO in the sample.

70. Determine which reagent is in excess and by how much if 100.0 g P_4O_6 is treated with 100 g $KMnO_4$ in HCl solution to form H_3PO_4 and $MnCl_2$?

71. 12 g of an impure sample of arsenious oxide was dissolved in water containing 7.5 g of sodium bicarbonate and the resulting solution was diluted to 250 mL. 25 mL of this solution was completely oxidized by 22.4 mL of a solution of iodine. 25 mL of this iodine solution reacted with same volume of a solution containing 24.8g of sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$) in one litre. Calculate the percentage of arsenious oxide in the sample. (Atomic mass of As = 75)
(Roorkee 1999)

72. H_2O_2 is reduced rapidly by Sn^{2+}, the products being Sn^{4+} and water. H_2O_2 decomposes slowly at room temperature to yield O_2 and water. Calculate the volume of O_2 produced at 20°C and 1.0 atm when 200 g of 10% by mass H_2O_2 in water is treated with 100 millilitre of 2.0 *M* Sn^{2+} and then the mixture is allowed to stand until no further reaction occurs.

73. A 1.7225 g of metal (bivalent) salt $A_x(CO_3)_y(OH)_z$ was dissolved to prepare 100 mL solution. 50 mL of this solution required 10 mL 1.0 *N* H_2SO_4 solution to reach the equivalence point using phenolphthalein as indicator. Another 50 mL solution using methyl orange as indicator required 15 mL of same acid. Deduce the formula of salt.

74. A 3.0 g sample of Cu_2O is dissolved in dil. H_2SO_4 where it undergoes disproportionation quantitatively. The solution is filtered off and 8.3 g pure KI crystals are added to clear filtrate in order to precipitate CuI with evolution of I_2. The solution is again filtered and boiled till all the I_2 is expelled. Now excess of an oxidizing agent is added to filtrate which liberates I_2 again. The liberated I_2 this time requires 10 mL of 1.0 *N* $Na_2S_2O_3$ solution. Calculate % by mass of Cu_2O in sample.

75. 10 mL of 1.0 *M* aqueous solution of Br_2 is added to excess of NaOH in order to disproportionate quantitatively to Br^- and BrO_3^-. The resulting solution is made free from Br^- ion by extraction and excess of OH^- neutralized by acidifying the solution. This solution requires 1.5 g of an impure CaC_2O_4 sample for complete redox change. Calculate % purity of CaC_2O_4 sample.

76. 2 g sample of NaOCl and $CaOCl_2$ are dissolved in water to prepare 100 mL solution. 10 mL of this sample requires 10 mL of 0.15 *M* acidified $Na_2C_2O_4$ for end point. The clear solution is now treated with excess of $AgNO_3$ solution which precipitates 0.287 g AgCl. Calculate mass percentage of NaOCl and $CaOCl_2$ in mixture.

77. 6.32 g of $KMnO_4$ are allowed to react with a mixture of 4 g of KCl and mg of KBr in presence of concentrated H_2SO_4. If the oxidizing agent is just sufficient to react with both halides completely to liberate halogen, what is the vlaue of *m*? (Atomic mass: $K = 39$, $Br = 80$)

78. 1 g of moist sample of KCl and $KClO_3$ was dissolved in water to make 250 mL solution, 25 mL of this solution was treated with SO_2 to reduce chlorate to chloride and excess of SO_2 was removed by boiling. The total chloride was precipitated as silver chloride. The mass of precipitate was 0.1435 g. In another experiment, 25 mL of original solution was heated with 30 mL of 0.2 *N* ferrous sulphate solution and unreacted ferrous sulphate required 37.5 mL of 0.08 *N* solution of an oxidant for complete oxidation. Calculate the molar ratio of chlorate to chloride in the given mixture. Fe^{2+} reacts with ClO_3^- according to equation.

$$ClO_3^- + 6Fe^{2+} + 6H^+ \longrightarrow Cl^- + 6Fe^{3+} + 3H_2O$$

79. An acid solution of $KReO_4$ sample containing 26.83 mg of combined rhenium was reduced by passage through a column of granulated zinc. The effluent solution including the washings from the column, was then titrated with 0.05 *N* $KMnO_4$. 11.45 mL of the standard $KMnO_4$ was required for the reoxidation of all the rhenium to the perrhenate ion ReO_4^-. Assuming that rhenium was the only element reduced, what is the oxidation state to which rhenium was reduced by the zinc column?

SOLUTIONS (Numerical Problems)

1. We have,

Eq. mass of oxidant or reductant

$$= \frac{\text{Molar mass of oxidant or reductant}}{\text{No. of '}e\text{' lost or gained by one molecule of oxidant or reductant}}$$

(a) $\because \quad 2Fe^{2+} \longrightarrow (Fe^{3+})_2 + 2e$

$\therefore$ Eq. mass of $FeSO_4 = \frac{\text{Molar mass of } FeSO_4}{1} = \frac{152}{1}$

$= \mathbf{152}$

$\because \quad 6e + Cl^{5+} \longrightarrow Cl^-$

$\therefore$ Eq. mass of $KClO_3 = \frac{\text{Molar mass of } KClO_3}{6}$

$= \frac{122.5}{6} = \mathbf{20.42}$

(b) $\because \quad S^{4+} \longrightarrow S^{6+} + 2e$

$\therefore$ Eq. mass of $Na_2SO_3 = \frac{M}{2} = \frac{126}{2} = \mathbf{63}$

$\because \quad 3e + Cr^{6+} \longrightarrow Cr^{3+}$

$\therefore$ Eq. mass of $Na_2CrO_4 = \frac{M}{3} = \frac{162}{3} = \mathbf{54}$

(c) $\because \quad 2(Fe^{(8/3)+})_3 \longrightarrow 3Fe_2^{3+} + 2e$

$\therefore$ Eq. mass of $Fe_3O_4 = \frac{M}{1} = \frac{232}{1} = \mathbf{232}$

$\because \quad 3e + Mn^{7+} \longrightarrow Mn^{4+}$

$\therefore$ Eq. mass of $KMnO_4 = \frac{M}{3} = \frac{158}{3} = \mathbf{52.67}$

(d) $\because \quad 2I^- \longrightarrow I_2^0 + 2e$

$\therefore$ Eq. mass of $KI = \frac{M}{1} = \frac{166}{1} = \mathbf{166}$

$\because \quad 6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$

$\therefore$ Eq. mass of $K_2Cr_2O_7 = \frac{M}{6} = \frac{294}{6} = \mathbf{49}$

(e) $\because \quad 2e + Mn^{4+} \longrightarrow Mn^{2+}$

$\therefore$ Eq. mass of $Mn^{4+} = \frac{\text{Atomic mass of Mn}}{2} = \frac{55}{2}$

$= \mathbf{27.5}$

(f) $\because \quad 10e + 2N^{5+} \longrightarrow N_2^0$

$\therefore$ Eq. mass of $NO_3^- = \frac{\text{Ionic Molar mass}}{5} = \frac{62}{5} = \mathbf{12.4}$

(g) $\because \quad 6e + N_2^0 \longrightarrow 2N^{3-}$

$\therefore$ Eq. mass of $N_2 = \frac{\text{Molar mass of } N_2}{6} = \frac{28}{6} = \mathbf{4.67}$

(h) $\because \quad 2S_2^{2+} \longrightarrow S_4^{(5/2)+} + 2e$

$\therefore$ Eq. mass of $Na_2S_2O_3 = \frac{M}{1} = \frac{158}{1} = \mathbf{158}$

$\because \quad 2e + I_2^0 \longrightarrow 2I^-$

$\therefore$ Eq. mass of $I_2 = \frac{M}{2} = \frac{254}{2} = \mathbf{127}$

(i) $\because$

$$\begin{array}{c} FeC_2O_4 \longrightarrow Fe^{3+} + CO_2 \\ Fe^{2+} \longrightarrow Fe^{3+} + e \\ C_2^{3+} \longrightarrow 2C^{4+} + 2e \\ \hline FeC_2O_4 \longrightarrow Fe^{3+} + 2C^{4+} + 3e \end{array}$$

$\therefore$ Eq. mass of $FeC_2O_4 = \frac{M}{3} = \frac{144}{3} = \mathbf{48}$

2. (i) $Mn^{7+} + 3e \longrightarrow Mn^{4+}$; Eq. mass $= M/3$

(ii) $Mn^{7+} + 5e \longrightarrow Mn^{2+}$; Eq. mass $= M/5$

(iii) $Mn^{7+} + 1e \longrightarrow Mn^{6+}$; Eq. mass $= M/1$

3. Meq. of sodium bromate $= 85.5 \times 0.672 = 57.456$

(i) $\because$ Meq. of $NaBrO_3 = 57.456$

$\therefore \quad \frac{w}{E} \times 1000 = 57.456$

$\therefore \quad \frac{w}{151/6} \times 1000 = 57.456 \qquad \left(\because E_{NaBrO_3} = \frac{M}{6}\right)$

$\therefore \quad w = \mathbf{1.446\ g}$

Also, Molarity $= \frac{\text{Normality}}{\text{Valency factor}} = \frac{0.672}{6} = \mathbf{0.112}M$

(ii) Similarly use valency factor 5 in place of 6 in this problem and get

$w = \mathbf{1.735\ g}$

and $\quad M = \mathbf{0.1344}M$

The term valency factor = No. of electrons lost or gained by one molecule of reductant or oxidant

4. The reactions for redox change are

$$5e + Mn^{7+} \longrightarrow Mn^{2+}$$

$$Fe^{2+} \longrightarrow Fe^{3+} + 1e$$

Now Meq. of $KMnO_4$ = Meq. of $FeSO_4$

$0.05 \times 5 \times v = \frac{2}{152/1} \times 1000 \quad \Big| \quad \because$ Meq. $= N \times V$ in mL

$\therefore \quad v = \mathbf{52.63\ mL} \quad \Big| \quad$ and Meq. $= \frac{\text{Mass}}{\text{Eq.mass}} \times 1000$

5. For Sn, $\quad Sn^{2+} \longrightarrow Sn^{4+} + 2e$

For $Cr_2O_7^{2-} \quad 6e + Cr_2^{6+} \longrightarrow 2Cr^{3+}$

(a) Meq. of $SnCl_2 = 2000 \times 0.1$

$\therefore \quad \frac{w}{E} \times 1000 = 200$

$\therefore \quad \frac{w}{189.7/2} \times 1000 = 200 \qquad \left[\because E_{SnCl_2} = \frac{M_{SnCl_2}}{2}\right]$

$\therefore \quad w_{SnCl_2} = \mathbf{18.97\ g}$

(b) Normality of $K_2Cr_2O_7$

$= \frac{4.9}{M/6} \times \frac{1}{0.1} = \frac{4.9}{294/6 \times 0.1} = \mathbf{1N} \quad \Big| \quad N = \frac{\text{Eq.}}{\text{litre}}$

6. For redox change:

$$\mathrm{Mn}^{2+} \longrightarrow \mathrm{Mn}^{4+} + 2e$$

$$3e + \mathrm{Mn}^{7+} \longrightarrow \mathrm{Mn}^{4+}$$

$\because$ Meq. of $KMnO_4$ = Meq. of $MnSO_4$

$$[\because N = M \times \text{valency factor}]$$

$$N \times 16 = 20 \times 0.2 \times 2$$

$\therefore$ $N = \mathbf{0.5}$

$\therefore$ $M = \frac{0.5}{3} = \mathbf{0.167}$

$$[\because \text{valency factor for } KMnO_4 = 3]$$

7. The redox changes are:

$$\mathrm{Sn} \longrightarrow \mathrm{Sn}^{4+} + 4e$$

$$6e + \mathrm{Cr}_2^{6+} \longrightarrow 2\mathrm{Cr}^{3+}$$

$\therefore$ Meq. of Sn = Meq. of $K_2Cr_2O_7$

or $\frac{1}{E_{\mathrm{Sn}}} \times 1000 = \frac{1}{10} \times V$

or $\frac{1}{\frac{118.7}{4}} \times 1000 = \frac{1}{10} \times V$ $\left(\because \text{Eq. mass of Sn} = \frac{\text{At. mass}}{4}\right)$

or $V = \mathbf{336.98\ mL}$

8. Reactions for redox change are:

$$5e + \mathrm{Mn}^{7+} \longrightarrow \mathrm{Mn}^{2+}$$

$$\mathrm{Fe}^{2+} \longrightarrow \mathrm{Fe}^{3+} + 1e$$

It is to be noted here that only $FeSO_4 \cdot 7H_2O$ will react with $KMnO_4$ to bring in redox change.

$\because$ Meq. of $FeSO_4 \cdot 7H_2O$ = Meq. of $KMnO_4$

$$\frac{w}{E} \times 1000 = 5.4 \times 0.1 \quad \therefore \quad \frac{w}{\frac{278}{1}} \times 1000 = 0.54$$

$\therefore$ $w = 0.150\,\mathrm{g}$

$\therefore$ Mass of $Fe_2(SO_4)_3 \cdot 9H_2O = 5.5 - 0.150\,\mathrm{g} = 5.350\,\mathrm{g}$

$\therefore$ Mole of $Fe_2(SO_4)_3 \cdot 9H_2O = \frac{5.350}{562} = \mathbf{9.5 \times 10^{-3}\ mol}$

$$(\because \text{Molar mass of } Fe_2(SO_4)_3 \cdot 9H_2O = 562)$$

9. $MnO_2 \xrightarrow{HCl} Cl_2 \xrightarrow{KI} I_2 \xrightarrow{Na_2S_2O_3} NaI + Na_2S_4O_6$

Redox changes are:

$$2e + \mathrm{I}_2^0 \longrightarrow 2\mathrm{I}^-$$

$$2(\mathrm{S}^{2+})_2 \longrightarrow (\mathrm{S}^{5/2+})_4 + 2e$$

$$2e + \mathrm{Mn}^{4+} \longrightarrow \mathrm{Mn}^{2+}$$

The reactions suggest that,

Meq. of MnO_2 = Meq. of Cl_2 formed
= Meq. of I_2 liberated
= Meq. of $Na_2S_2O_3$ used

$\therefore$ $\frac{w}{M/2} \times 1000 = 0.1 \times 1 \times 30$

$[\because N_{Na_2S_2O_3} = M_{Na_2S_2O_3}$ since valency factor = 1, see redox changes for $Na_2S_2O_3]$

or $w = \frac{0.1 \times 1 \times 30 \times M}{2000} = \frac{0.1 \times 1 \times 30 \times 87}{2000}$ $(\because M_{MnO_2} = 87)$

$$w_{MnO_2} = 0.1305$$

$\therefore$ Purity of $MnO_2 = \frac{0.1305}{0.5} \times 100 = \mathbf{26.1\%}$

10. The element forming acidic oxide is non-metal say *A*. It forms isomorphous of K_2SO_4 with KOH, *i.e.*, K_2AO_4.

$\therefore$ $A^0 \longrightarrow A^{6+} + 6e$

$\therefore$ Atomic mass of *A*
= Eq. mass of A × No. of 'e' lost $= 13.16 \times 6 = \mathbf{78.96}$

11.

$$\mathrm{Sn}^{2+} \longrightarrow \mathrm{Sn}^{4+} + 2e$$

$$6e + (\mathrm{Cr}^{6+})_2 \longrightarrow 2\mathrm{Cr}^{3+}$$

Since, Sn^{2+} is oxidized by $K_2Cr_2O_7$

$\therefore$ Meq. of Sn^{2+} = Meq. of $K_2Cr_2O_7$ used for tin

$$= N \times V_{\text{in mL}}$$

$$= \frac{2.5}{\frac{294.2}{6} \times 0.50} \times 10 = 1.0197$$

$$\left(\because N = \frac{2.5}{\frac{294.2}{6} \times 0.5}\right)$$

$\therefore$ $\frac{w_{Sn^{2+}}}{118/2} \times 1000 = 1.0197$

$\therefore$ $w_{Sn^{2+}} = 0.06\,\mathrm{g}$

$\therefore$ $\%\ \mathrm{Sn} = \frac{0.06}{0.4} \times 100 = \mathbf{15\%}$

12. Redox changes are:

$$\mathrm{Mn}^{7+} + 5e \longrightarrow \mathrm{Mn}^{2+}$$

$$\mathrm{O}_2^{1-} \longrightarrow \mathrm{O}_2^0 + 2e$$

$\therefore$ Eq.mass of $H_2O_2 = \frac{34}{2}$

Now, Meq. of $KMnO_4$ = Meq. of H_2O_2

$$N.(X) = \frac{X}{100 \times 34/2} \times 1000$$

$\therefore$ $N = \mathbf{0.588}$

13.

$$A^{n-} \longrightarrow A^{a+} + (a+n)e$$

$$6e + (\mathrm{Cr}^{6+})_2 \longrightarrow 2\mathrm{Cr}^{3+}$$

$\therefore$ Meq. of A^{n-} = Meq. of $Cr_2O_7^{2-}$

or $3.26 \times 10^{-3} \times (a+n) = 1.68 \times 10^{-3} \times 6$

$\therefore$ $a + n = 3$ or $\mathbf{a = 3 - n}$

14. Redox changes are:

$$5e + \mathrm{Mn}^{7+} \longrightarrow \mathrm{Mn}^{2+}$$

$$(\mathrm{O}^-)_2 \longrightarrow \mathrm{O}_2^0 + 2e$$

(a) $\therefore$ Meq. of H_2O_2 = Meq. of $KMnO_4$

$$\frac{w \times 1000}{34/2} = \frac{0.316}{M/5} \times 1000$$

$\therefore$ $\frac{w \times 2 \times 1000}{34} = \frac{0.316 \times 5 \times 1000}{158}$

$\therefore$ $w_{H_2O_2} = 0.17\,\mathrm{g}$

$\because$ 0.2 g impure sample of H_2O_2 has 0.17 g pure H_2O_2

$\therefore$ % of $H_2O_2 = \frac{0.17 \times 100}{0.2} = \mathbf{85\%}$

(b) Now, $\text{Eq. of } O_2 = \text{Eq. of } KMnO_4$

$$\frac{w}{32/2} = \frac{0.316 \times 5}{158}$$

$$\therefore \quad w_{O_2} = 0.16\,g$$

$$\therefore \quad \frac{750}{760} \times V = \frac{0.16}{32} \times 0.0821 \times 300$$

$$\therefore \quad V_{O_2} = \mathbf{124.79\ mL}$$

15. Redox changes are: $5e + Mn^{7+} \longrightarrow Mn^{2+}$

$$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$$

$\therefore$ Meq. of oxalate ion

$$= \text{Meq. of } KMnO_4\ \frac{w}{E} \times 1000 = 90 \times \frac{1}{20}$$

$$\left[E_{C_2O_4^{2-}} = \frac{\text{Ionic mass}}{2}\right]$$

$$\frac{w}{\frac{88}{2}} \times 1000 = \frac{9}{2}$$

$$\therefore \quad w_{C_2O_4^{2-}} = 0.198\,g$$

$\therefore$ 0.3 g $C_2O_4^{2-}$ sample has oxalate ion $= 0.198\,g$

$\therefore$ % of $C_2O_4^{2-}$ in sample $= \frac{0.198 \times 100}{0.3} = \mathbf{66\%}$

16. Redox changes are: $2e + (O^-)_2 \longrightarrow 2O^{2-}$

$$2I^- \longrightarrow I_2 + 2e$$

$$2(S^{2+})_2 \longrightarrow (S^{5/2+})_4 + 2e$$

and $\quad 2e + I_2^0 \longrightarrow 2I^{1-}$

$$H_2O_2 \xrightarrow{KI} I_2 + H_2O \xrightarrow{Na_2S_2O_3} d\, Na_2S_4O_6 + 2I^-$$

$\therefore$ Meq. of H_2O_2 = Meq. of KI used = Meq. of I_2 liberated
= Meq. of $Na_2S_2O_3$ used

$\therefore$ Meq. of H_2O_2 = Meq. of $Na_2S_2O_3$ used

$$N \times 50 = 20 \times 0.1 \quad \therefore \quad N_{H_2O_2} = 0.04$$

$\therefore$ Strength of $H_2O_2 = N \times E = 0.04 \times \frac{34}{2} = \mathbf{0.68\ g\ litre^{-1}}$

17. Redox changes are:

For $H_2C_2O_4$ $\quad (C^{3+})_2 \longrightarrow 2C^{4+} + 2e$

For $KMnO_4$ $\quad 5e + Mn^{7+} \longrightarrow Mn^{2+}$

Meq. of oxalic acid in 10 mL solution = Meq. of $KMnO_4$ used for it $= 8.5 \times \frac{1}{10}$

$\therefore$ Meq. of oxalic acid in 200 mL solution $= 8.5 \times \frac{1}{10} \times \frac{200}{10}$

$$\therefore \quad \frac{w}{E} \times 1000 = 17$$

Formula of oxalic acid is
$H_2C_2O_4 \cdot 2H_2O$
$\therefore$ Molar mass = 126

$\therefore \quad \frac{w}{126/2} \times 1000 = 17$
$\therefore \quad w_{H_2C_2O_4} = 1.071\,g$

$\therefore$ % purity of oxalic acid $= \frac{1.071}{1.2} \times 100 = \mathbf{89.25\%}$

18. (a) The redox changes are

$$2e + (O^-)_2 \longrightarrow 2O^{2-}$$

$$2I^- \longrightarrow I_2 + 2e$$

$$2(S^{2+})_2 \longrightarrow (S^{5/2+})_4 + 2e$$

$$I_2 + 2e \longrightarrow 2I^-$$

Meq. of H_2O_2 = Meq. of I_2 = Meq. of $Na_2S_2O_3$

$$N \times 25 = 0.1 \times 20 \quad \therefore \quad N_{H_2O_2} = 0.08$$

Mass of H_2O_2 in one litre $= 0.08 \times \frac{34}{2} = 1.36\,g$

$\therefore$ % by mass = 0.136%

Also concentration of H_2O_2 in terms of volume
= 0.448 volume

(b) Follow problem 18 (a)
[Ans. 1.344]

19. The given reactions are:

$$\underset{(ppt.)}{MnO_2} + Na_2C_2O_4 + 2H_2SO_4 \longrightarrow MnSO_4 + 2CO_2 + Na_2SO_4 + 2H_2O$$

$\therefore$ Meq. of MnO_2 = Meq. of $Na_2C_2O_4 = 10 \times 0.2 \times 2 = 4$

$\because \quad Mn^{4+} + 2e \longrightarrow Mn^{2+}$

$\therefore$ Valence factor of $MnO_2 = 2$ $\therefore$ mM of $MnO_2 = \frac{4}{2} = 2$

Now, $2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow \underset{(ppt.)}{5MnO_2} + K_2SO_4 + 2H_2O$

Since, Eq. mass of MnO_2 is derived from $KMnO_4$ and $MnSO_4$ both, thus it is better to proceed by mole concept.

$$\text{mM of } KMnO_4 = \text{mM of } MnO_2 \times \frac{2}{5} = \frac{4}{5}$$

Also, $5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$

$\therefore$ mM of H_2O_2 = mM of $KMnO_4 \times \frac{5}{2} = \frac{4}{5} \times \frac{5}{2} = 2$

$$\therefore \quad M \times 20 = 2$$

$$M_{H_2O_2} = \mathbf{0.1}$$

20. $\underset{CaCO_3}{\text{Limestone}} \xrightarrow{\text{oxalic acid}} CaC_2O_4 \xrightarrow{KMnO_4} \text{decolorizes}$

$\therefore$ Redox changes are:

For CaC_2O_4 $\quad (C^{3+})_2 \longrightarrow 2C^{4+} + 2e$

For $KMnO_4$ $\quad 5e + Mn^{7+} \longrightarrow Mn^{2+}$

$\therefore$ Meq. of $CaCO_3$ = Meq. of CaC_2O_4 = Meq. of $KMnO_4$

$\because$ Meq. of $CaCO_3$ = Meq. of CaO
(since CaO is present in $CaCO_3$)

$\therefore$ Meq. of CaO = Meq. of $KMnO_4$

$$\frac{w}{56/2} \times 1000 = 45 \times 0.2$$

Mass of CaO = 0.252 g

$\therefore$ % of CaO in limestone $= \frac{0.252}{0.56} \times 100 = \mathbf{45\%}$

21. The redox changes are:

For $FeSO_4$ $\quad Fe^{2+} \longrightarrow Fe^{3+} + 1e$

For $KMnO_4$ $\quad 5e + Mn^{7+} \longrightarrow Mn^{2+}$

$\therefore$ Meq. of $FeSO_4 \cdot 7H_2O$ in 25 mL solution

$$= \text{Meq. of } KMnO_4 = 20 \times \frac{1}{10}$$

$\therefore$ Meq. of $FeSO_4 \cdot 7H_2O$ in 1 litre solution

$$= 20 \times \frac{1}{10} \times \frac{1000}{25} = 80$$

$$\therefore \frac{w}{E} \times 1000 = 80$$

(Molar mass of $FeSO_4 \cdot 7H_2O = 278$) $\therefore \dfrac{w}{\frac{278}{1}} \times 1000 = 80$

$\therefore \quad w = 22.24$ g

$\because$ 25 g sample has $FeSO_4 \cdot 7H_2O = 22.24$ g

$\therefore$ % of $FeSO_4 \cdot 7H_2O$ in sample $= 22.24 \times \dfrac{100}{25} = \mathbf{88.96\%}$

22. Redox changes are:

For $KMnO_4$ $\quad 5e + Mn^{7+} \longrightarrow Mn^{2+}$

For X^{n+} $\quad X^{n+} \longrightarrow X^{5+} + (5-n)e$

Now,

Meq. of X^{n+} = Meq. of $KMnO_4$

$2.68 \times 10^{-3} \times (5-n) \times 1000$

$\because$ Meq. = mole × valency factor × 1000

$$= 1.61 \times 10^{-3} \times 5 \times 1000$$

$\therefore \quad n = 1.99$

$n = \mathbf{2}$

Now, $\quad X^{2+} \longrightarrow X^{5+} + 3e$

If a is atomic mass of X,

$\because \quad$ Eq. mass of $XCl_2 = 56$

$\therefore$ Molar mass of $XCl_2 = 56 \times$ valency factor $= 56 \times 3$

or $\quad a + 71 = 56 \times 3$

$\therefore \quad a = \mathbf{97}$

23. Bleaching powder $\xrightarrow{KI + HCl} I_2 \xrightarrow{Na_2S_2O_3} I^- + Na_2S_4O_6$

The redox changes are: $\quad 2e + I_2 \longrightarrow 2I^-$

$$2(S^{2+})_2 \longrightarrow (S^{5/2+})_4 + 2e$$

Meq. of bleaching powder = Meq. of available Cl_2

= Meq. of I_2 liberated

= Meq. of $Na_2S_2O_3$ used

$\therefore$ Meq. of available Cl_2 in 25 mL bleaching powder solution

$$= \text{Meq. of } Na_2S_2O_3 \text{ used} = 24.35 \times \frac{1}{10}$$

$\therefore$ Meq. of available Cl_2 in 500 mL bleaching powder solution

$$= 24.35 \times \frac{1}{10} \times \frac{500}{25} = 48.7$$

$\therefore \dfrac{w}{71/2} \times 1000 = 48.7 \quad \therefore \quad w_{Cl_2} = 1.729\text{g}$

$\therefore$ % of available Cl_2 in bleaching powder

$$= \frac{1.729}{5.7} \times 100 = \mathbf{30.33\%}$$

24. Redox changes are:

$$(S^{2+})_2 \longrightarrow 2S^{6+} + 8e$$

$$3e + Mn^{7+} \longrightarrow Mn^{4+}$$

$\therefore$ Meq. of $KMnO_4$ = Meq. of $S_2O_3^{2-}$

$$0.1 \times 3 \times V = \frac{0.158}{158/8} \times 1000$$

($\because$ Molar mass of $Na_2S_2O_3 = 158$)

$\therefore \quad V = \mathbf{26.67\ mL}$

25. Let Meq. of $Fe_2(SO_4)_3$ and FeC_2O_4 are a and b respectively. $KMnO_4$ will oxidize only FeC_2O_4 as:

$$2Fe^{2+} \longrightarrow Fe_2^{3+} + 2e$$

$$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$$

Note that valence factor for $Fe_2(SO_4)_3$ is 2 and for FeC_2O_4 is 3.

Meq. of FeC_2O_4 of valence factor 3

= Meq. of Fe^{2+} (v.f. = 1)

+ Meq. of $Ca_2O_4^{2-}$ (v.f. = 2)

$$b = \frac{b}{3} + \frac{2b}{3}$$

$$b = \text{Meq. of } KMnO_4$$

$$b = 40 \times \frac{1}{16} = \frac{40}{16} \qquad ...(1)$$

Fe_2^{3+} from $Fe_2(SO_4)_3$ and Fe_2^{3+} obtained by oxidation of FeC_2O_4 will be converted to Fe^{2+} as,

$$2e + (Fe^{3+})_2 \longrightarrow 2Fe^{2+}$$

The CO_2 formed during oxidation of FeC_2O_4 with $KMnO_4$ escapes out.

Now, Meq. of Fe^{2+} so obtained are again oxidized by $KMnO_4$.

$\therefore$ Meq. of Fe^{2+} of $Fe_2(SO_4)_3$ reduction +

Meq. of Fe^{2+} of FeC_2O_4

= Meq. of $KMnO_4$

$$a + \frac{b}{3} = 60 \times \frac{1}{16} = \frac{60}{16} \qquad ...(2)$$

By Eqs. (1) and (2), $\quad a = \dfrac{140}{48}, \quad b = \dfrac{40}{16}$

$$\therefore \frac{\text{Meq. of } Fe_2(SO_4)_3 \text{ of valence factor 2}}{\text{Meq. of } FeC_2O_4 \text{ of valence factor 3}} = \frac{140}{48} \times \frac{16}{40} = \frac{7}{6}$$

$\therefore$ Ratio of Meq. of $Fe_2(SO_4)_3$: Meq. of FeC_2O_4 = **7 : 6**

26. Let a mole of Cu^{2+} and b mole of $C_2O_4^{2-}$ be present in solution.

Case I: The solution is oxidized by $KMnO_4$ which reacts with only $C_2O_4^{2-}$.

$$5e + Mn^{7+} \longrightarrow Mn^{2+}$$

$$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$$

$\therefore \quad$ Meq. of $C_2O_4^{2-}$ = Meq. of $KMnO_4$

$\therefore \quad b \times 2 \times 1000 = 0.02 \times 5 \times 22.6$

$\therefore \quad b = 1.13 \times 10^{-3} \qquad ...(1)$

Case II: After oxidation of $C_2O_4^{2-}$, the resulting solution is neutralized by Na_2CO_3, acidified with dilute CH_3COOH and then treated with excess of KI. The liberated I_2 required $Na_2S_2O_3$ for its neutralization, *i.e.*,

$$Cu^{2+} \xrightarrow{KI} I_2 \xrightarrow{Na_2S_2O_3} Na_2S_4O_6 + I^-$$

$\therefore$ Meq. of Cu^{2+} = Meq. of I_2 liberated

= Meq. of $Na_2S_2O_3$ used

$\therefore$ Meq. of Cu^{2+} = Meq. of $Na_2S_2O_3$ used

$$a \times 1 \times 1000 = 11.3 \times 0.05 \times 1$$

$$\therefore \quad a = 5.65 \times 10^{-4}$$

$\therefore$ Molar ratio of

$$\frac{Cu^{2+}}{C_2O_4^{2-}} = \frac{a}{b} = \frac{5.65 \times 10^{-4}}{1.13 \times 10^{-3}} = \frac{1}{2}$$

Redox changes are:

$$2Cu^{2+} + 2e \longrightarrow (Cu^+)_2$$

$$2I^- \longrightarrow I_2 + 2e$$

and $2e + I_2 \longrightarrow 2I^{-1}$

$$2(S^{2+})_2 \longrightarrow (S^{5/2+})_4 + 2e$$

27. For KI + KIO_3 reaction:

$$I^{5+} + 4e \longrightarrow I^+$$

$$I^- \longrightarrow I^+ + 2e$$

$\therefore$ valence factor of KI = 2 and valence factor of KIO_3 = 4

Now, Meq. of KI in 20 mL $= 30 \times \frac{1}{10} \times 4 = 12$

$\therefore$ Meq. of KI in 50 mL $= 12 \times \frac{50}{20} = 30$

Now, Meq. of KI left after treatment with $AgNO_3$

$$= 50 \times \frac{1}{10} \times 4 = 20$$

$\therefore$ Meq. of KI (v.f. = 2) used by $AgNO_3 = 30 - 20 = 10$

But in its reaction with $AgNO_3$ valence factor of KI = 1

$$AgNO_3 + KI \longrightarrow AgI + KNO_3$$

$\therefore$ Meq. of KI used by $AgNO_3$ (v.f. = 1) $= \frac{10 \times 1}{2} = 5$

$\therefore$ Meq. of $AgNO_3 = 5$

$$\frac{w}{170} \times 1000 = 5$$

$$\therefore \quad w = \mathbf{0.85\ g}$$

$\therefore$ % purity of $AgNO_3$ in sample $= \frac{0.85 \times 100}{1} = \mathbf{85\%}$

Alternative method:

milli mole of KIO_3 used by 20 mL of KI stock solution

$$= 30 \times \frac{1}{10} = 3$$

$\therefore$ milli mole of KIO_3 used by 50 mL of KI stock solution

$$= 3 \times \frac{50}{20} = 7.5$$

milli mole of KIO_3 used by KI left in 50 mL solution after reaction with

$$AgNO_3 = \frac{1}{10} \times 50 = 5$$

$\because$ Mole ratio of KIO_3 and KI is 1 : 2 in reaction

$\therefore$ milli mole of KI in 50 mL stock solution $= 7.5 \times 2 = 15$

$\therefore$ milli mole of KI left in 50 mL solution after reaction with $AgNO_3 = 5 \times 2 = 10$

$\therefore$ milli mole of KI used for $AgNO_3 = 15 - 10 = 5$

$\therefore$ m mole of $AgNO_3 = 5$

($\because$ mole ratio of KI and $AgNO_3$ reaction is 1 : 1)

Now for $AgNO_3$: $\frac{w}{M} \times 1000 = 5$

$$\therefore \quad \frac{w}{170} \times 1000 = 5$$

$$\therefore \quad w_{AgNO_3} = 0.85$$

$$\therefore \quad \%\text{ of } AgNO_3 = 0.85 \times \frac{100}{1} = \mathbf{85\%}$$

28. Meq. of MnO_2 = Meq. of oxalic acid added − Meq. of oxalic acid left (in 250 mL)

$$= 1 \times 50 - 0.1 \times 32 \times 10$$

$$= 18$$

$$\therefore \quad \frac{w}{E} \times 1000 = 18 \quad \text{or} \quad w_{MnO_2} = \frac{18 \times 86.9}{2 \times 1000} = 0.7821\text{ g}$$

$$\left(\because E = \frac{86.9}{2}\right)$$

$$\therefore \quad \%\text{ of } MnO_2 = \frac{0.7821}{1.6} \times 100 = \mathbf{48.88\%}$$

Also Meq. of MnO_2 = Meq. of O_2 = 18

$$\therefore \quad \frac{w}{8} \times 1000 = 18$$

$$w_{O_2} = \mathbf{0.144\ g}$$

$$\therefore \quad \%\text{ of available } O_2 = \frac{0.144}{1.6} \times 100 = \mathbf{9}$$

29.

$$KIO_3 + 5KI \longrightarrow 3K_2O + 3I_2$$

i.e. $2I^{5+} + 10e \longrightarrow I_2^0$

$$2I^- \longrightarrow I_2^0 + 2e$$

Now the liberated I_2 reacts with $Na_2S_2O_3$ to give

$$I_2 + 2e \longrightarrow 2I^-$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e$$

$\because$ millimole ratio is $I_2 : S_2O_3 :: 1 : 2$,

Thus, m. mole of I_2 liberated = m. mole of $Na_2S_2O_3$ used $\times \frac{1}{2} = 45 \times M \times \frac{1}{2}$

(M is molarity of thiosulphate)

Also m. mole of $KIO_3 = \frac{0.1}{214} \times 1000$

Now, m. mole ratio is $KIO_3 : I_2 :: 1 : 3$

$$\text{Thus,} \quad \frac{\frac{0.1}{214} \times 1000}{\frac{45\,M}{2}} = \frac{1}{3}$$

$$\therefore \quad M = \frac{0.1 \times 1000 \times 3 \times 2}{214 \times 45}$$

$$M = \mathbf{0.062}$$

30. 1. Pyrolusite contains MnO_2.

2. Meq. of oxalic acid added to pyrolusite $= 65 \times 1 = 65$

3. MnO_2 reacts with oxalic acid as,

$$2e + Mn^{4+} \longrightarrow Mn^{2+}$$

$$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$$

4. Excess of oxalic acid is oxidized by $KMnO_4$

Meq. of oxalic acid left in 100 mL $= 50 \times \frac{1}{10} = 5$

$\therefore$ Meq. of oxalic acid left in 500 mL $= 5\times\frac{500}{100} = 25$

$\therefore$ Meq. of oxalic acid used for $MnO_2 = 65 - 25 = 40$

$\therefore$ Meq. of $MnO_2 = 40$

$\because$ Molar mass of $MnO_2 = 87$, Eq. mass $= \frac{87}{2}$

$\therefore \quad \frac{w}{87/2}\times 1000 = 40 \quad \therefore \quad w_{MnO_2} = 1.74$ g

$\therefore$ % of MnO_2 in pyrolusite $= \frac{1.74}{2.6}\times 100 =$ **66.92%**

31. **Case I:** $Fe^{2+} \xrightarrow{\text{Zn dust + } H_2SO_4} Fe^{2+}$ (*i.e.*, no change)

$$2e + (Fe^{3+})_2 \xrightarrow{\text{Zn dust + } H_2SO_4} 2Fe^{2+}$$

$\because$ Zn dust is used as reducing agent and thus,

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

Let a Meq. of Fe^{2+} and b Meq. of Fe^{3+} be present in 25 mL solution. In case I, after reduction with Zn,

Meq. of Fe^{2+} + Meq. of Fe^{2+} from $Fe^{3+} = a + b$

Now these are oxidized by $K_2Cr_2O_7$

$\therefore$ Total Meq. of Fe^{2+} = Meq. of $K_2Cr_2O_7$

$$a + b = 34.25\times\frac{1}{10}$$

$$\therefore \quad a + b = 3.425 \qquad ...(1)$$

Case II: If reduction is not made, the solution contains Fe^{2+} and Fe^{3+} of which only Fe^{2+} are oxidized by $K_2Cr_2O_7$.

$\therefore$ Meq. of Fe^{2+} = Meq. of $K_2Cr_2O_7$

$$a = 22.45\times\frac{1}{10}$$

$$a = 2.245 \qquad ...(2)$$

$\therefore$ By Eq. (1), $b = 3.425 - 2.245 = 1.18$

$\because$ Meq. of $FeSO_4$ (in 25 mL) $= a = 2.245$	Meq. of $Fe_2(SO_4)_3$ (in 25 mL) $= b = 1.18$
$\therefore \frac{w}{M/1}\times 1000 = 2.245$	$\therefore \frac{w}{M/2}\times 1000 = 1.18$
$\because$ Molar mass of $FeSO_4 = 152$	$\because$ Molar mass of $Fe_2(SO_4)_3 = 400$
$\therefore$ Mass of $FeSO_4$ in 25 mL $= 0.341$ g	$\therefore$ Mass of $Fe_2(SO_4)$ in 25 mL $= 0.236$ g
$\therefore$ Strength of $FeSO_4$ = **13.64 g / litre**	$\therefore$ Strength of $Fe_2(SO_4)_3$ = **9.45 g / litre**

32.

$$MnSO_4\cdot 4H_2O \longrightarrow Mn_3O_4$$

$$3Mn^{2+} \longrightarrow (Mn^{8/3+})_3 + 2e$$

The residue Mn_3O_4 is dissolved in $FeSO_4$ which is reduced from $Mn^{8/3+}$ to $Mn^{2+}\cdot(Mn^{8/3+})_3 + 2e \longrightarrow 3Mn^{2+}$. The excess of $FeSO_4$ is titrated by $KMnO_4$. The normality of $KMnO_4$ is determined by another $FeSO_4$.

For normality of $KMnO_4$: Meq. of $KMnO_4$
= Meq. of $FeSO_4$

$$25\times N = 30\times 0.1 \quad \therefore \quad N = \frac{3}{25}$$

Now Meq. of $FeSO_4$ added to $Mn_3O_4 = 100\times 0.1 = 10$

Meq. of $FeSO_4$ left after reaction with Mn_3O_4
= Meq. of $KMnO_4$ used
$= 50\times\frac{3}{25} = 6$

$\therefore$ Meq. of $FeSO_4$ used for $Mn_3O_4 = 10 - 6 = 4$

$\therefore$ Meq. of $Mn_3O_4 = 4$

$\therefore$ Meq. of $MnSO_4\cdot 4H_2O = 4$

$\therefore \quad \frac{w}{3M/2}\times 1000 = 4$

$\because \quad E = \frac{M}{2/3}$ for $MnSO_4$ as valence factor is $\frac{2}{3}$

$\therefore \quad \frac{w\times 2}{3\times 223}\times 1000 = 4 \quad \therefore \quad w =$ **1.338 g**

33. For acid-base reaction in 25 mL solution:

Meq. of H_2SO_4 + Meq. of $H_2C_2O_4$ = Meq. of NaOH

$$a + b = 35.5\times\frac{1}{10} = 3.55 \qquad ...(1)$$

For redox change: Meq. of oxalic acid = Meq. of $KMnO_4$

$$b = 23.45\times\frac{1}{10} = 2.345$$

$\therefore$ Meq. of $H_2SO_4 = a$ (in 25 mL)	and Meq. of oxalic acid (in 25 mL) $= b = 2.345$
$= 3.55 - 2.345 = 1.205$	$N_{H_2C_2O_4} = \frac{2.345}{25} = 0.0938$
$\therefore N_{H_2SO_4} = \frac{1.205}{25} = 0.0482$ and Strength $= N\times E = 0.0482\times 49$ = **2.362 g litre^{-1}**	Strength $= N\times E$ $= 0.0938\times 63$ = **5.909 g litre^{-1}**

34.

$$N_{HCl} = \frac{4}{\frac{36.5\times 100}{1.2\times 1000}} = 1.315$$

($\because$ 4% by mass solution means that 100 g solution has 4 g solute)

Now Meq. of MnO_2 = Meq. of HCl

= Meq. of Cl_2 formed $= \frac{1.78}{11.2}\times 1000 = 158.93$

($\because$ Eq. mass of $Cl_2 = M/2$; $2Cl^- \longrightarrow Cl_2 + 2e$)

$\therefore$ Meq. of HCl $= 158.93$

$N\times V = 158.93$

$\therefore \quad V = \frac{158.93}{1.315} =$ **120.85 mL**

$\because$ HCl is also used to give $MnCl_2$ and thus, volume used is double than required for reduction of MnO_2;

$= 2\times 120.85 =$ **241.7 mL**

Also Meq. of $MnO_2 = 158.93$

$\therefore \quad \frac{w}{87/2}\times 1000 = 158.93$

$\therefore$ Mass of MnO_2 = **6.9134 g**

35. The redox changes are:

For $FeCl_3$ $\quad e + Fe^{3+} \longrightarrow Fe^{2+}$

For $N_2H_6SO_4$ $\quad (N^{2-})_2 \longrightarrow N_2^0 + 4e$

For $KMnO_4$ $\quad 5e + Mn^{7+} \longrightarrow Mn^{2+}$

Meq. of $N_2H_6SO_4$ in 10 mL solution

$= $ Meq. of $FeCl_3$ reacting with $N_2H_6SO_4$

$= $ Meq. of Fe^{2+} formed $=$ Meq. of $KMnO_4$

$\therefore$ Meq. of $N_2H_6SO_4$ in 10 mL solution $= 20\times\frac{1}{50}\times 5 = 2$

$$\therefore \quad \frac{w}{M/4}\times 1000 = 2$$

($\because$ Molar mass of $N_2H_6SO_4 = 130$)

$$\therefore \quad w = \frac{2\times 130}{4000} = 0.065$$

$\therefore$ Mass of $N_2H_6SO_4$ in 10 mL $= 0.065$ g

$\therefore$ Mass of $N_2H_6SO_4$ in 1000 mL $=$ **6.5 g litre^{-1}**

36. The redox changes are:

For reduction of Fe_2O_3 by zinc dust

$$2e + (Fe^{3+})_2 \longrightarrow 2Fe^{2+}$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$

Oxidant + $ne \longrightarrow$ Reductant

Meq. of Fe_2O_3 in 25 mL

$= $ Meq. of Fe^{3+} in $Fe_2O_3 =$ Meq. of Fe^{2+} formed

$= $ Meq. of oxidant used to oxidize Fe^{2+} again

$\therefore$ Meq. of Fe_2O_3 in 25 mL $=$ Meq. of oxidant

$= 17\times 0.0167\times n$

where n is no. of electrons gained by 1 molecule of oxidant.

$\therefore$ Meq. of Fe_2O_3 in 100 mL $= 17\times 0.0167\times n\times\frac{100}{25}$

$$\therefore \quad \frac{1\times 55.2\times 1000}{100\times M/2} = 17\times 0.0167\times n\times 4$$

$\because$ Molar mass of $Fe_2O_3 = 160$

$$\therefore \quad n = \frac{1\times 55.2\times 2\times 1000}{100\times 160\times 17\times 0.0167\times 4} = 6$$

$\therefore$ No. of electrons gained by one molecule of oxidant $=$ **6**

37. Redox changes are:

For $CuFeS_2$ $\quad e + Fe^{3+} \longrightarrow Fe^{2+}$

For $K_2Cr_2O_7$ $\quad 6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$

$\therefore$ Meq. of $CuFeS_2 =$ Meq. of $Fe^{2+} =$ Meq. of $K_2Cr_2O_7$

$= 42\times 0.01\times 6 = 2.52$

$$\therefore \quad \frac{w}{183.5/1}\times 1000 = 2.52$$

($\therefore$ Molar mass of $CuFeS_2 = 183.5$)

$\therefore$ Mass of $CuFeS_2 = 0.4624$ g

$$\therefore \quad \% \text{ of } CuFeS_2 = \frac{0.4624\times 100}{0.5} = \mathbf{92.48\%}$$

38. Let mass of $H_2C_2O_4 = a$ g in 1 litre

mass of $NaHC_2O_4 = b$ g in 1 litre

For acid-base reaction:

Now (Meq. of $H_2C_2O_4$ + Meq. of $NaHC_2O_4$) in 10 mL

$= 3\times 0.1$

$\therefore$ Meq. of $H_2C_2O_4$ + Meq. of $NaHC_2O_4$ in one litre

$= 3\times 0.1\times 100 = 30$

$$\therefore \frac{a}{45}\times 1000 + \frac{b}{112/1}\times 1000 = 30$$

$$\therefore \frac{1000a}{45} + \frac{1000b}{112} = 30 \quad ...(1)$$

E of $H_2C_2O_4 = \frac{M}{2}$

$= \frac{90}{2} = 45$

E of $NaHC_2O_4 = \frac{M}{1}$

(as acid salt)

$= \frac{112}{1} = 112$

For redox change : $C_2^{3+} \longrightarrow 2C^{4+} + 2e$

$$5e + Mn^{7+} \longrightarrow Mn^{2+}$$

Meq. of $H_2C_2O_4$ + Meq. of $NaHC_2O_4$ in 10 mL $= 4\times 0.1$

$\therefore$ Meq. of $H_2C_2O_4$ + Meq. of $NaHC_2O_4$ in 1 litre

$= 4\times 0.1\times 100 = 40$

$$\therefore \frac{a}{45}\times 1000 + \frac{b}{112/2}\times 1000 = 40$$

$$\therefore \frac{1000a}{45} + \frac{2000b}{112} = 40 \quad ...(2)$$

$\because$ Eq. mass of $H_2C_2O_4 = \frac{M}{2}$

and Eq. mass of $NaHC_2O_4$ (as reductant) $= \frac{M}{2}$

Solving Eqs. (1) and (2), we get

$a =$ **0.90 g**

$b =$ **1.12 g**

Note : Also given $a + b = 2.02$ and thus Eq. (1) or (2) can be used to find a and b by using $a + b = 2.02$.

39. Let V mL of reducing agent be used for $KMnO_4$ in different medium which act as oxidant.

Acid medium $\quad n_1e + Mn^{7+} \longrightarrow Mn^{a+} \quad \therefore \; n_1 = 7 - a$

Neutral medium $\quad n_2e + Mn^{7+} \longrightarrow Mn^{b+} \quad \therefore \; n_2 = 7 - b$

Alkaline medium $\quad n_3e + Mn^{7+} \longrightarrow Mn^{c+} \quad \therefore \; n_3 = 7 - c$

$\therefore$ Meq. of reducing agent $=$ Meq. of $KMnO_4$ in acid

$= $ Meq. of $KMnO_4$ in neutral

$= $ Meq. of $KMnO_4$ in alkali

$= 1\times n_1\times 20 \quad = 1\times n_2\times 33.3 \quad = 1\times n_3\times 100$

$n_1 = 1.665 \; n_2 = 5n_3$

$\because \; n_1, n_2, n_3$ are integers and $n_1 \ngtr 7$, $\quad \therefore \; n_3 = 1$

$\therefore \quad n_1 = 5, \; n_2 = 3$ and $n_3 = 1$

Therefore, different oxidation states of Mn are:

Acid medium $\quad 5e + Mn^{7+} \longrightarrow Mn^{a+} \quad \therefore \; a = \mathbf{+2}$

Neutral medium $\quad 3e + Mn^{7+} \longrightarrow Mn^{b+} \quad \therefore \; b = \mathbf{+4}$

Alkaline medium $\quad 1e + Mn^{7+} \longrightarrow Mn^{c+} \quad \therefore \; c = \mathbf{+6}$

Now same volume of reducing agent is treated with $K_2Cr_2O_7$ and therefore,

Meq. of reducing agent $=$ Meq. of $K_2Cr_2O_7$

$$20\times 5 = 1\times 6\times V$$

$$\therefore \; V = \frac{100}{6} = \mathbf{16.67\ mL}$$

$\therefore \; 6e + Cr_2^{6+} \longrightarrow 2Cr^{3+}$

$\therefore \; N = M \times$ Valence factor

Note : The conditions are valid only when Mn in each medium exist as monomeric atom, *i.e.*, not as Mn_2.

40. Redox changes are:

$$Fe \longrightarrow Fe^{2+} + 2e \qquad (\text{in } H_2SO_4)$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e \qquad (\text{with } K_2Cr_2O_7)$$

$$6e + Cr_2^{6+} \longrightarrow 2Cr^{3+}$$

Meq. of Fe^{2+} in 20 mL = Meq. of $K_2Cr_2O_7$

$$= 30 \times \frac{1}{30} = 1$$

∴ Meq. of Fe^{2+} of valence factor one in 100 mL

$$= \frac{1 \times 100}{20} = 5$$

∴ Meq. of Fe^{2+} of valence factor two in 100 mL

$$= 5 \times 2 = 10$$

∴ Meq. of Fe = Meq. of Fe^{2+}

$$\frac{w}{M/2} \times 1000 = 10$$

$$\therefore \quad \frac{w}{\frac{56}{2}} \times 1000 = 10$$

$$\therefore \quad w = \frac{56 \times 10}{2 \times 1000} = 0.28\,g$$

∴ % of Fe in wire $= \frac{0.28}{0.2828} \times 100 = \mathbf{99.0\%}$

41. When medium is reported and conc. of medium is desired, then first balance the equation using ion electron method.

$$4Cl_2 + S_2O_3^{2-} + 10OH^- \longrightarrow 2SO_4^{2-} + 8Cl^- + 5H_2O$$

Mole before reaction	0.15	0.01	0.30	0	0	0
Mole after reaction	$(0.15 - 4 \times 0.01)$ $= 0.11$	0 0	$(0.3 - 0.01 \times 10)$ 0.2	0.02 0.02	0.08 0.08	0.05 0.05

Since, mole ratio for combination is

$$Cl_2 : S_2O_3^{2-} : OH^- :: 4 : 1 : 10$$

∴ **$[OH^-]$ left after reaction is 0.2 mole.**

42. Meq. of NH_3 formed = Meq. of HCl used for NH_3

$$= 50 \times 0.15 - 32.10 \times 0.10 = 4.29$$

Note : These Meq. of NH_3 are derived using valence factor of $NH_3 = 1$. (an acid-base reaction)

In redox change valence factor of NH_3 is 8;

$$8e + N^{5+} \longrightarrow N^{3-}$$

Thus, Meq. of NH_3 for valence factor $8 = 8 \times 4.29$

Also, Meq. of NO_3^- = Meq. of $NH_3 = 8 \times 4.29 = 34.32$

$$\therefore \quad N_{NO_3^-} = \frac{34.32}{25} = \mathbf{1.37} \qquad (N \times V \text{ in mL} = \text{Meq.})$$

$$\text{Also,} \quad M_{NO_3^-} = \frac{1.37}{8} = \mathbf{0.1716} \qquad (N = M \times V \text{ factor})$$

43.

$$2NaClO_2 + Cl_2 \longrightarrow 2NaCl + 2ClO_2$$

Thus, mole ratio of $\frac{NaClO_2}{ClO_2} = \frac{2}{2}$

Also mole of $NaClO_2 = 2 \times 3.78$ (Mole $= M \times V_{\text{in } l}$)

∴ Mole of $ClO_2 = \mathbf{2 \times 3.78}$

Further % yield of the reaction = 97%

∴ Mole of ClO_2 actually formed $= \frac{2 \times 3.78 \times 97}{100}$

$$= 7.33 \text{ mol}$$

44. For $FeSO_4$ $\quad Fe^{2+} \xrightarrow{\text{Oxidation}} Fe^{3+} \xrightarrow{\text{Reduction}} Fe^{2+}$

$$\text{For } FeC_2O_4 \begin{cases} Fe^{2+} \xrightarrow{\text{Oxidation}} Fe^{3+} \xrightarrow{\text{Reduction}} Fe^{2+} \\ C_2O_4^{2-} \xrightarrow{\text{Oxidation}} CO_2 \uparrow \end{cases}$$

Let mM or Meq. of $FeSO_4$ and FeC_2O_4 be a and b respectively.

∴ Meq. of

Fe^{2+} + Meq. of Fe^{2+} + Meq. of $C_2O_4^{2-}$ = Meq. of

in $FeSO_4$ in FeC_2O_4 in FeC_2O_4 $KMnO_4$ used

$$a \times 1 \; + \; b \times 1 \; + \; b \times 2 \; = 40 \times \frac{1}{15} = \frac{8}{3}$$

$$\therefore \quad a + 3b = \frac{8}{3} \qquad ...(1)$$

After reduction of mixture only Fe^{2+} ions are formed from Fe^{3+} since CO_2 escapes out in air.

∴ Meq. of Fe^{2+} of $FeSO_4$ + Meq. of Fe^{2+} of FeC_2O_4

= Meq. of $KMnO_4$ used

$$a \times 1 \; + \; b \times 1 = 25 \times \frac{1}{15} = \frac{5}{3}$$

$$\therefore \quad a + b = 5/3 \qquad ...(2)$$

By Eqs. (1) and (2), $\quad a = 7/6, \quad b = 1/2$

∴ Ratio of Fe in $FeSO_4$ and $FeC_2O_4 = \frac{a}{b} = \mathbf{\frac{7}{3}}$

45. Redox changes are:

$$6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$

Meq. of $K_2Cr_2O_7$ in 1 mL = Meq. of Fe

$$= \frac{0.006}{56} \times 1000 = \frac{6}{56}$$

∴ Meq. of $K_2Cr_2O_7$ in 15.05 mL

$$= \frac{6}{56} \times 15.05 = 1.612$$

∴ Meq. of Fe^{2+} left unused = Meq. of $K_2Cr_2O_7$ used

$$= 1.612$$

Now Meq. of ferrous ammonium sulphate added

$$= 50 \times 0.12 = 6$$

Meq. of ferrous ammonium sulphate left unused = 1.612

∴ Meq. of ferrous ammonium sulphate used for sample

$$= 6 - 1.612 = 4.388$$

$$\therefore \quad \text{Meq. of Cr} = 4.388 \quad \text{or} \quad \frac{w}{E} \times 1000 = 4.388$$

$$\therefore \quad w_{Cr} = \frac{4.388 \times 52}{1000 \times 3} = 0.0761 \qquad (\because E_{Cr} = 52/3)$$

$$\therefore \quad \%\,Cr = \frac{0.0761}{0.5} \times 100 = \mathbf{15.20\%}$$

$$\text{Also} \quad \text{Meq. of } Cr_2O_3 = 4.388 \quad \text{or} \quad \frac{w}{E} \times 1000 = 4.388$$

$$w_{Cr_2O_3} = \frac{4.388 \times 152}{6 \times 1000} = 0.1112\,g \left(\because E_{Cr_2O_3} = \frac{152}{6}\right)$$

$$\therefore \quad \%\,Cr_2O_3 = \frac{0.1112}{0.5} \times 100 = \mathbf{22.23\%}$$

46. Redox changes are:

$$e + \mathrm{Fe}^{3+} \longrightarrow \mathrm{Fe}^{2+}$$
$$2\mathrm{N}^{-} \longrightarrow (\mathrm{N}^{+})_2 + 4e$$
$$5e + \mathrm{Mn}^{7+} \longrightarrow \mathrm{Mn}^{2+}$$

Meq. of Fe^{2+} formed by $\mathrm{NH_2OH}$ in 50 mL dilute solution

$= \text{Meq. of } \mathrm{KMnO_4} \text{ used} = 12 \times 0.02 \times 5 = 1.2$

$\therefore$ Meq. of $\mathrm{NH_2OH}$ in 50 mL dilute solution = 1.2

$\therefore$ Meq. of $\mathrm{NH_2OH}$ in 1000 mL dilute solution

$$= 1.2 \times \frac{1000}{50} = 24$$

$\therefore$ Meq. of $\mathrm{NH_2OH}$ in 10 mL of original solution

= Meq. of $\mathrm{NH_2OH}$ in 1000 mL dilute solution = 24

($\because$ Meq. of solute does not change on dilution)

$$\therefore \quad \frac{w}{33/2} \times 1000 = 24$$

$$w_{\mathrm{NH_2OH}} = 0.396\,\mathrm{g}$$

$\therefore$ Mass of $\mathrm{NH_2OH}$ in 10 mL original solution = 0.396 g

$\therefore$ Mass of $\mathrm{NH_2OH}$ in 1 litre original solution

$$= \frac{0.396 \times 1000}{10} = \mathbf{39.6\ g / litre}$$

47. $\therefore$ Meq. of $\mathrm{NaHSO_3}$ = Meq. of $\mathrm{NaIO_3}$

$$= N \times V = \frac{5.8}{198/6} \times 1000$$

[Eq. mass of $\mathrm{NaIO_3} = M/6$; because $\mathrm{I}^{5+} + 6e \longrightarrow \mathrm{I}^{-}$]

Meq. of $\mathrm{NaHSO_3} = 175.76$

$$\therefore \quad \frac{w}{M/2} \times 1000 = 175.76$$

$$\therefore \quad w_{\mathrm{NaHSO_3}} = \frac{175.76 \times 104}{2000} = \mathbf{9.14\ g}$$

Also Meq. of I^{-} formed in I step using valence factor 6

$= 175.76$

In II step valence factor of I^{-} is 1 and valence factor of $\mathrm{IO_3^{-}}$ is 5.

Thus, Meq. of I^{-} formed using valence factor 1 $= \frac{175.76}{6}$

Also Meq. of $\mathrm{NaIO_3}$ used in step II $= \frac{175.76}{6}$

$$\therefore \quad N \times V = \frac{175.76}{6}$$

$$\text{or} \quad \frac{5.8}{198/5} \times V = \frac{175.76}{6} \quad \therefore \quad V_{\mathrm{NaIO_3}} = \mathbf{200\ mL}$$

48. Meq. of oxalate salt as acid in 30 mL = Meq. of NaOH used

$= 27 \times 0.12$

Meq. of oxalate salt as acid in one litre $= \frac{27 \times 0.12 \times 1000}{30}$

$$\text{or} \quad \frac{9.15}{\text{Molar mass of salt}/Y} \times 1000 = \frac{27 \times 0.12 \times 1000}{30} \quad \text{...(1)}$$

($\because$ Y is replaceable H-atom $\therefore E_{\text{salt}} = M/Y$)

Also Meq. of oxalate salt as reductant in 30 mL

= Meq. of $\mathrm{KMnO_4}$ used $= 36 \times 0.12$

$\therefore$ Meq. of oxalate salt as reductant in 1 litre

$$= \frac{36 \times 0.12 \times 1000}{30}$$

$$\text{or} \quad \frac{9.15}{\frac{\text{Molar mass of salt}}{2z}} \times 1000 = \frac{36 \times 0.12 \times 1000}{30} \quad \text{...(2)}$$

$[\because (\mathrm{C}_2^{3+})_z \longrightarrow (2\mathrm{C}^{4+})_z + 2Ze \quad \therefore E_{\text{salt}} = M/2Z]$

$\therefore$ By Eqs. (1) and (2), $\quad \frac{Y}{2Z} = \frac{27}{36}$

$\therefore \quad 4Y = 6Z$ ...(3)

Also, Total cationic charge = total anionic charge

$\therefore \quad X + Y = 2Z$ ...(4)

By Eqs. (3) and (4), $X : Y : Z :: 1 : 3 : 2$

These are in simplest ratio.

$\therefore$ Molecular formula is $\mathrm{KH_3(C_2O_4)_2 \cdot }n\mathrm{H_2O}$.

Now Molar mass of salt $= 39 + 3 + 176 + 18n = 218 + 18n$ ...(5)

By Eq. (1) and putting, $\quad Y = 3$

$M = 254.16$ ...(6)

$\therefore$ By Eqs. (5) and (6), $\quad n = 2$

$\therefore$ Oxalate salt is $\mathbf{KH_3(C_2O_4)_2 \cdot 2H_2O}$

49. Metal is M

$$M \longrightarrow M^{n+} + ne$$
$$2e + 2\mathrm{H}^{+} \longrightarrow \mathrm{H_2}$$

$\therefore$ Meq. of metal or Meq. of M^{n+} = Meq. of $\mathrm{H_2}$

$$= \frac{43.9}{11200} \times 1000$$

($\because$ 11200 mL $\mathrm{H_2}$ = 1 equivalent)

$$\frac{0.1}{51/n} \times 1000 = 3.92$$

$\therefore \quad n = 2$

Now $\quad M^{2+} \longrightarrow M^{a+} + (a-2)e$

$$5e + \mathrm{Mn}^{7+} \longrightarrow \mathrm{Mn}^{2+}$$

$\therefore$ Meq. of M^{2+} = Meq. of $\mathrm{KMnO_4}$

$$\frac{0.1}{51/(a-2)} \times 1000 = 58.8 \times 0.1 \quad \therefore \quad a = 5$$

$\therefore$ Different oxidation states of metal are **2** and **5.**

50. For the reaction: $\mathrm{Fe} + \mathrm{Fe_2(SO_4)_3} \longrightarrow 3\mathrm{FeSO_4}$

$\because$ 964 g $\mathrm{Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O}$ gives 3×152 g $\mathrm{FeSO_4}$

$\therefore$ 1.25 g $\mathrm{Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O}$ gives

$$= \frac{3 \times 152 \times 1.25}{964}\,\mathrm{g}$$

$= 0.5913$ g $\mathrm{FeSO_4}$

$\mathrm{FeSO_4}$ formed is now oxidized by $\mathrm{KMnO_4}$

$\therefore$ Meq. of $\mathrm{FeSO_4}$ = Meq. of $\mathrm{KMnO_4}$

$$\frac{0.5913}{152/1} \times 1000 = 0.107 \times V \quad \therefore \quad V = \mathbf{36.36\ mL}$$

Similarly, if Cu is used

$$\mathrm{Cu} + \mathrm{Fe_2(SO_4)_3} \longrightarrow 2\mathrm{FeSO_4} + \mathrm{CuSO_4}$$

$\because$ 964 g salt gives $= 2 \times 152$ g $\mathrm{FeSO_4}$

$\therefore$ 1.25 g salt gives $= \frac{2 \times 152 \times 1.25}{964}$ g $= 0.3942$ g $\mathrm{FeSO_4}$

$\therefore$ Meq. of $\mathrm{FeSO_4}$ = Meq. of $\mathrm{KMnO_4}$

$$\frac{0.3942}{152/1}\times 1000 = 0.107\times V \quad \therefore \quad V = \mathbf{24.24\ mL}$$

51. For, $Fe_3O_4 \longrightarrow 3FeO;\quad 2e + Fe_3^{8/3+} \longrightarrow 3Fe^{2+}$ ...(i)

Thus, valence factor for Fe_3O_4 is 2 and for FeO is 2/3

For, $Fe_2O_3 \longrightarrow 2FeO;\quad 2e + Fe_2^{3+} \longrightarrow 2Fe^{2+}$ ...(ii)

Thus, valence factor for Fe_2O_3 is 2 and for FeO is 1.

Let Meq. of Fe_3O_4 and Fe_2O_3 be a, b respectively.

$\therefore$ Meq. of Fe_3O_4 + Meq. of Fe_2O_3

= Meq. of I_2 liberated = Meq. of hypo used

$$a + b = \frac{11\times 0.5\times 100}{20} = 27.5 \qquad \text{...(iii)}$$

Now, the Fe^{2+} ions are again oxidized to Fe^{3+} by $KMnO_4$. Note that in the change $Fe^{2+} \rightarrow Fe^{3+} + e$; valence factor of Fe^{2+} is 1.

Thus, Meq. of Fe^{2+} (from Fe_3O_4) +

Meq. of Fe^{2+} (from Fe_2O_3)

= Meq. of $KMnO_4$ used

[If valence factor for Fe^{2+} is 2/3 from Eq. (1),
then Meq. of Fe^{2+} (from Fe_3O_4) = a
If valence factor for Fe^{2+} is 1 then Meq. of Fe^{2+}
(from Fe_3O_4) = $3a/2$
Similarly, from Eq. (ii), Meq. of Fe^{2+} from Fe_2O_3 = b]

$$\therefore \quad \frac{3a}{2} + b = 0.25\times 5\times 12.8\times \frac{100}{50} = 32$$

or $3a + 2b = 64$ ...(iv)

From Eqs. (iii) and (iv),

Meq. of $Fe_3O_4 = a = 9$ and Meq. of $Fe_2O_3 = b = 18.5$

$$\therefore w_{Fe_3O_4} = \frac{9\times 232}{2\times 1000} = 1.044\text{ g} \qquad w_{Fe_2O_3} = \frac{18.5\times 160}{2\times 1000} = 1.48\text{ g}$$

$$\therefore \quad \%\text{ of }Fe_3O_4 = \frac{1.044\times 100}{3} = \mathbf{34.8}$$

and
$$\%\text{ of }Fe_2O_3 = \frac{1.48\times 100}{3} = \mathbf{49.33}$$

52. $Ca + H_2C_2O_4 \longrightarrow CaC_2O_4$

The Meq. of $H_2C_2O_4$ solution added to precipitate Ca as CaC_2O_4 is derived as:

25 mL of $H_2C_2O_4$ is diluted 4 folds, *i.e.*, to 100 mL

Now Meq. of dil. $H_2C_2O_4$ in 25 mL

= Meq. of $KMnO_4$ used

$= 24.1\times 0.1025 = 2.47025$

$\therefore$ Meq. of $H_2C_2O_4$ in 100 mL dilute solution

$$= \frac{2.47025\times 100}{25} = 9.881$$

$\therefore$ Meq. of $H_2C_2O_4$ in 25 mL conc. solution = 9.881

Meq. of $H_2C_2O_4$ left after precipitation of $Ca_2C_2O_4$ in one fourth filtrate

= Meq. of $KMnO_4$ used $= 5\times 0.1025$

$\therefore$ Total Meq. of $H_2C_2O_4$ left $= 5\times 0.1025\times 4 = 2.05$

$\therefore$ Meq. of $H_2C_2O_4$ used for Ca $= 9.881 - 2.05 = 7.831$

$\therefore$ Meq. of Ca = 7.831

$$\frac{w}{40/2}\times 1000 = 7.831 \quad \therefore \quad w_{Ca} = 0.1566\text{ g}$$

$$\therefore \quad \%\text{ of Ca in substance} = \frac{0.1566}{1.048}\times 100 = \mathbf{14.94\%}$$

53. Meq. of Fe^{2+} = Meq. of $KMnO_4$

Meq. of $Fe^{2+} = 47.2\times 0.112 = 5.2864$

$\therefore \quad Fe^{2+} \longrightarrow Fe^{3+} + e$

Meq. of $Fe^{2+} = 5.2864$ (valence factor = 1)

Fe ore on dissolution in H_2SO_4 show valence factor 2

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

$\therefore$ Meq. of Fe^{2+} of valence factor $2 = 5.2864\times 2$

$\therefore$ Meq. of Fe $= 5.2864\times 2$

$$\frac{w}{\frac{56}{2}}\times 1000 = 5.2864\times 2 \quad \therefore \quad w_{Fe} = 0.296\text{ g}$$

$$\therefore \quad \%\text{ purity of Fe} = \frac{0.296\times 100}{0.804} = \mathbf{36.82\%}$$

Now $Fe_3O_4 \longrightarrow 3Fe$

3×56 g Fe is obtained from 232 g Fe_3O_4

$$\therefore 0.296\text{ g Fe is obtained} = \frac{232\times 0.296}{56\times 3} = 0.409\text{ g }Fe_3O_4$$

$$\therefore \quad \%\text{ of }Fe_3O_4 = \frac{0.409}{0.804}\times 100 = \mathbf{50.87\%}$$

54. Meq. of reductant in 25 mL = Meq. of $KMnO_4$

$= 20\times 0.01\times 5$

$\therefore$ Meq. of reductant in 1 litre $= 20\times 0.01\times 5\times 40 = 40$

Reductant shows the change $A_2^{+a} \longrightarrow 2A^{+b} + 2e$

$$\therefore \quad \text{Eq. mass of reductant} = \frac{\text{Molar mass}}{2}$$

$\because$ Meq. of reductant = 40

$$\therefore \quad \frac{w}{M/2}\times 1000 = 40 \quad \therefore \quad \frac{2.52\times 2\times 1000}{M} = 40$$

$$\therefore \quad M = \mathbf{126}$$

55. Meq. of H_2SO_4 = Meq. of NaOH

$N\times 10.27 = 10.35\times 0.1297 \therefore N_{H_2SO_4} = 0.1307$

$V_{H_2SO_4}$ used for $KNaCO_3 = 41.72 - 1.91$ mL

Meq. of H_2SO_4 used for $NaKCO_3$ = Meq. of H_2SO_4 added − Meq. of H_2SO_4 used by NaOH

$= (0.1307\times 41.72) - 1.91\times 0.1297 = 5.2050$

Also for the change

$$NaKC_4H_4O_6\cdot 4H_2O \longrightarrow NaKCO_3 + CO_2\uparrow + H_2O\uparrow$$

Now Meq. of $NaKCO_3$ using valency factor 2 during its neutralization with $H_2SO_4 = 5.2050$

$$\therefore \quad \text{Mass of }NaKCO_3 = \frac{5.2050\times 122}{2\times 1000} = 0.3175\text{ g}$$

$\therefore$ For 1 : 1 mole ratio of conversion, mass of Rochelle salt

$$= \frac{282}{122}\times 0.3175 = 0.7339\text{ g}$$

$$\therefore \quad \%\text{ purity of Rochelle salt} = \frac{0.7339}{0.9546}\times 100 = \mathbf{76.87\%}$$

56. The reactions are:

$$5e + Mn^{7+} \longrightarrow Mn^{2+} \quad \text{and} \quad 2I^- \longrightarrow I_2 + 2e$$

$$6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$$

Let mass of $KMnO_4$ and $K_2Cr_2O_7$ be a and b g respectively.

$\therefore$ Meq. of $KMnO_4$ + Meq. of $K_2Cr_2O_7$ = Meq. of I_2

= Meq. of hypo $= 60 \times 0.1$

$$\therefore \quad \frac{a}{158/5} \times 1000 + \frac{b}{294/6} \times 1000 = 6 \quad \text{...(i)}$$

Also given $\quad a + b = 0.24 \quad$ ...(ii)

$\therefore \quad a = 0.098\,g \quad$ *i.e.*, mass of $KMnO_4$

$b = 0.142\,g \quad$ *i.e.*, mass of $K_2Cr_2O_7$

Also, mass of Mn in 0.098 g $KMnO_4 = \frac{55 \times 0.098}{158}$

$= 0.034\,g$

Mass of Cr in 0.142 g $K_2Cr_2O_7 = \frac{52 \times 2 \times 0.142}{294} = 0.050\,g$

$\therefore \quad$ % of Mn in sample $= \frac{0.034 \times 100}{0.24} =$ **14.17%**

$\therefore \quad$ % of Cr in sample $= \frac{0.050 \times 100}{0.24} =$ **20.83%**

57. The redox changes are :

$$5e + Mn^{7+} \longrightarrow Mn^{2+}$$
$$6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$$
$$2I^- \longrightarrow I_2^0 + 2e$$
$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e$$

Let $K_2Cr_2O_7$ and $KMnO_4$ be a and b g respectively

$\therefore \quad a + b = 0.5 \quad$ ...(1)

Further $\quad$ Meq. of $KMnO_4$ + Meq. of $K_2Cr_2O_7$

= Meq. of KI = Meq. of I_2 liberated = Meq. of $Na_2S_2O_3$

$$\frac{a}{294/6} \times 1000 + \frac{b}{158/5} \times 1000 = 100 \times 0.15 \text{...(2)}$$

By Eqs. (1) and (2) $\quad a = 0.073, \quad b = 0.427$

$\therefore$ % of $K_2Cr_2O_7$ = **14.6%** and % of $KMnO_4$ = **85.4%**

58. Meq. of H_2O_2 = Meq. of I_2

$(w/17) \times 1000 = [0.508/(254/2)] \times 1000 \quad \therefore w = 0.068\,g$

$$H_2O_2 \longrightarrow H_2O + (1/2)O_2$$

$\because$ 34 g H_2O_2 gives 11.2 litre O_2,

$\therefore$ 0.068 g gives $\quad (11.2 \times 0.068)/34 = 22.4$ mL O_2

$\therefore \quad$ Volume strength of $H_2O_2 = 22.4/5 =$ **4.48%**

59. Let Molar mass of AO and A_2O_3 be m and n respectively.

$\therefore \quad m = a + 16 \quad$ ...(1)

and $\quad n = 2a + 48 \quad$ ...(2)

where a is Atomic mass of A.

Now suppose X and Y g of AO and A_2O_3 are present in mixture

Then $\quad X + Y = 2.198 \quad$ ...(3)

Also $\quad$ Meq. of AO + Meq. of A_2O_3 = Meq. of $K_2Cr_2O_7$

$$\frac{X}{(a+16)/5} \times 1000 + \frac{Y}{(2a+48)/8} \times 1000 = 0.015 \times 6 \times 1000 \quad \text{...(4)}$$

$\because$
$$A^{2+} \longrightarrow A^{7+} + 5e$$
$$A_2^{3+} \longrightarrow 2A^{7+} + 8e$$
$$6e + Cr_2^{6+} \longrightarrow 2Cr^{3+}$$

$$\therefore \quad \text{By Eq. (4),} \quad \frac{5X}{a+16} + \frac{8Y}{2a+48} = 0.09 \quad \text{...(5)}$$

Also, mole AO_4^- by AO + mole of AO_4^- by $A_2O_3 = 0.0187$

$$\frac{X}{a+16} + \frac{2Y}{2a+48} = 0.0187 \quad \text{...(6)}$$

$\because$ Mole ratio of $AO : AO_4^- :: 1:1, A_2O_3 : AO_4^{-1} :: 1:2$

Solving Eqs. (3), (5) and (6) $\quad a =$ **100**

60. In (a): $\quad Se^{4+} \longrightarrow Se^{6+} + 2e$

$10e + 2Br^{5+} \longrightarrow Br_2^0 \quad \therefore$ Eq. mass $KBrO_3 = M/5$;

(valency factor = 5)

In (b): $6e + Br^{5+} \longrightarrow Br^{1-} \quad \therefore$ Eq. mass $KBrO_3 = M/6$;

$As^{3+} \longrightarrow As^{5+} + 2e \quad$ (valency factor = 6)

Let Meq. of BrO_3^- of valency factor 6 = Meq. of AsO_2^-

$$= 5.1 \times \frac{1}{25} \times 2 = 0.408$$

Meq. of BrO_3^- of valency factor 5 added

$$= 20 \times \frac{1}{60} \times 5 = \frac{5}{3} = 1.67$$

Left Meq. of BrO_3^- of valency factor $5 = \frac{0.408 \times 5}{6} = 0.34$

$\therefore$ Meq. of BrO_3^- used for $SeO_3^{2-} = 1.67 - 0.34 = 1.33$

$\therefore$ Meq. of $SeO_3^{2-} = 1.33$ or $\frac{w}{127/2} \times 1000 = 1.33$

$\therefore \quad W_{SeO_3^{2-}} = \mathbf{0.084\ g}$

61. Meq. of I_2 used $= 20.10 \times 0.05 = 1.005$

Let Meq. of As_2O_3 and Meq. of As_2O_5 in mixture be a and b respectively. On addition of I_2 to mixture, As_2^{3+} is converted to As_2^{5+}.

$\therefore$ Meq. of As_2O_3 = Meq. of I_2 used = 1.005

= Meq. of As^{5+} formed

or $\quad a = 1.005 \quad$ ...(1)

After reaction with I_2, mixture contains all the arsenic in +5 oxidation state which is then titrated using KI + hypo. Thus,

Meq. of As_2O_3 as As^{5+} + Meq. of As_2O_5 as As^{5+}

= Meq. of liberated I_2 = Meq. of hypo used

or $\quad a + b = \frac{1.1113}{248} \times 1000$ or $a + b = 4.481$ ...(2)

By Eqs. (1) and (2), $\quad b = 4.481 - 1.005 = 3.476$

$\therefore$ Mass of $As_2O_3 = \frac{\text{Meq.} \times \text{Eq. mass}}{1000} = \frac{1.005 \times 198}{4 \times 1000}$

$= 0.0497\,g$

and $\quad$ Mass of $As_2O_5 = \frac{3.476 \times 230}{4 \times 1000} = 0.1999\,g$

$\therefore \quad$ Mass of mixture $= 0.0497 + 0.1999 =$ **0.2496 g**

62. (a) $\quad Cu^0 \longrightarrow Cu^{2+} + 2e$

$$N^{5+} + e \longrightarrow N^{4+}$$

$\therefore$ Eq. of Cu = Eq. of NO_2

$$\frac{w}{63.6/2} = \frac{1 \times 1.04}{0.0821 \times 298}$$

$$\left(\because \text{mole of } NO_2 = \text{Eq. of } NO_2 = \frac{PV}{RT}\right)$$

$\therefore \quad w_{Cu} = \mathbf{1.35\ g}$

$\therefore \quad w_{Zn} = 1.50 - 1.35 = \mathbf{0.15\ g}$

$$\%\text{ of Cu} = \frac{1.35}{1.5} \times 100 = 90\%$$

$$\therefore \quad \%\text{ of Zn} = \frac{0.15}{1.5} \times 100 = \mathbf{10\%}$$

(b) Thus, 1 g brass contains 0.9 g Cu and 0.1 g Zn

$\therefore$ Meq. of HNO_3 = Meq. of Zn	and Meq. of HNO_3 = Meq. of Cu
or $3 \times 8 \times V_1 = \frac{0.1}{65/2} \times 1000$	or $3 \times V_2 = \frac{0.9}{63.6/2} \times 1000$
$\therefore \quad V_1 = 0.128$ mL	$\therefore \quad V_2 = 9.43$ mL
$(\because N^{5+} + 8e \rightarrow N^{3-})$	

$\therefore$ Total volume of HNO_3 used $= 0.128 + 9.43 = \mathbf{9.558\ mL}$

63. Meq. of alkali added $= 30 \times 0.04 = 1.2$

Meq. of alkali left $= 22.48 \times 0.024 = 0.54$

$\therefore$ Meq. of alkali used for SO_2 and H_2O_2

$$= 1.2 - 0.54 = 0.66$$

$$\therefore \quad \text{Mass of alkali used} = \frac{0.66 \times 40}{1000} = 0.0264\ \text{g}$$

$\because$ 80 g NaOH reacts with 64 g SO_2.

$$\therefore \quad 0.0264\ \text{g NaOH reacts} = \frac{64 \times 0.0264}{80} = 0.021\text{g } SO_2$$

Now $\because$ 64 g SO_2 required = 32 g S

$$\therefore \quad 0.021\ \text{g } SO_2 \text{ required} = \frac{32 \times 0.021}{64} = 0.0105\text{g}$$

$$\therefore \quad \%\text{ of S} = \frac{0.0105}{5.6} \times 100 = \mathbf{0.1875\%}$$

64. Since, Cu will react with ferric sulphate to reduce Fe^{3+} to Fe^{2+}. The reduced state of iron is further oxidized by $KMnO_4$.

Thus, Meq. of $KMnO_4$ used

= Meq. of iron sulphate oxidized
= Meq. of ferric sulphate used by Cu
= Meq. of Cu

$\therefore$ Meq. of Cu = Meq. of $KMnO_4$ used

$$\frac{0.108}{63.6/n} \times 1000 = 33.7 \times 0.1$$

$\therefore \quad n \approx 2$ (integer)

It is thus, clear that during reduction of Fe^{3+}, Cu is oxidized to Cu^{2+}. Thus reaction is:

$$\mathbf{Cu + Fe_2(SO_4)_3 \longrightarrow CuSO_4 + 2FeSO_4}$$

65. The reactions are

$$H_2O + 2KI + O_3 \longrightarrow 2KOH + I_2 + O_2$$

Also $\quad 2e + I_2 \longrightarrow 2I^-$

and $\quad 2(S^{2+})_2 \longrightarrow (S^{5/2+})_4 + 2e$

$\therefore$ Meq. of I_2 = Meq. of $Na_2S_2O_3 = 1.5 \times 0.01 = 1.5 \times 10^{-2}$

or $\quad \text{mM of } I_2 = \frac{1.5 \times 10^{-2}}{2} = 7.5 \times 10^{-3}$

$\therefore \quad \text{mM of } O_3 = \text{mM of } I_2 = 7.5 \times 10^{-3}$

$(\because$ Mole ratio of $O_3 : I_2 :: 1:1)$

$$\therefore \quad P'_{O_3} = \frac{nRT}{V} = \frac{7.5 \times 10^{-6} \times 0.0821 \times 300}{10}$$

$$= 184.725 \times 10^{-7}\ \text{atm}$$

$\therefore$ Vol. % of $O_3 = 184.725 \times 10^{-7} \times 100 = \mathbf{1.847 \times 10^{-3}\%}$

66. $\quad O_3 + 2KI + H_2O \longrightarrow 2KOH + I_2 + O_2$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

$\therefore$ Millimole of O_3 = Millimole of I_2

$$= \frac{1}{2} \times \text{mM of } Na_2S_2O_3$$

$(\text{mM} = M \times V_{\text{in mL}})$

$$= \frac{1}{2} \times 40 \times \frac{1}{10} = 2\ \text{mM} = 0.002\ \text{mole}$$

Total millimole of O_2 and O_3 in mixture are calculated from

$$PV = nRT$$

$$1 \times 1 = n \times 0.0821 \times 273 \quad \therefore \quad n = 0.044\ \text{mole}$$

$\therefore \quad$ Mole of $O_2 = 0.044 - 0.002 = 0.042$

Now $\quad$ mass of $O_2 = 0.042 \times 32\text{g} = 1.344$ g

mass of $O_3 = 0.002 \times 48\text{g} = 0.096$g

$$\therefore \quad \%\text{ of } O_3 = \frac{0.096}{1.44} \times 100 = 6.7\%$$

No. of photon or molecules of ozone

$$= \frac{0.096 \times 6.023 \times 10^{23}}{48} = \mathbf{1.2 \times 10^{21}}$$

67. Meq. of MnO_4^- added $= 200 \times 0.75 \times 5 = 750$

$\because \quad Mn^{7+} + 5e \longrightarrow Mn^{2+} \qquad \therefore \quad N = M \times 5$

Meq. of MnO_4^- left unused = Meq. of Fe^{2+} used

$$= 175 \times 1 \times 1 = 175$$

$\because \quad Fe^{2+} \longrightarrow Fe^{3+} + e \qquad \therefore \quad N = M \times 1$

Now Meq. of MnO_4^- used $= 750 - 175 = 575$

MnO_4^- is used for Cu_2S and CuS to give.

For Cu_2S: $\quad Cu_2^+ \longrightarrow 2Cu^{2+} + 2e$

$$S^{2-} \longrightarrow S^{4+} + 6e$$

$$Cu_2S \longrightarrow 2Cu^{2+} + S^{4+} + 8e$$

For CuS: $\quad S^{2-} \longrightarrow S^{4+} + 6e$

Let Cu_2S and CuS be a and b g respectively

$$\therefore \quad a + b = 10 \qquad \text{...(1)}$$

$\therefore$ Meq. of MnO_4^- used = Meq. of Cu_2S + Meq. of CuS

$$575 = \frac{a}{159.2/8} \times 1000 + \frac{b}{95.6/6} \times 1000 \qquad \text{...(2)}$$

$\therefore$ Solving Eqs. (1) and (2), $a = 4.206$g

$b = 5.794$ g

$$\therefore \quad \%\text{ of CuS in mixture} = \frac{5.794}{10} \times 100 = \mathbf{57.94\%}$$

68. **NaCN vs. $KMnO_4$:** $C^{2+} \longrightarrow C^{4+} + 2e$

$$3e + Mn^{7+} \longrightarrow Mn^{4+}$$

Meq. of $KMnO_4$ added $= 50 \times 0.33 \times 3 = 49.5$

(v.f. of $KMnO_4 = 3$)

Meq. of $KMnO_4$ (v.f. = 5) left after reaction with NaCN

$= $ Meq. of $FeSO_4$ used $= 500 \times 0.06 \times 1 = 30$

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$

$$Mn^{7+} + 5e \longrightarrow Mn^{2+}$$

$\therefore$ Meq. of $KMnO_4$ (v.f. = 3) left $= \frac{30 \times 3}{5} = 18$

$\therefore$ Meq. of NaCN in sample $= 49.5 - 18 = 31.5$

$$\frac{w}{49/2} \times 1000 = 31.5$$

$\therefore$ $w = 0.7718\,g$

$\therefore$ % of NaCN $=$ **77.18**

69. Suppose mass of $BaCO_3$, $CaCO_3$ and CaO are a, b, c be respectively.

$$a + b + c = 1.249 \quad ...(1)$$

For the reactions $BaCO_3 \longrightarrow BaCrO_4$

and $3e + Cr^{6+} \longrightarrow Cr^{3+}$

$$2I^- \longrightarrow I_2 + 2e$$

Meq. of $BaCO_3$ = Meq. of $BaCrO_4$ = Meq. of I_2

or $\frac{a}{197/3} \times 1000 = 20 \times 0.05 \times \frac{100}{10}$

$\therefore$ $a = 0.657\,g$ ...(2)

The Eq. mass of $BaCrO_4$ is $M/3$ and thus for $BaCO_3$ it should be $M/3$.

Also for acid-base reaction

Meq. of $BaCO_3$ + Meq. of $CaCO_3$ = Meq. of CO_2

$$\frac{a}{197/2} \times 1000 + \frac{b}{100/2} \times 1000 = \frac{168 \times 44}{22400 \times 22} \times 1000$$

$\therefore$ $200a + 394b = 295.5$ ...(3)

By Eqs. (2) and (3) $b = 0.416\,g$

$\therefore$ By Eq. (1) $0.657 + 0.416 + c = 1.249$

$\therefore$ $c = 0.176$

or % of CaO $= \frac{0.176 \times 100}{1.249} =$ **14.09%**

70. $5e + Mn^{7+} \longrightarrow Mn^{2+}$

$$(P^{3+})_4 \longrightarrow 4P^{5+} + 8e$$

Thus, Meq. of $KMnO_4 = \frac{100 \times 5 \times 1000}{158} = 3164.56$

Meq. of $P_4O_6 = \frac{100 \times 8 \times 1000}{219.9} = 3638.02$

$\therefore$ Meq. of P_4O_6 in excess $= 473.46$

$\therefore$ $\frac{w \times 8 \times 1000}{219.9} = 473.46$ $\therefore$ $w_{P_4O_6}$ in excess $=$ **13.01 g**

71. As_2O_3 sample $= 12.0\,g$. It reacts with $NaHCO_3$ to give Na_3AsO_3. Its reaction with I_2 shows the changes:

$$(As^{3+})_2 \longrightarrow (As^{5+})_2 + 4e;$$

$$I_2 + 2e \longrightarrow 2I^-$$

Meq. of As_2O_3 in 25 mL = Meq. of $I_2 = 22.4 \times N$ ...(1)

Also N of I_2 can be evaluated as:

Meq. of I_2 = Meq. of hypo $= N \times V$

The reaction are: $I_2 + 2e \longrightarrow 2I^-$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e$$

$$N \times 25 = \frac{24.8}{248 \times 1} \times 25$$

$\therefore$ $N_{I_2} = \frac{N}{10}$

$\therefore$ Meq. of As_2O_3 in 25 mL $= 22.4 \times \frac{1}{10} = 2.24$

or Meq. of As_2O_3 in 250 mL $= 2.24 \times \frac{250}{25} = 22.4$

or $\frac{w}{E} \times 1000 = 22.4$

$$\frac{w}{\frac{198}{4}} \times 1000 = 22.4$$

$\therefore$ $w_{As_2O_3} = \frac{22.4 \times 198}{4 \times 1000} = 1.1088$

$\therefore$ % of $As_2O_3 = \frac{1.1088}{12} \times 100 =$ **9.24%**

72. $Sn^{2+} \longrightarrow Sn^{4+} + 2e$

$$2e + (O^-)_2 \longrightarrow 2O^{2-}$$

Meq. of H_2O_2 used = Meq. of $Sn^{2+} = 100 \times 2 \times 2 = 400$

$\therefore$ Meq. of H_2O_2 taken $= \frac{200 \times 10 \times 2 \times 1000}{100 \times 34} = 1176.47$

$\therefore$ Meq. of H_2O_2 left $= 1176.47 - 400 = 776.47$

m mole of H_2O_2 left $= \frac{776.47}{2}$

Now $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$

or m mole of O_2 formed $= \frac{776.47}{2 \times 2} = 194.12$

$\therefore$ $V = \frac{nRT}{P} = \frac{194.12 \times 10^{-3} \times 0.0821 \times 293}{1} =$ **4.67 litre**

73. For $A_x(CO_3)_y(OH)_z$: $2x = 2y + z$ ...(1)

The reaction of salt with H_2SO_4 uses carbonate ions as well as hydroxide ions.

In case of phenolphthalein : Half of the salt is neutralized as carbonate is converted to bicarbonate and OH^- ions are completely neutralized.

Meq. of $H_2SO_4 = \frac{1}{2}$ Meq. of salt for carbonate +

Meq. of salt for OH^-

$$\frac{10 \times 1 \times 100}{50} = \frac{1}{2} \times \frac{1.7225 \times 1000}{\frac{M}{2y}} + \frac{1.7225 \times 1000}{\frac{M}{z}}$$

or $20 = \frac{1722.5y}{M} + \frac{1722.5z}{M}$ ...(2)

In case of methyl orange : Salt is completely neutralized.

$$\frac{15 \times 1 \times 100}{50} = \frac{1.7225 \times 1000}{\frac{M}{2y}} + \frac{1.7225 \times 1000}{\frac{M}{z}}$$

or $$30=\frac{3445y}{M}+\frac{1722.5z}{M} \qquad ...(3)$$

By subtracting Eq. (2) from Eq. (3).

$$10=\frac{1722.5y}{M} \qquad ...(4)$$

By Eqs. (2) and (4), $10=\frac{1722.5z}{M}$ ...(5)

$\therefore$ By Eqs. (4) and (5), $y=z$ ...(6)

Also from Eqs. (1) and (6), $x=1.5y$

Thus for simplest ratio $x:y:z::1.5:1:1$ or $3:2:2$

Therefore formula of salt is $\boldsymbol{A_3(CO_3)_2(OH)_2}$

74. $$(Cu^+)_2 \longrightarrow Cu^{2+} + Cu$$

The solution after dissolution of Cu_2O in dil. H_2SO_4 contains Cu^{2+} and Cu ions. Cu^{2+} ions react with KI to give CuI_2 which is converted to CuI and I_2.

$$Cu^{2+} + 2I \longrightarrow CuI_2 \longrightarrow CuI + \frac{1}{2}I_2$$

Millimole of KI taken $=\frac{8.3}{166}\times 1000 = 50$

Now, KI left unused reacts with oxidizing agent to liberate I_2 again.

$$2I^- \xrightarrow{\text{Oxidant}} I_2 \xrightarrow{2Na_2S_2O_3} Na_2S_4O_6 + 2NaI$$

$\therefore$ Millimole of KI left = Millimole of $Na_2S_2O_3$ used

(mole ratio of I^- to $Na_2S_2O_3$ is 1 : 1)

$= 10\times 1.0 = 10$

Therefore, millimole of KI used for $Cu^{2+} = 50 - 10 = 40$

$\therefore$ Millimole of $Cu_2O = 20$

$$\begin{bmatrix} Cu_2^+ \longrightarrow 2Cu^{2+} \\ \therefore \text{Mole ratio } Cu_2^+ : Cu^{2+} :: 1:2 \end{bmatrix}$$

or $$\frac{w}{M}\times 1000 = 20$$

$$\frac{w\times 1000}{142} = 20 \quad \therefore \ w_{Cu_2O} = 2.84$$

$\therefore$ % of $Cu_2O = \frac{2.84\times 100}{3} = \mathbf{94.67}$

75. $3Br_2 + 6OH^- \longrightarrow 5Br^- + BrO_3^- + 3H_2O$

(mole ratio $Br_2 : BrO_3^- :: 3:1$)

BrO_3^- and $C_2O_4^{2-}$ reacts to give redox change as:

$6e + Br^{5+} \longrightarrow Br^-$ (valence factor of $BrO_3^- = 6$)

$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$

Millimole of Br_2 taken $= 10\times 1.0 = 10$

$\therefore$ Millimole of BrO_3^- formed $=\frac{10}{3}$

Also, Meq. of CaC_2O_4 = Meq. of $BrO_3^- = \frac{10}{3}\times 6 = 20$

or $\frac{w\times 1000}{128/2} = 20 \quad \therefore \ w_{CaC_2O_4} = 1.28\,g$

$\therefore$ % of $CaC_2O_4 = \frac{1.28}{1.5}\times 100 = \mathbf{85.33}$

76. $2e + Cl^+ \longrightarrow Cl^-$ (OCl^- changes to Cl^-)

$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$ ($C_2O_4^{2-}$ change to CO_2)

Let *a* and *b* millimole of NaOCl and $CaOCl_2$ be present in mixture.

Meq. of NaOCl + Meq. of $CaOCl_2$ = Meq. of $Na_2C_2O_4$

$$2a + 2b = 10\times 0.15\times 2\times \frac{100}{10} = 30$$

$\therefore$ $2a + 2b = 30$ ...(1)

Also millimole of Cl^- from NaOCl +

millimole of Cl^- from $CaOCl_2$

= millimole of AgCl

or $$a + 2b = \frac{0.287}{143.5}\times 1000\times \frac{100}{10} = 20$$

$a + 2b = 20$ ...(2)

By Eqs. (1) and (2), $a = 10, b = 5$

$\therefore$ % of NaOCl $= 10\times 74.5\times 10^{-3}\times \frac{100}{2} = \mathbf{37.25}$

% of $CaOCl_2 = 5\times 127\times 10^{-3}\times \frac{100}{2} = \mathbf{31.75}$

77. Equivalent of $KMnO_4 = \frac{6.32}{31.6} = 0.2$

Equivalent of KCl $= \left[\frac{4}{74.5}\right] = 0.0537$

Equivalent of KBr $= \left[\frac{m}{119}\right]$

$\therefore$ $0.2 = 0.0537 + \frac{m}{119} \quad \therefore \ m = \mathbf{17.41\,g}$

78. Let mM of Cl^- and ClO_3^- be *a* and *b* respectively

$\therefore$ $a + b = $ mM of AgCl $= \frac{0.1435}{143.5}\times 1000 = 1$

Also, Meq. of $KClO_3 = 6a \quad \because 6e + Cl^{5+} \longrightarrow Cl^-$

and Meq. of $FeSO_4$ used for $KClO_3$

$= 30\times 0.2 - 37.5\times 0.08 = 6 - 3 = 3$

$\therefore$ $6a = 3$

$\therefore$ $a = \frac{1}{2}$ and $b = \frac{1}{2}$

i.e., $\mathbf{5\times 10^{-3}}$ **mole each, (1 : 1)**

79. Meq. of $KMnO_4$ = Meq. of ReO_4^{1-} = Meq. of Re

11.45×0.05 = Meq. of ReO_4^{1-} = Meq. of Re

$\therefore$ Meq. of Re from Re^{n+} to $ReO_4^- = 0.5725$

or $$\frac{26.83\times 10^{-3}}{186.2/(7-n)}\times 1000 = 0.5725$$

$\therefore$ $$7 - n = \frac{0.5725\times 186.2}{26.83\times 10^{-3}\times 1000} = 4 \quad \therefore n = 3$$

$\therefore$ Oxidation state is Re^{3+}.

• SINGLE INTEGER ANSWER PROBLEMS •

1. 'n' factor of FeC_2O_4 during its oxidation by acidified $KMnO_4$ is ....
2. An element A in a compound has oxidation state A^{n-}. If 1.68×10^{-3} mole of $K_2Cr_2O_7$ are required for complete oxidation of 3.26×10^{-3} mole of ABD for oxidation to A^{n-} to elemental state. The value of n is ....
3. 1.6 g pyrolusite ore was titrated with $50\,cm^3$ of 1.0 N oxalic acid and some sulphuric acid. The oxalic acid left was raised to 250 mL in a flask 25 mL of this solution when treated with 0.1 N $KMnO_4$ required 32 mL of the solution. The percentage of available oxygen in pyrolusite is :
4. 1 g sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with Zn dust. The resultant solution is cooled and made upto 100 mL. An aliquot of 25 mL of this solution requires 17 mL of 0.0167M solution of an oxidant for titration. The number of electrons taken up by oxidant in the above titration is ....
5. 0.31 g of an alloy of Fe + Cu was dissolved in excess dilute H_2SO_4 and the solution was made upto 100 mL. 20 mL of this solution required 3 mL of $\frac{N}{30} K_2Cr_2O_7$ solution for exact oxidation. The % purity (in closest value) of Fe in wire is :
6. The reaction $Cl_2(g) + S_2O_3^{2-} \longrightarrow SO_4^{2-} + Cl^-$ to be carried out in basic medium. 1.5 mole of Cl_2 are allowed to react can with 0.1 mole of $S_2O_3^{2-}$ in presence of 3.0 mole of OH^-. Mole of OH^- left after the reaction is ....
7. Equivalent mass of O_3 in the reaction : $2O_3 \longrightarrow 3O_2$ is ....
8. 'n' factor for H_2S during its oxidation to SO_2 is ....
9. 'n' factor for Cu_2S in the reaction
   $$Cu_2S + KMnO_4 \longrightarrow Cu^{2+} + SO_2 + Mn^{2+} \text{ is:}$$
10. A 5.6 g sample of limestone is dissolved in acid and calcium is precipitated as calcium oxalate. The precipitate is filtered, washed with water and dissolved in dil. H_2SO_4. The solution required 40 mL of 0.25 N $KMnO_4$ solution for titration. The % of CaO in limestone is ....
11. 80 mL of M/24 $K_2Cr_2O_7$ solution oxidises 22.4 mL H_2O_2 solution. The volume strength of H_2O_2 solution is ....
12. 10 mL of 0.2 M solution of $K_xH(C_2O_4)_y$ requires 8 mL of 0.2 M acidified $KMnO_4$ solution. The value of x is ....
13. 'n' factor for SO_2 in $FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$ is ....
14. 30 mL of 0.3 M $MnSO_4$ is completely oxidised by 3 mL of $KMnO_4$ of unknown normality, each forming Mn^{4+} oxidation state. The normality of $KMnO_4$ is ....
15. 2 M solution of HNO_3 is reduced to NO by suitable reductant. The normality of HNO_3, if HNO_3 is used like this is ....
16. 'n' factor for S in SO_2 is 4 and in SO_3 is 6. The 'n' factor of S in $SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$ is ....
17. 'n' factor of C_2H_5OH in the reactions is....
    $$C_2H_5OH \longrightarrow CH_3CHO$$
18. 4 mole each of Hg^{2+} and I^- will form how much mole of $[HgI_4]^{2-}$
19. 2.5 mole of $Fe_2(C_2O_4)_3$ requires how much mole of $KMnO_4$ for its complete oxidation in acidic medium?
20. C_3H_8 is completely oxidised to CO_2 and H_2O, the ratio of equivalent mass of CO_2 formed and C_3H_8 taken is.....
21. The number of mole of $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$ oxidised by 4 mole of acidified $KMnO_4$ is.....
22. CrO_5 reacts with H_2SO_4 to give $Cr_2(SO_4)_3$, H_2O and O_2. The mole of O_2 released during the reaction of 4 mole of CrO_5 with excess of H_2SO_4.
23. 2 mole of FeC_2O_4 are oxidised by 'X' mole of $KMnO_4$ whereas 2 mole of $FeSO_4$ are oxidised by 'Y' mole of $KMnO_4$. The ratio of X : Y is.....
24. Number of H_2O_2 mole needed to convert two mole of $Cr(OH)_3$ in alkaline medium to sodium chromate is.....
25. 6×10^{-3} mole $K_2Cr_2O_7$ reacts completely with 9×10^{-3} mole X^{n+} to give XO_3^- and Cr^{3+}. The value of n is ......
26. Mole of $KMnO_4$ required to oxidise a mixture of 2 mole each of $FeSO_4$, FeC_2O_4 and $Fe_2(C_2O_4)_3$ in acid medium.
27. Mole of $K_2Cr_2O_7$ required to oxidise one mole of $Fe_2(C_2O_4)_3$ in acid medium.
28. Equivalent mass of nitrogen in the reaction :
    $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$ is $\frac{M}{X}$. The value of X is ....
29. A 1.10 g sample of copper ore is dissolved and Cu^{2+} formed are titrated with excess of KI. The liberated iodine requires 12.12 mL of 0.10 N $Na_2S_2O_3$ solution for titration. The % of copper by mass in sample is ....
30. 9.824 g of $FeSO_4.(NH_4)_2SO_4.X\,H_2O$ were dissolved in 250 mL of solution. 20 mL of this solution required 20 mL of $KMnO_4$ containing 3.52 g of 90% by mass $KMnO_4$ dissolved per litre. The value of 'X' is ....

31. A 0.56 g sample of limestone is dissolved in acid and calcium is precipitated as calcium oxalate. The precipitate is filtered, washed and dried and then dissolved in H_2SO_4. The solution required 4mL of 0.25 N $KMnO_4$ for oxidation of oxalate. The % of CaO in limestone is ....

32. Hydrogen peroxide in aqueous solution decomposes on warming to give oxygen according to the equation.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

under conditions where 1 mole of gas occupies 50 dm^3, 100 cm^3, of XM solution of H_2O_2 produces 5 dm^3 of O_2. Thus X is ....

33. 15g sample of an alloy containing Cu (at mass 63.6) and Zn reacts completely with $3M$ HNO_3 as :

$$Cu + HNO_3 \longrightarrow Cu^{2+} + NO_2(g) + H_2O$$

$$Zn + HNO_3 \longrightarrow Zn^{2+} + NH_4^+ + H_2O$$

The liberated $NO_2(g)$ was found to occupy 4.647 litre at 1 atm and 300 K. The mass of Zn (to the closest value) in alloy is ....

34. n-factor of Mn_2O_7 in the change :

$2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$ is ....

35. n-factor for Fe_3O_4 in its reaction during its oxidation to Fe_2O_3 is ....

36. Number of mole of As_2S_3 required to reduce 56 mole of HNO_3 according to equation :

$As_2S_3 + HNO_3 \longrightarrow H_3AsO_4 + H_2SO_4 + NO$

37. Reaction of Br_2 with Na_2CO_3 in aqueous solution gives sodium bromide and sodium bromate with evolution of CO_2 gas. The number of sodium bromide molecules involved in the balanced chemical equation is : **[IIT 2011]**

ANSWERS

1. Three **2.** Three **3.** Nine **4.** Six **5.** Nine **6.** Two **7.** Eight **8.** Six **9.** Eight **10.** Five **11.** Five **12.** Three
13. Five **14.** Two **15.** Six **16.** Two **17.** Two **18.** One **19.** Three **20.** Three **21.** Five **22.** Seven **23.** Three **24.** Three
25. One **26.** Four **27.** One **28.** Six **29.** Seven **30.** Six **31.** Five **32.** Two **33.** Nine **34.** Six **35.** One **36.** Six
37. Five

OBJECTIVE PROBLEMS (One Answer Correct)

1. Four mole of Cl_2 undergoes disproportionation involving in all six moles electrons. The No. of mole of Cl_2 losing electron and gaining electrons are respectively :

(a) 1, 3
(b) 3, 1
(c) 2, 2
(d) none of these

2. Number of mole of $K_2Cr_2O_7$ in acidic medium required to oxidise one mole of Cu_3P to $CuSO_4$ and H_3PO_4 is :

(a) 11/6
(b) 6/11
(c) 3/5
(d) 5/3

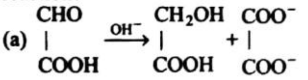
3. Equivalent mass of As_2S_5 in $As_2S_5 + HNO_3 \longrightarrow H_2SO_4 + NO_2 + H_3AsO_4 + H_2O$ is :

(a) $M/20$
(b) $M/40$
(c) $M/10$
(d) $M/5$

4. 4 mole of FeC_2O_4 are oxidised separately by acidified $KMnO_4$ and $K_2Cr_2O_7$. The mole ratio of $KMnO_4$ and $K_2Cr_2O_7$ is :

(a) 6/5
(b) 5/6
(c) 24/5
(d) $5/2n$

5. Which of the following is not disproportionation reaction?

(a)


$$\begin{matrix} CHO \\ | \\ COOH \end{matrix} \xrightarrow{OH^-} \begin{matrix} CH_2OH \\ | \\ COOH \end{matrix} + \begin{matrix} COO^- \\ | \\ COO^- \end{matrix}$$

(b) $KO_2 + H_2O + CO_2 \longrightarrow KHCO_3 + O_2$
(c) $KClO_3 \longrightarrow KClO_4 + KCl$
(d) $PbO_2 + H_2O \longrightarrow PbO + H_2O_2$

6. Which of the following is intermolecular redox change?

(a) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$
(b) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$
(c) $2KClO_3 \longrightarrow 2KCl + 3O_2$
(d) $PbO_2 + H_2O \longrightarrow PbO + H_2O_2$

7. For the reaction : $4CrO_5 + 6H_2SO_4 \longrightarrow 2Cr_2(SO_4)_3 + 6H_2O + 7O_2$, which statement is wrong :

(a) It is disproportionation reaction
(b) It is intramolecular redox
(c) CrO_5 acts as oxidant and reductant both
(d) Cr acts as oxidant whereas O acts as reductant

8. In which of the reaction oxygen is not an oxidant :

(a) $N_2 + \frac{1}{2}O_2 \longrightarrow N_2O$
(b) $C + O_2 \longrightarrow CO_2$
(c) $F_2 + \frac{1}{2}O_2 \longrightarrow F_2O$
(d) $C + \frac{1}{2}O_2 \longrightarrow CO$

9. The equilibrium : $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$ exist at $pH = 4$. The concentration of $[CrO_4^{2-}]$ at equilibrium is :

(a) $4 \times K_c \times [Cr_2O_7^{2-}]$
(b) $2 \times \sqrt{K_c \cdot [Cr_2O_7^{2-}]}$
(c) $10^4 \times \sqrt{K_c \times [Cr_2O_7^{2-}]}$
(d) $10^{-8} \times K_c \times [Cr_2O_7^{2-}]$

10. 1 mole each of FeC_2O_4 and $FeSO_4$ is oxidised separately by 1 M $KMnO_4$ in acid medium. The volume ratio of $KMnO_4$ used for FeC_2O_4 and $FeSO_4$ is :

(a) 1
(b) 2
(c) 3
(d) 4

11. What is wrong about 6.07% strength H_2O_2?

(a) Its normality is 3.57 N
(b) Its molarity is 1.785 M
(c) Its volume strength is 20 volume
(d) Volume strength = 5.6 × molarity

12. A 100 mL sample of blackish water was made ammoniacal and the sulphide ion in solution were titrated with 16.50 mL of 0.02000 M $AgNO_3$. The concentration of H_2S in the water in ppm is :

(a) 5.60
(b) 560
(c) 56
(d) 0.560

13. Titration of I_2 produced from 0.1045 g of primary standard KIO_3 required 30.72 mL of sodium thiosulphate as shown below:

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$
$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

The molarity of sodium thiosulphate ion is :

(a) 0.095
(b) 0.079
(c) 0.084
(d) 0.064

14. The mass of 1 g-equivalent of V_2O_5 used in the reaction $Zn + V_2O_5 \longrightarrow ZnO + V$ is : (atomic mass of $V = A$)

(a) $\frac{A}{5}$
(b) $\frac{A+80}{5}$
(c) $\frac{2A+80}{5}$
(d) $\frac{2A+80}{10}$

15. An element A forms an acidic oxide which with KOH forms a salt isomorphous to K_2SO_4. If eq. mass of A is 13, the atomic mass of A is :

(a) 78
(b) 80
(c) 26
(d) 52

16. Equivalent mass of Fe_3O_4 and Fe_2O_3 in the change $Fe_3O_4 \longrightarrow Fe_2O_3$ is respectively. M_1 and M_2 are molar mass of Fe_3O_4 and Fe_2O_3 respectively :

(a) $M_1, \frac{3M_2}{2}$
(b) $\frac{M_1}{3}, \frac{M_2}{2}$
(c) $\frac{M_1}{2}, \frac{M_2}{3}$
(d) $M_1, \frac{3M_2}{2}$

17. A definite amount of reducing agent is oxidised by 20 mL of 1 M $KMnO_4$ in acid medium, then the same amount of reducing agent is oxidised to same state by how many mL of 1 M $KMnO_4$ in neutral medium it self changing to Mn^{4+} state :

(a) 3 mL
(b) 33.3 mL
(c) 12 mL
(d) 24 mL

18. 5 g mixture $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ is completely oxidised by 5.5 mL of 0.1 M $KMnO_4$ in acid medium. The % of $FeSO_4 \cdot 7H_2O$ in mixture is :

(a) 15.29 (b) 3.058
(c) 20.24 (d) 25.29

19. The number of mole of $KMnO_4$ that will be needed to react with one mole of sulphite ions in acidic solution is:

(a) 2/5 (b) 3/5
(c) 4/5 (d) 1

20. Mole of H_2O_2 required for decolorising 1 mole of acidified $KMnO_4$ are :

(a) 1/2 (b) 3/2
(c) 5/2 (d) 7/2

21. 2 mole, equimolar mixture of $Na_2C_2O_4$ and $H_2C_2O_4$ required V_1 L of 0.1 M $KMnO_4$ in acidic medium for complete oxidation. The same amount of the mixture required V_2L of 0.1 M NaOH. The ratio of V_1 to V_2 is :

(a) 2 : 1 (b) 4 : 5
(c) 5 : 4 (d) 2 : 5

22. If a g of $NaHC_2O_4$ is completely reduced by 100 mL of 0.02 M $KMnO_4$ in acid medium and b g of $NaHC_2O_4$ required to neutralise completely 100 mL of 0.2 M NaOH, then :

(a) $a = b$ (b) $2a = b$
(c) $a = 2b$ (d) $b = 4a$

23. Ratio of mole of $FeSO_4$ oxidised by equal volume of equimolar $K_2Cr_2O_7$ and $KMnO_4$ solution in acidic medium is :

(a) 6 : 5 (b) 5 : 6
(c) 5 : 3 (d) 3 : 5

24. When BrO_3^- ion reacts with Br^- ion in acid medium, Br_2 is liberated. The equivalent mass of Br_2 in the reaction is :

(a) $\frac{5M}{3}$ (b) $\frac{3M}{5}$
(c) $\frac{4M}{6}$ (d) $\frac{5M}{8}$

25. In Fe^{2+} *vs* MnO_4^- titration, HNO_3 is not used because it :

(a) oxidises Mn^{2+} (b) reduces MnO_4^-
(c) oxidises Fe^{2+} (d) reduces Fe^{3+} formed

26. 1 mole of equimolar mixture of $Fe_2(C_2O_4)_3$ and FeC_2O_4 requires X mole of $KMnO_4$ in acid medium for complete oxidation. The value of X is :

(a) 0.9 (b) 0.6
(c) 1.2 (d) 0.8

27. Number of MnO_4^- ions present in 1 litre of 5 N $KMnO_4$ is :

(a) N_A (b) $5N_A$
(c) $\frac{2N_A}{10}$ (d) $\frac{5N_A}{10}$

28. 1 litre solution of KIO_3 of unknown molarity is given to titrate with KI in strong acid medium. 50 mL solution of KIO_3 requires 10 mL of 0.1 M KI for complete reduction to I_2. The molarity of KIO_3 solution is :

(a) $4 \times 10^{-3} M$ (b) $4 \times 10^{-4} M$
(c) $4 \times 10^{-5} M$ (d) $4 \times 10^{-2} M$

29. 10g of Fe_3O_4 is oxidised completely by 50 mL of 0.1 M $KMnO_4$ solution. The mass in g of Fe_2O_3 in Fe_3O_4 is :

(a) 1.8 (b) 8.2
(c) 4.1 (d) 5.9

30. How many mole of $KMnO_4$ are needed to oxidise a mixture of 1 mole each of $FeSO_4$, FeC_2O_4 and $Fe_2(C_2O_4)_3$ completely in acid medium :

(a) 5 (b) 2
(c) 4 (d) 6

31. The anion nitrate is converted into NH_4^+ ion. The equivalent mass of NO_3^- is :

(a) 6.20 (b) 7.75
(c) 10.5 (d) 21.0

32. If Cl_2 is passed into hot NaOH solution, oxidation number of chlorine changes from :

(a) 0 to + 5 (b) 0 to −2
(c) 0 to +1 (d) 0 to + 7

33. M is the molar mass of $KMnO_4$. The equivalent mass of $KMnO_4$ when it is converted into K_2MnO_4 is :

(a) M (b) $M/3$
(c) $M/5$ (d) $M/7$

34. The equivalent mass of $MnSO_4$ is half its molar mass when it is converted to :

(a) Mn_2O_3 (b) MnO_2
(c) MnO_4^- (d) MnO_4^{2-}

35. The number of mole of $KMnO_4$ that will be needed to react completely with one mole of ferrous oxalate in acidic medium is :

(a) $\frac{3}{5}$ (b) $\frac{2}{5}$
(c) $\frac{4}{5}$ (d) 1

36. 9×10^{-3} mole of X^{n+} are oxidised to XO_3^- by 6×10^{-3} mole of $K_2Cr_2O_7$. If atomic mass of X is A, then equivalent mass of X^{n+} will be :

(a) A (b) $\frac{A}{2}$
(c) $\frac{A}{3}$ (d) $\frac{A}{4}$

37. If molar mass of $AsCl_3$ is 228.5. It is oxidised to $AsCl_5$. The equivalent mass of $AsCl_3$ is :

(a) 228.5 (b) 114.25
(c) 76.16 (d) 57.12

38. In the disproportionation : $H_3PO_2 \longrightarrow PH_3 + H_3PO_3$; the *n* factor of H_3PO_2 is :

(a) $\frac{3}{4}$ (b) $\frac{4}{3}$

(c) $\frac{2}{3}$ (d) $\frac{3}{2}$

39. Number of mole of $KMnO_4$ required for 1 mole of Hg_2S in the reaction :

$$Hg_2S + MnO_4^- + H^+ \longrightarrow Hg^{2+} + SO_4^{2-} + Mn^{2+} + H_2O$$

are same as required for the change 5 mole of :

(a) N_2 to NO_2 (b) C_2H_5OH to CH_3CHO

(c) NO to HNO_3 (d) NH_3 to NO

40. Photosynthesis is a redox reaction *i.e.*,

$XCO_2 + XH_2O \xrightarrow[\text{Chlorophyll}]{h\nu} (CH_2O)_n + XO_2$; which one is not correct about it :

(a) carbon is reduced and oxygen is oxidised

(b) it may be classified as intermolecular redox reaction

(c) O_2 released comes from H_2O

(d) equivalent mass of CO_2 is 11 and of H_2O is 4.5

41. In standardisation of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent mass of $K_2Cr_2O_7$ is : **(IIT 2001)**

(a) *M*/2 (b) *M*/6

(c) *M*/6 (d) *M*

42. In alkaline medium, MnO_4^- oxidises I^- to : **(IIT 2004)**

(a) IO_3^- (b) I_2

(c) IO_4^- (d) IO^-

43. Consider a titration of potassium dichromate solution with acidified Mohr's salt. The number of mole of Mohr's salt required per mole of dichromate is : **(IIT 2007)**

(a) 3 (b) 4

(c) 5 (d) 6

44. The oxidation number of Mn in the product of alkaline oxidative fusion of MnO_2 is : **(IIT 2009)**

(a) 2 (b) 4

(c) 6 (d) 8

SOLUTIONS (One Answer Correct)

1. (a) $2e + \text{Cl}_2 \longrightarrow 2\text{Cl}^- \times 3$

(The lowest oxidation state of Cl is $-$I)

$$\begin{array}{l} \text{Cl}_2 \longrightarrow 2\text{Cl}^{3+} + 6e \\ \hline 4\text{Cl}_2 \longrightarrow 6\text{Cl}^- + 2\text{Cl}^{3+} \end{array}$$

2. (a) $6\text{Cu}_3\text{P} + 124\text{H}^+ + 11\text{Cr}_2\text{O}_7^{2-} \longrightarrow 18\text{Cu}^{2+} +$

$6\text{H}_3\text{PO}_4 + 22\text{Cr}^{3+} + 53\text{H}_2\text{O}$

3. (b) $(\text{As}^{5+})_2 \longrightarrow 2\text{As}^{5+}$, No redox

$(\text{S}^{2-})_5 \longrightarrow 5\text{S}^{6+} + 40e$, $E_{\text{As}_2\text{S}_5} = M/40$

4. (a) $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e$ $\quad \text{Mn}^{7+} + 5e \longrightarrow \text{Mn}^{2+}$

$$\begin{array}{l} (\text{C}^{3+})_2 \longrightarrow 2\text{C}^{4+} + 2e \\ \hline \text{FeC}_2\text{O}_4 \longrightarrow \text{Fe}^{3+} + 2\text{C}^{4+} + 3e \end{array} \quad (\text{Cr}^{6+})_2 + 6e \longrightarrow 2\text{Cr}^{3+}$$

$\therefore$ 4 mole $\text{FeC}_2\text{O}_4 \equiv \frac{12}{5}$ mole KMnO_4

$\equiv 2$ mole $\text{K}_2\text{Cr}_2\text{O}_7$

5. (d) It is intermolecular redox change.

6. (d) —do—

7. (a) $3e + \text{Cr}^{6+} \longrightarrow \text{Cr}^{3+}$

$\text{O}^{-1} \longrightarrow \text{O}_2^0 + 2e$

8. (c) F_2 is oxidant and O_2 is reductant (0 to +2)

9. (c) $K_c = \dfrac{[\text{CrO}_4^{2-}]^2[\text{H}^+]^2}{[\text{Cr}_2\text{O}_7^{2-}]}$

$\therefore \quad [\text{CrO}_4^{2-}] = \sqrt{10^8 \times [\text{Cr}_2\text{O}_7^{2-}] \times K_c}$

10. (c) $\text{Fe}^{2+} + \text{C}_2\text{O}_4^{2-} \longrightarrow \text{Fe}^{3+} + 2\text{CO}_2^{4+} + 3e$

$\text{Mn}^{7+} + 5e \longrightarrow \text{Mn}^{2+}$

$\text{Fe}^{2+} + \text{SO}_4^{2-} \longrightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + e$

Meq. of FeC_2O_4 = Meq. of KMnO_4,

$1 \times 3 \times 1000 = 1 \times 5 \times V_1$

Meq. of FeSO_4 = Meq. of KMnO_4

$1 \times 1 \times 1000 = 1 \times 5 \times V_2$

$\therefore \quad \dfrac{V_1}{V_2} = 3$

11. (d) 6.07% strength of H_2O_2 means 6.07 g H_2O_2 in 100 mL solution.

20 volume H_2O_2 means of 1 mL H_2O_2 solution gives 20 mL O_2

Also, % strength $= \frac{17}{56} \times$ vol. strength;

volume strength $= 5.6 \times N = 11.2 \times M$

12. (c) Meq. of H_2S = Meq. of S^{2-} = Meq. of AgNO_3

$= 16.50 \times 0.02 = 0.33$

$\frac{w}{17} \times 1000 = 0.33 \quad \therefore \; w_{\text{H}_2\text{S}} = 5.6 \times 10^{-3}$

$\therefore$ ppm of $\text{H}_2\text{S} = \dfrac{5.6 \times 10^{-3} \times 10^6}{10^2} = 56$

13. (a) $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$

$$\begin{array}{l} 3\text{I}_2 + 6\text{S}_2\text{O}_3^{2-} \longrightarrow 6\text{I}^- + 3\text{S}_4\text{O}_6^{-2} \\ \hline \text{IO}_3^- + 6\text{S}_2\text{O}_3^{2-} + 6\text{H}^+ \longrightarrow \text{I}^- + 3\text{S}_4\text{O}_6^{2-} \end{array}$$

Mole of $\text{KIO}_3 = 6$ mole of $\text{S}_2\text{O}_3^{2-}$

Mole of $\text{KIO}_3 = \dfrac{0.1045}{214} = 4.88 \times 10^{-4}$

$\therefore$ Mole of $\text{S}_2\text{O}_3^{2-}$ used $= 4.88 \times 10^{-4} \times 6$

Mole of $\text{S}_2\text{O}_3^{2-} = 2.93 \times 10^{-3}$

$\dfrac{M \times 30.72}{1000} = 2.93 \times 10^{-3}$

$\therefore \quad M = 0.095$

14. (d) $10e + (\text{V}^{5+})_2 \longrightarrow 2\text{V}^0$

$\therefore \quad E = \dfrac{M}{10} = \dfrac{2A + 80}{10}$

15. (a) $A \longrightarrow$ oxide of $A \xrightarrow{\text{KOH}}$ Isomorph of K_2SO_4, *i.e.*, K_2AO_4

$A^\circ \longrightarrow A^{6+} + 6e$

$\therefore$ atomic mass = eq. mass × v. f. $= 13 \times 6 = 78$

16. (a) $2(\text{Fe}^{8/3+})_3 \longrightarrow 3(\text{Fe}^{3+})_2 + 2e$

$\therefore \quad E_{\text{Fe}_3\text{O}_4} = \dfrac{M}{1}$ and $E_{\text{Fe}_2\text{O}_3} = \dfrac{M}{2/3}$

17. (b) $\text{Mn}^{7+} + 5e \longrightarrow \text{Mn}^{2+}$ (Acid med.)

$\text{Mn}^{7+} + 3e \longrightarrow \text{Mn}^{4+}$ (Neutral med.)

$\therefore$ Meq. of KMnO_4 in acid medium

= Meq. of KMnO_4 in neutral medium.

$1 \times 5 \times 20 = 1 \times 3 \times V$

$\therefore \quad V = 33.3$ mL

18. (a) Meq. of KMnO_4 = Meq. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

$5.5 \times 0.1 \times 5 = \dfrac{w}{278} \times 1000 \quad (\text{Mn}^{7+} + 5e \longrightarrow \text{Mn}^{2+})$

$\therefore \quad w = 0.7645 \quad (\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + 1e)$

$\therefore$ % of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = \dfrac{0.7645}{5} \times 100 = 15.29$

19. (a) $\text{S}^{4+} \longrightarrow \text{S}^{6+} + 2e \quad \times 5$

$\text{Mn}^{7+} + 5e \longrightarrow \text{Mn}^{2+} \quad \times 2$

20. (c) $\text{Mn}^{7+} + 5e \longrightarrow \text{Mn}^{2+} \quad \times 2$

$(\text{O}^{-1})_2 \longrightarrow \text{O}_2^0 + 2e \quad \times 5$

21. (d) Let mole of $\text{Na}_2\text{C}_2\text{O}_4$ and $\text{H}_2\text{C}_2\text{O}_4$ be a, b respectively, then $a + b = 2$ and $a = b$ (equimolar)

Eq. of $\text{Na}_2\text{C}_2\text{O}_4 + \text{H}_2\text{C}_2\text{O}_4 = V_1 \times 0.1 \times 5$

$(\text{Mn}^{7+} + \text{Se} \longrightarrow \text{Mn}^{2+})$

$2a + 2b = 0.5V_1 \quad (\because a = b) \quad$ ...(i)

$\therefore \quad V_1 = 8$ L

Eq. of $\text{H}_2\text{C}_2\text{O}_4 = V_2 \times 0.1 \times 1$

$2b = 0.1V_2$

$\therefore \quad V_2 = 20\,\text{L}$

$\therefore \quad \frac{V_1}{V_2} = \frac{8}{20} = \frac{2}{5}$

22. (d) Meq. of $NaHC_2O_4$ = Meq. of $KMnO_4$

$$\frac{a \times 2}{M} \times 1000 = 100 \times 0.02 \times 5 = 10$$

Also Meq. of $NaHC_2O_4$ = Meq. of NaOH

$$\frac{b \times 1 \times 1000}{M} = 100 \times 0.2 = 20$$

$\therefore \quad \frac{2a}{b} = \frac{10}{20}$

or $\quad b = 4a$

23. (a) $6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$

$5e + Mn^{3+} \longrightarrow Mn^{2+}$

$Fe^{2+} \longrightarrow Fe^{3+} + e$

One mole of $K_2Cr_2O_7$ will oxidise 6 mole Fe^{2+}

One mole of $KMnO_4$ will oxidise 5 mole Fe^{2+}

24. (b)

$$\begin{array}{l} 10e + 2Br^{5+} \longrightarrow (Br^0)_2 \\ \quad 2Br^- \longrightarrow (Br^0)_2 + 2a \\ \hline 2Br^{5+} + 10Br^- \longrightarrow 6Br_2 \end{array}$$

$$\begin{aligned} 6 \text{ mole of } Br_2 &= 2 \text{ mole } Br^{5+} \\ &= 10 \text{ eq. } Br^{5+} \\ &= 10 \text{ eq. } Br_2 \end{aligned}$$

$\therefore \quad 1 \text{ mole } Br_2 = \frac{10}{6} \text{ eq. } Br_2 = \frac{5}{3} \text{ eq. } Br_2$

$\therefore \quad n = \frac{5}{3}$

$\therefore \quad E_{Br_2} = \frac{M}{5/3} = \frac{3M}{5}$

25. (c) HNO_3 will also oxidise Fe^{2+}

26. (a) $KMnO_4$ will oxidise Fe^{2+} to Fe^{3+} and $C_2O_4^{2-}$ to CO_2

$(C_2^{3+})_3 \longrightarrow 6C^{4+} + 6e$

$(C_2^{3+}) \longrightarrow 2C^{4+} + 2e$

and $\quad Fe^{2+} \longrightarrow Fe^{3+} + e$

Meq. of $C_2O_4^{2-}$ in $Fe_2(C_2O_4)_3$ + Meq. of FeC_2O_4

= Meq. of $KMnO_4$

$= X \cdot 5$ $\quad$ (Total mole of $FeC_2O_4 = 0.5$ and mole of $Fe_2(C_2O_4)_3 = 0.5$)

$0.5 \times 6 + 0.5 \times 3 = X \cdot 5$

$\therefore \quad X = 0.9$

27. (a) Eq. of $KMnO_4 = 5 \times 1 = 5$

$\therefore$ mole of $KMnO_4 = 1$ $\quad$ (mole × V. f. = Eq.)

28. (a) $10e + 2I^{5+} \longrightarrow (I^0)_2$

$2I^- \longrightarrow (I^0)_2 + 2e$

Meq. of KIO_3 = Meq. of I^-

$50 \times M \times 5 = 10 \times 0.1 \times 1$

$\therefore \quad \text{Molarity} = \frac{1}{250} = 4 \times 10^{-3}\,\text{M}$

29. (b) Meq. of Fe^{2+} in $Fe_3O_4 = 50 \times 0.1 \times 5 = 25$ = Meq. of FeO

mm of Fe^{2+} in $Fe_3O_4 = 25$ = mm of FeO

$\therefore \quad w_{FeO} = \frac{25 \times 72}{1000} = 1.8\,\text{g}$

$\therefore \quad w_{Fe_2O_3} = 10 - 1.8 = 8.2\,\text{g}$

30. (b) $Mn^{7+} + 5e \longrightarrow Mn^{2+}$

$Fe^{2+} \longrightarrow Fe^{3+} + e$

$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$

$[(C^{3+})_2]_3 \longrightarrow 6C^{4+} + 6e$

Eq. of $KMnO_4$ = Eq. of $FeSO_4$ + Eq. of FeC_2O_4 + Eq. of $Fe_2(C_2O_4)_3$

$= 1 \times 1 + 1 \times 3 + 1 \times 6$

$M \times 5 = 10$

$M = 2$

31. (b) $8e + N^{+5} \longrightarrow N^{-3}$

$\therefore \quad E_{NO_3^-} = \frac{62}{8} = 7.75$

32. (a) $Cl_2 + OH^- \longrightarrow ClO_3^- + Cl^-$

33. (a) $Mn^{7+} + e \longrightarrow Mn^{6+}$

$\therefore \quad E = \frac{M}{1}$

34. (b) $Mn^{2+} \longrightarrow Mn^{4+} + 2e$

$\therefore \quad E = \frac{M}{2}$

35. (a)

$$\begin{array}{l} \quad Fe^{2+} \longrightarrow Fe^{3+} + e \\ \quad (C^{3+})_2 \longrightarrow 2C^{4+} + 2e \\ \hline FeC_2O_4 \longrightarrow Fe^{3+} + 2C^{4+} + 3e] \times 5 \end{array}$$

$Mn^{7+} + 5e \longrightarrow Mn^{2+}] \times 3$

or 5 mole $FeC_2O_4 \equiv 3$ mole $KMnO_4$

36. (d) $6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$

$X^{n+} \longrightarrow X^{5+} + (5-n)e$

$\therefore$ Meq of $K_2Cr_2O_7$ = Meq of X^{+n}

$6 \times 6 \times 10^{-3} = 9 \times 10^{-3} \times (5-n)$

$\therefore n = 1$

$\therefore X^{1+} \longrightarrow X^{5+} + 4e$

$\therefore E \text{ of } X^{n+} = \frac{A}{4}$

37. (b) $As^{3+} \longrightarrow As^{5+} + 2e$

$\therefore \text{Eq. mass} = \frac{\text{molar mass}}{2} = \frac{228.5}{2} = 114.25$

38. (b)

$$\begin{array}{l} 4e + P^{+1} \longrightarrow P^{-3} \\ \quad P^{+1} \longrightarrow P^{+3} + 2e \\ \hline 3P^{+} \longrightarrow P^{-3} + 2P^{+3} \end{array}$$

$3H_3PO_2 \longrightarrow PH_3 + 2H_3PO_3$

3 mole H_3PO_2 = 1 mole PH_3

= 4 eq. PH_3 = 4 eq. H_3PO_2

$\therefore$ 1 mole $H_3PO_2 = \frac{4}{3}$eq. H_3PO_2

or n factor $= \frac{4}{3}$

39. (b) $(Hg^{+1})_2 \longrightarrow 2Hg^{2+} + 2e$

$S^{-2} \longrightarrow S^{6+} + 8e$

$Hg_2S \longrightarrow 2Hg^{2+} + S^{6+} + 10e$

for (b) $(C^{-2})_2 \longrightarrow (2C^{-1}) + 2e$

$\therefore$ $5C_2H_5OH \longrightarrow 10CH_3CHO$

$5e + Mn^{7+} \longrightarrow Mn^{2+}$

40. (d) $4e + C^{4+} \longrightarrow C^0$

$\underset{\text{(of } H_2O)}{2(O^{-2})} \longrightarrow O_2^0 + 4e$

$\therefore$ Equivalent mass of $CO_2 = \frac{44}{4} = 11$

and Equivalent mass of $H_2O = \frac{18}{2} = 9$

41. (b) $6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$

$\therefore$ $E = M/6$

42. (a) $2MnO_4^- + I^- + H_2O \longrightarrow IO_3^- + 2MnO_2 + 2OH^-$

43. (d) $Fe^{2+} \longrightarrow Fe^{3+} + e] \times 6$

$6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$

44. (c) $2MnO_2 + 4KOH + O_2 \longrightarrow K_2MnO_4 + 2H_2O$

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. 100 mL of 0.1 M $NaHC_2O_4$ is neutralised by V_1 mL of 0.1 M NaOH and V_2 mL of a M $KMnO_4$ separately, then for complete neutralisation :

(a) volume of NaOH required = 200 mL

(b) if M of $KMnO_4$ is 0.1 M then $\frac{V_1}{V_2} = 5:1$

(c) if M of $KMnO_4$ is 0.1 M then $V_2 = 20$ mL

(d) if M of $KMnO_4$ is 0.2 M then $V_2 = 2$ mL

2. A mixture of $Na_2C_2O_4$ and $H_2C_2O_4$ requires 100 mL of 0.1 M $KMnO_4$ for complete neutralisation. The same mixture on neutralisation by a base requires 50 mL of 0.2 M NaOH solution. Which one are correct?

(a) Mole ratio of $Na_2C_2O_4$ and $H_2C_2O_4 = 4:1$

(b) Equivalent ratio of $Na_2C_2O_4$ and $H_2C_2O_4 = 4:1$

(c) Mole of $C_2O_4^{2-}$ in mixture $= 25 \times 10^{-3}$

(d) Mole ratio of $Na_2C_2O_4$ and $H_2C_2O_4 = 1:4$

3. Quantitative estimation of Fe^{2+} can be made by $KMnO_4$ in acidified medium. In which medium it can be estimated by $KMnO_4$?

(a) In H_2SO_4 (b) In HNO_3

(c) In HCl (d) all of these

4. Which are correct about the reaction?

$$FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$$

(a) Eq. mass of FeS_2 is $M/11$

(b) Eq. mass of $SO_2 = M/5$

(c) 1 mole of FeS_2 requires 7/4 mole of O_2

(d) S has – 2 oxidation state in FeS_2

5. Which of the following are primary standards?

(a) As_2O_3 (b) $H_2C_2O_4$

(c) NaOH (d) Na_2CO_3

6. Which of the followings are not valid reactions for iodometric titrations?

(a) $O_3 + 2I^- + 2H^+ \longrightarrow O_2 + I_2 + H_2O$

(b) $8HNO_3 + 6I^- \longrightarrow 6NO_3^- + 2NO + 2I_2 + 4H_2O$

(c) $CuSO_4 + 2KI \longrightarrow Cu_2I_2 + I_2 + K_2SO_4$

(d) $Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

7. In which of the following reactions O_2 is oxidant?

(a) $F_2 + \frac{1}{2}O_2 \longrightarrow F_2O$ (b) $3O_3 \longrightarrow 2O_2$

(c) $CO + \frac{1}{2}O_2 \longrightarrow CO_2$ (d) $N_2 + O_2 \longrightarrow 2NO$

8. Reduction of the metal centre in aqueous permanganate ion involves : **(IIT 2011)**

(a) 3 electrons in neutral medium

(b) 5 electrons in neutral medium

(c) 3 electrons in alkaline medium

(d) 5 electrons in acidic medium

SOLUTIONS (More Than One Answer Correct)

1. (b, c) Meq. of $NaHC_2O_4 = 100 \times 0.1 = 10$

Meq. of NaOH required $= 10 = V_1 \times 0.1 \times 1$

(v.f. of NaOH = 1)

$$V_1 = 100 \text{ mL}$$

Meq. of $KMnO_4$ required $= 10 = V_2 \times a \times 5$

(v.f. of $KMnO_4 = 5$)

$$\therefore \quad V_2 = \frac{10}{5a} \quad \therefore \quad \frac{V_1}{V_2} = \frac{100 \times 5a}{10}$$

if $M_{KMnO_4} = 0.1M$, then $10 = V_2 \times 0.1 \times 5$

$$\therefore \quad V_2 = 20 \text{ mL}$$

2. (a,b,c) Meq. of $KMnO_4 = 100 \times 0.1 \times 5 = 50$

$$= \underset{a}{\text{Meq. of } Na_2C_2O_4} + \underset{b}{\text{Meq. of } H_2C_2O_4}$$

$$\therefore \quad a + b = 50$$

Meq. of NaOH $= 50 \times 0.2 = 10 =$ Meq. of $H_2C_2O_4$

$$\therefore \quad b = 10$$

$$\therefore \quad a = 40$$

milli mole of $Na_2C_2O_4 = \frac{a}{2}$

$\therefore$ milli mole of $C_2O_4 = \frac{a}{2} + \frac{b}{2} = \frac{a+b}{2} = \frac{40+10}{2} = 25$

milli mole of $H_2C_2O_4 = \frac{b}{2}$

3. (a) HNO_3 also oxidises Fe^{2+} whereas $KMnO_4$ oxidises HCl.

4. (a,b,c) $2Fe^{2+} \longrightarrow (Fe^{3+})_2 + 2e$

Eq. mass of $FeS_2 = \frac{M}{22/2} = \frac{M}{11}$

$$2(S^{-1})_2 \longrightarrow 4(S^{4+}) + 20e$$

Eq. mass of $SO_2 = \frac{M}{20/4} = \frac{M}{5}$

$$\therefore \quad 4e + O_2^0 \longrightarrow 2(O^{-2})$$

$$\therefore \quad 4\,FeS_2 + 7O_2 \longrightarrow 2Fe_2O_3$$

S has −1 oxidation state.

5. (a,b) Primary standard solutions are those whose solution of exact normality can be prepared by weighing desired amount of its pure sample.

6. (b) In strong acidic medium either I produced in reaction tend to be oxidised to I^- or starch used to detect end point is decomposed and hydrolysed.

7. (c,d) In the reaction of F_2 and O_2, F_2 is oxidant.

8. (a,c,d)

In acidic medium : $Mn^{7+} + 5e \longrightarrow Mn^{2+}$

In neutral medium : $Mn^{7+} + 3e \longrightarrow Mn^{4+}$

In alkaline solution : $Mn^{7+} + e \longrightarrow Mn^{6+}$

Note that in **alkaline medium,** Mn^{6+} is further reduced to Mn^{4+}

$$Mn^{6+} + 2e \longrightarrow Mn^{4+}$$

Thus over all reaction may give

$$Mn^{7+} + 3e \longrightarrow Mn^{4+}$$

COMPREHENSION BASED PROBLEMS

Comprehension 1: Estimation of $CuSO_4$ is made by iodometric titrations. In a given titration $CuSO_4$ reacts with KI in acidic medium to liberate I_2.

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

Mercuric per iodate $Hg_5(IO_6)_2$ reacts with a mixture of KI and HCl following the equation:

$$Hg_5(IO_6)_2 + 34KI + 24HCl \longrightarrow 5K_2HgI_4 + 8I_2 + 24KCl + 12H_2O$$

The liberated iodine is titrated against $Na_2S_2O_3$ solution. One mL of which is equivalent to 0.0499 *g* of $CuSO_4 \cdot 5H_2O$. Molar mass of $Hg_5(IO_6)_2 = 1448.5$ and molar mass of $CuSO_4 \cdot 5H_2O = 249.5$.

[1] Equivalent mass of $CuSO_4 \cdot 5H_2O$ is :

(a) $\frac{M}{2}$
(b) $\frac{M}{1}$
(c) $\frac{M}{3}$
(d) M

[2] The reaction of $Na_2S_2O_3$ and I_2 gives oxidation product as:

(a) I^-
(b) $S_2O_3^{2-}$
(c) $S_4O_6^{2-}$
(d) SO_4^{2-}

[3] Volume in mL of $Na_2S_2O_3$ solution will be required to react with I_2 liberated from 0.76245 g of $Hg_5(IO_6)_2$:

(a) 40 mL
(b) 10 mL
(c) 20 mL
(d) 30 mL

Comprehension 2: 2.5 g sample of copper is dissolved in excess of H_2SO_4 to prepare 100 mL of 0.02 *M* $CuSO_4$ (*aq.*). 10 mL of 0.02 *M* solution of $CuSO_4$ (*aq.*) is mixed with excess of KI to show the following changes.

$$CuSO_4 + 2KI \longrightarrow K_2SO_4 + CuI_2$$

$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

The liberated iodine is titrated with hypo ($Na_2S_2O_3$) and requires *V* mL of 0.1 *M* hypo solution for its complete reduction.

[1] The volume (*V*) of hypo required is :

(a) 2 mL
(b) 20 mL
(c) 1 mL
(d) 10 mL

[2] Percentage of purity of sample is :

(a) 10.16
(b) 5.08
(c) 2.54
(d) 1.27

[3] The mass of I_2 liberated in the reaction of 10 mL of 0.02 *M* solution with KI_{excess} is :

(a) 0.051 g
(b) 0.0254 g
(c) 0.102 g
(d) 0.204 g

[4] The colour of solution developed during addition of KI $CuSO_4$ is :

(a) violet due to dissolution of liberated I_2
(b) brownish yellow due to dissolution of liberated I_2
(c) red due to the formation of CuI_2
(d) brown due to the formation of Cu_2I_2

[5] Select the correct statement :

1. The reaction belongs to iodometric titration
2. The reaction belongs to iodimetric titration
3. Cu_2I_2 formed during the reaction is white
4. Starch is used as indicator in this titration

(a) 1, 3, 4
(b) 2, 3, 4
(c) 1, 3
(d) 2, 3

Comprehension 3: $K_2Cr_2O_7$ acts as a good oxidizing agent in acidic medium.

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 14H^+ + 6e^- \longrightarrow \underset{\text{Green}}{2Cr^{3+}} + 7H_2O$$

In alkaline solution, orange colour of $Cr_2O_7^{2-}$ changes to yellow colour due to formation of CrO_4^{2-} and again yellow colour changes to orange colour on changing the solution to acidic medium.

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 2OH^- \longrightarrow \underset{\text{Yellow}}{2CrO_4^{2-}} + H_2O$$

$$\underset{\text{Yellow}}{2CrO_4^{2-}} + 2H^+ \longrightarrow \underset{\text{Orange}}{2Cr_2O_7^{2-}} + H_2O$$

CrO_4^{2-} and $Cr_2O_7^{2-}$ exist in equilibrium at pH = 4 and are interconvertible by altering the pH of the solution. When heated with H_2SO_4 and metal chloride, $K_2Cr_2O_7$ gives vapours of chromyl chloride (CrO_2Cl_2). Chromyl chloride (CrO_2Cl_2) when passed into aqueous NaOH solution, yellow colour solution of CrO_4^{2-} is obtained. This on reaction with lead acetate gives yellow ppt. of $PbCrO_4$.

When H_2O_2 is added to an acidified solution of dichromate ion, a complicated reaction occurs. The products obtained depend on the pH and concentration of Cr.

$$Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO(O_2)_2 + 5H_2O$$

A deep blue-violet coloured peroxo compound, $CrO(O_2)_2$, called chromic peroxide is formed. This decomposes rapidly in aqueous solution into Cr^{3+} and oxygen.

[1] What happens when a solution of potassium chromate is treated with an excess of dilute nitric acid?

(a) Cr^{3+} and $Cr_2O_7^{2-}$ are formed
(b) $Cr_2O_7^{2-}$ and H_2O are formed
(c) CrO_4^{2-} is reduced to +3 state of Cr
(d) CrO_4^{2-} is reduced to 0 state of Cr

[2] Which of the following statement is wrong when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4?

(a) A deep red vapour is evolved
(b) The vapour when passed through NaOH solution gives a yellow solution of Na_2CrO_4
(c) Chlorine gas is formed
(d) Chromyl chloride is formed

[3] The CrO_3 on reaction with HCl and NaOH(*aq.*) gives respectively:

(a) CrO_2Cl_2, CrO_4^{2-} (b) $Cr(OH)_2, CrO_4^{2-}$

(c) $Cl_2, Cr_2O_7^{2-}$ (d) $Cl_2, Cr(OH)_3$

[4] Number of mole of $K_2Cr_2O_7$ reduced by one mole of Sn^{2+} ions in acidic medium is :

(a) $\frac{1}{3}$ (b) 3

(c) $\frac{1}{6}$ (d) 6

[5] The equivalent mass of barium in $BaCrO_4$ used as an oxidizing agent in acidic medium is (atomic mass of Ba = 137.34 and Cr = 52)

(a) 137.34 (b) 85.78

(c) 114.45 (d) 68.67

[6] The equivalent mass of KIO_3 in the reaction

$$2Cr(OH)_3 + OH^- + KIO_3 \longrightarrow 2CrO_4^{2-} + KI + 5H_2O$$

(a) Molar mass (b) $\frac{M}{3}$

(c) $\frac{M}{6}$ (d) $\frac{M}{2}$

[7] When H_2O_2 is added to an acidified solution of $K_2Cr_2O_7$, then :

(a) solution turns green due to formation of Cr_2O_3 and reduction of Cr takes place

(b) solution turns blue due to formation of $CrO(O_2)_2$ and no redox change

(c) a deep blue-violet coloured compound $CrO(O_2)_2$ due to reduction of Cr

(d) solution gives green ppt. $CrO(O_2)_2$ due to oxidation of Cr

[8] The colour of $Cu_2Cr_2O_7$ solution in water is :

(a) green (b) blue

(c) orange (d) black

[9] Which statement about CrO_5 is wrong?

(a) Oxidation number of Cr in CrO_5 is +6

(b) CrO_5 has butterfly structure

(c) It has one oxygen atom attached with double bond with Cr and four oxygen atoms attached with single bond with chromium

(d) It has four peroxide bond

[10] The $[CrO_4^{2-}]$ ions at equilibrium for the reaction

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+ \text{ at pH} = 4 \text{ is :}$$

(a) $10^{-4}[Cr_2O_7^{2-}] \cdot K_C$

(b) $10^{-8}[Cr_2O_7^{2-}] \cdot K_C$

(c) $10^{+4}[(Cr_2O_7^{2-}) \cdot K_C]^{1/2}$

(d) $10^{-4}[Cr_2O_7^{2-}]^{1/2} \cdot K_C$

Comprehension 4 : Redox changes are of three types. These includes, intermolecular redox reaction, intramolecular redox reactions and disproportionation.

The equivalent mass '*E*' of reductant or oxidant is given by the expression :

$$E_{\text{red/oxi}} = \frac{\text{Molar mass of reductant or oxidant}}{\text{Number of electron lost or gained by 1 molecule of reductant or oxidant}}$$

[1] The equivalent mass of cyanogen $(CN)_2$ in the redox change is :

$$(CN)_2 + H_2O \longrightarrow HCN + HOCN$$

(a) $\frac{M}{2}$ (b) M

(c) $\frac{M}{3}$ (d) $\frac{M}{24}$

[2] The equivalent mass of $KClO_3$ in the redox reaction is :

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

(a) $\frac{M}{6}$ (b) $\frac{M}{2}$

(c) $\frac{M}{3}$ (d) $\frac{M}{5}$

[3] The equivalent mass of $Fe_2(C_2O_4)_3$ in the redox reaction is :

$$5Fe_2(C_2O_4)_3 + 6KMnO_4 + 24H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + 6MnSO_4 + 30CO_2 + 24H_2O$$

(a) $\frac{M}{2}$ (b) $\frac{M}{6}$

(c) $\frac{M}{3}$ (d) $\frac{M}{4}$

Comprehension 5 : Bleaching powder and bleach solution are produced on a large scale and used in several household products. The effectiveness of bleach solution is often measured by iodometry. **(IIT 2012)**

[1] Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is :

(a) Cl_2O (b) Cl_2O_7

(c) ClO_2 (d) Cl_2O_6

[2] 25 mL of household bleach solution was mixed with 30 mL of 0.50 *M* KI and 10 mL of 4 *N* acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 *N* $Na_2S_2O_3$ was used to reach the end point. The molarity of the household bleach solution is :

(a) 0.48 *M* (b) 0.96 *M*

(c) 0.24 *M* (d) 0.024 *M*

SOLUTIONS

Comprehension 1

[1] (d) $2Cu^{2+} + 2e \longrightarrow (Cu^{2+})_2$

[2] (c) $2S_2O_3^{2-} \longrightarrow \underset{\text{oxidation product}}{S_4O_6^{2-}} + 2e$

[3] (a) $\because$ 1 mole $Hg_5(IO_6)_2$ or 1448.5 g gives = 8 mole I_2

$\therefore$ 0.7245 g $Hg_5(IO_6)_2$ will give

$$= \frac{8 \times 0.7245}{1448.5} \text{ mole } I_2$$

$$= 4.0 \times 10^{-3} \text{ mole } I_2$$

This I_2 is titrated with $Na_2S_2O_3$ as,

$$2e + I_2 \longrightarrow 2I^-$$

$$2S_2^{2+} \longrightarrow S_4^{5/2+} + 2e$$

Meq. of $Na_2S_2O_3$ = Meq. of $I_2 = 4 \times 10^{-3} \times 10^3 \times 2 = 8$

Meq. of $Na_2S_2O_3$ in one mL = Meq. of $CuSO_4$

$$= \frac{0.0499}{249/1} \times 1000 = 0.20$$

$\therefore$ $0.20 \times V = 8$ $\therefore$ $V = 40$ **mL**

Comprehension 2

[1] (a) The reactions are :

$$2(Cu^{2+}) + 2e \longrightarrow (Cu^+)_2, E = \frac{M}{1}$$

$$2(I^{-1}) \longrightarrow I_2 + 2e, E_{I^-} = \frac{M}{1}$$

$$2(S^{2+})_2 \longrightarrow (S^{5/2+})_4 + 2e,$$

$$E_{Na_2S_2O_3} = \frac{M}{1}$$

Meq. of $CuSO_4$ = Meq. of $Na_2S_2O_3$

= Meq. of I_2 liberated

$$10 \times 0.02 \times 1 = V \times 0.1 \times 1$$

$\therefore$ $V = 2$ mL

[2] (b) Meq. of $CuSO_4$ in 100 mL = $100 \times 0.02 = 2$

$\therefore$ $w_{CuSO_4} = \frac{2 \times 249.6}{1000} = 0.499 g$

$\therefore$ $w_{Cu} = \frac{0.499 \times 63.6}{249.6} = 0.127 g$

$\therefore$ % of Cu $= \frac{0.127}{2.5} \times 100 = 5.08$

[3] (b) Eq. of I_2 = Eq. of $CuSO_4$

$$= \frac{10 \times 0.02}{1000} = 2 \times 10^{-4}$$

$\therefore$ $\frac{w}{254/2} = 2 \times 10^{-4}$

$\therefore$ $w_{I_2} = 0.0254$ g

[4] (b) **Liberated iodine on dissolution in solution of Cu_2I_2 and KI develops brown colour.**

[5] (a) **If I_2 is used as intermediate, the process is iodometric.**

Comprehension 3

[1] (b) $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$

[2] (c) $4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \longrightarrow$

$$2CrO_2Cl_2 + 4NaHSO_4 + 2KHSO_4 + 3H_2O$$

[3] (a) $CrO_3 + 2HCl \longrightarrow CrO_2Cl_2 + H_2O$

$CrO_3 + 2NaOH \longrightarrow Na_2CrO_4 + H_2O$

[4] (a) $[Sn^{2+} \longrightarrow Sn^{4+} + 2e] \times 3$

$6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$

$\therefore$ 1 mole of $K_2Cr_2O_7$ will oxidise 3 mole of Sn^{2+}

[5] (b) $3e + Cr^{6+} \longrightarrow Cr^{3+}$; $E = \frac{M}{3} = \frac{253.34}{3} = 85.78$

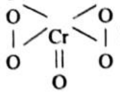
[6] (c) $6e + I^{5+} \longrightarrow I^-$; $E = \frac{M}{6}$

[7] (b) $Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO_5 + 5H_2O$

(Not a redox change)

[8] (a) Cu^{2+} ions are blue and $Cr_2O_7^{2-}$ ions are orange to give green colour

[9] (d)



has two per oxide (O—O) bonds

[10] (c)

$$K_C = \frac{[CrO_4^{2-}]^2[H^+]^2}{[Cr_2O_7^{2-}]}$$

$$\therefore \quad [CrO_4^{2-}]^2 = \frac{[Cr_2O_7^{2-}] \times K_C}{[H^+]^2} = \frac{K_C\,[Cr_2O_7^{2-}]}{(10^{-4})^2}$$

$$= 10^4[K_C \cdot Cr_2O_7^{2-}]^{1/2}$$

Comprehension 4

[1] (b) $2e + (C^{3+})_2 \longrightarrow 2C^{2+}$

$$\underline{(C^{3+})_2 \longrightarrow 2C^{4+} + 2e}$$

$$(C^{3+})_2 \longrightarrow 2C^{2+} + 2C^{4+}$$

$$2(CN)_2 + 2H_2O \longrightarrow 2HCN + 2HOCN$$

2 mole $(CN)_2$ = 2 mole HCN

= 2 × 1eq. HCN (V.f. for HCN = 1)

= 2 eq. $(CN)_2$

$\therefore$ 1 mole of $(CN)_2$ = 1 eq. $(CN)_2$

or V.f. for $(CN)_2$ = 1

$\therefore E = M$

[2] (a) $6e + Cl^{5+} \longrightarrow Cl^{-1}$

$$\underline{2(O^{-2})_3 \longrightarrow 3(O_2^0) + 12e}$$

$\therefore$ $2KClO_3 \longrightarrow 2KCl + 3O_2$

2 mole $KClO_3$ ≡ 2 mole KCl

≡ 2 × 6 eq. KCl

≡ 12eq. $KClO_3$

$\therefore$ 1 mole $KClO_3 \equiv 6$ eq. $KClO_3$

$\therefore$ v.f. for $KClO_3 \equiv 6$

$$\therefore \quad E_{KClO_3} = \frac{M}{6}$$

[3] (b) $(C_2^{3+})_3 \longrightarrow 6C^{4+} + 6e$

$$Mn^{7+} + 5e \longrightarrow Mn^{2+}$$

$$\therefore 5Fe_2(C_2O_4)_3 + 6KMnO_4 + 24H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + 6MnSO_4 + 3K_2SO_4 + 24H_2O$$

v.f. of $Fe_2(C_2O_4)_3 = 6$

Comprehension 5

13. (a) $\underset{\text{(Bleaching powder)}}{Ca(OCl)Cl} \longrightarrow Ca^{2+} + \bar{O}Cl + Cl^-$

Thus bleaching powder contains OCl^- *i.e.*, part of oxoacid HOCl and Cl^- *i.e.*, part of HCl.

Oxidation no. of Cl in oxoacid = +1.

Thus, oxide of Cl with same ox. no. is Cl_2O

$\therefore$ Anhydride of oxoacid (HOCl) is Cl_2O.

14. (c) $CaOCl_2(aq.) + 2KI \longrightarrow I_2 + Ca(OH)_2 + KCl$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

Thus Meq. of $Na_2S_2O_3$ used = Meq. of I_2 formed

= Meq. of bleaching powder

or 48×0.25 = Meq. of bleaching powder $= N \times 25$

$\therefore \quad N_{\text{Bleaching powder}} = 0.48$

$\because \quad Cl^+ + 2e \longrightarrow Cl^-$

Thus, n-factor for bleaching powder = 2

$$\therefore \quad M_{\text{Bleaching powder}} = \frac{0.48}{2} = 0.24$$

STATEMENT EXPLANATION PROBLEMS

Read the statements (S) and explanations (E) given below. Choose the correct choices a, b, c and d from the options

(a) S is correct but E is wrong

(b) S is wrong but E is correct

(c) Both S and E are correct and E is correct explanation of S

(d) Both S and E are correct but E is not correct explanation of S

1. S : The equivalent mass of NaCN in its conversion to NaOCN by $KMnO_4$ is $M/2$

E : The reaction is : $C^{2+} \longrightarrow C^{4+} + 2e$

2. S : The I_3^- reacts with H_3AsO_3 as:

$$H_3AsO_3 + KI_3 + H_2O \longrightarrow H_3AsO_4 + KI + 2HI$$

E : Equivalent mass of $KI_3 = 210$.

3. S : BrO_3^- shows two reactions as:

$$SeO_3^{2-} + BrO_3^- + H^+ \longrightarrow SeO_4^{2-} + Br_2 + H_2O$$

$$AsO_2^{2-} + BrO_3^- + H^+ \longrightarrow Br^- + AsO_4^- + H_2O$$

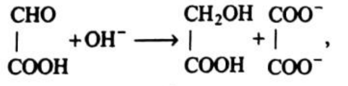
E : The ratio of equivalent mass of BrO_3^- in two reactions is 5/6.

4. S : One equivalent of MnO_2 reacts with 2 equivalent of HCl in the reaction:

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

E : One equivalent of MnO_2 reacts with one equivalent of HCl.

5. S : The reaction :



$$\begin{array}{c} CHO \\ | \\ COOH \end{array} + OH^- \longrightarrow \begin{array}{c} CH_2OH \\ | \\ COOH \end{array} + \begin{array}{c} COO^- \\ | \\ COO^- \end{array},$$

is Cannizzaro's reaction.

E : This is an example of disproportionation reaction.

6. S : In acidic medium, equivalent mass of $K_2Cr_2O_7$ is 49.

E : $(Cr^{6+})_2 + 6e \longrightarrow 2Cr^{3+}$; Thus, $E = \frac{M}{6}$.

7. S : Iodimetric titration are redox titrations.

E : The iodine solution acts as an oxidant to reduce the reductant.

$$I_2 + 2e \longrightarrow 2I^-$$

8. S : The redox titrations in which liberated I_2 is used as oxidant are called as iodometric titration.

E : Addition of KI of $CuSO_4$ liberates I_2 which is estimated against hypo solution.

9. S : $KMnO_4$ acts as oxidant as well as self indicator in its titration with ferrous ammonium sulphate solution in acidic medium.

E : $KMnO_4$ reduces itself to Mn^{2+} ions and oxidises Fe^{2+} to Fe^{3+} as well as after redox reaction is complete, the $KMnO_4$ at the equivalence point imparts pink colour.

10. S : The equivalence point refers the condition where equivalents of one species react with same number of equivalent of other species.

E : The end point of titration is exactly equal to equivalence point.

11. S : The equivalent mass of $KMnO_4$ when it is converted to K_2MnO_4 is equal to its molar mass.

E : $Mn^{7+} + e \longrightarrow Mn^{6+} \quad \therefore \quad E = \frac{M}{1}$

12. S : The number of equivalent per mole of H_2S used in its oxidation to SO_2 is six.

E : $S^{2-} \longrightarrow S^{4+} + 6 \;\therefore$ Equivalent = Mole × 6.

13. S : Starch is generally used as absorption indicator in iodometric or iodimetric titrations.

E : Starch imparts blue colour with iodine.

14. S : The colour of $KMnO_4$ discharges slowly in the beginning by the oxalic acid but fastens after sometime.

E : The Mn^{2+} ion act as auto catalyst for the reaction.

15. S : $KMnO_4$ has different equivalent mass in acid, neutral or alkaline medium.

E : In different medium change in oxidation number shown by manganese is altogether different.

ANSWERS (Statement Explanation Problems)

1. (c) $E = M/2$

2. (c) $E = M/2$ because $2e + (\mathrm{I}^{-1/3})_3 \longrightarrow 3\mathrm{I}^-$.

3. (a) (i) $E_{\mathrm{BrO_3^-}} = \dfrac{M}{5}$

(ii) $E_{\mathrm{BrO_3^-}} = \dfrac{M}{6}$

$$10e + 2\mathrm{Br}^{5+} \longrightarrow \mathrm{Br}^0;$$

$$6e + \mathrm{Br}^{5+} \longrightarrow \mathrm{Br}^{-1}$$

$$\therefore \quad \text{Ratio} = \frac{6}{5}$$

4. (a) 1 mole $MnO_2 \equiv$ 4 mole HCl

2 eq. $MnO_2 \equiv$ 4 eq. HCl

5. (c) Both are facts.

6. (c) One mole of $K_2Cr_2O_7$ shows a change of six N electrons.

7. (c) The electrons liberated during oxidation of species are used by I_2 to get itself reduced.

8. (c) $2\mathrm{KI} + \mathrm{CuSO_4} \longrightarrow \mathrm{CuI_2} + \mathrm{K_2SO_4}$

$$2\mathrm{CuI_2} \longrightarrow \mathrm{Cu_2I_2} + \mathrm{I_2}$$

$$\mathrm{I_2} + 2\mathrm{Na_2S_2O_3} \longrightarrow \mathrm{Na_2S_4O_6} + 2\mathrm{NaI}$$

9. (c) The explanation is correct reason of the statement.

10. (a) The equivalent point is nearly same but not exactly same to end point. However for all practical purposes the two are taken same.

11. (c) One mole of $KMnO_4$ shows a change of N electrons.

12. (c) Equivalent = Mole × valence factor.

13. (c) The explanation is correct reason of the statement.

14. (c) $KMnO_4$ is reduced to MnO_2 by oxalic acid. The redox change is catalysed by Mn^{2+} ions *i.e.*, autocatalysis.

15. (c) $5e + \mathrm{Mn}^{7+} \longrightarrow \mathrm{Mn}^{2+}$ (Acidic)

$3e + \mathrm{Mn}^{7+} \longrightarrow \mathrm{Mn}^{4+}$ (Alkaline or neutral)

$1e + \mathrm{Mn}^{7+} \longrightarrow \mathrm{Mn}^{6+}$ (Neutral or alkaline)

MATCHING TYPE PROBLEMS

Type I : Only one match is possible

1.

	Half Reactions		***n*-factor of reactant**
A.	$Bi_2S_3 \rightarrow Bi^{5+} + S$	(a)	6
B.	$FeS_2 \rightarrow Fe^{3+} + 2SO_2$	(b)	10
C.	$(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3$	(c)	11
D.	$Al_2(Cr_2O_7)_3 \rightarrow Al^{3+} + Cr^{3+}$	(d)	18

2.

	Reaction		***n*-factor of reactant**
A.	$Fe_3O_4 \rightarrow Fe_2O_3$	(a)	4/3
B.	$Fe_2O_3 \rightarrow Fe_3O_4$	(b)	2/3
C.	$P_2H_4 \rightarrow PH_3 + P_4H_2$	(c)	1
D.	$H_3PO_2 \rightarrow PH_3 + H_3PO_3$	(d)	5/3
E.	$I_2 \rightarrow I^- + IO_3^-$	(e)	6/5

Type II : More than one match are possible

3.

	Titration		**Reagents**
A.	Iodimetric	(a)	$AgNO_3$ *vs.* KCl
B.	Iodometric	(b)	N_2H_4 *vs.* I_2
C.	Redox	(c)	$CuSO_4$ *vs.* KI
D.	Acid-Base	(d)	$H_2C_2O_4$ *vs.* $KMnO_4$
E.	Precipitation	(e)	$H_2C_2O_4$ *vs.* NaOH

4.

	Reaction		**Equivalent mass of reactant**
A.	$Fe(SCN)_2 \rightarrow Fe^{3+} + SO_4^{2-} + CO_3^{2-} + NO_3^-$	(a)	$\frac{M}{28}$
B.	$As_2S_3 \rightarrow As^{5+} + SO_4^{2-}$	(b)	$\frac{M}{33}$
C.	$CrI_3 \rightarrow Cr_2^{6+} + I^{5+}$	(c)	$\frac{M}{27}$
D.	$CrI_3 \rightarrow Cr_2^{6+} + I^{7+}$	(d)	$\frac{M}{21}$
E.	$CrI_3 \rightarrow Cr^{6+} + I^{7+}$		

Type III : Only one match from each list

5.

List A	**List B**	**List C**
A. CH_4	(i) $E = M/8$	(a) $C^{2+} \rightarrow C^{4+}$
B. CO	(ii) $E = M/2$	(b) $C^{4-} \rightarrow C^{4+}$
C. $C_2O_4^{2-}$	(iii) $E = M/12$	(c) $C^{3+} \rightarrow C^{4+}$
D. C_2H_4		(d) $C^{2-} \rightarrow C^{4+}$

6.

Redox change	**Equivalent mass**	**Number of electrons involved in change**
A. $MnO_2 \rightarrow Mn_2O_3$	i. $E_{MnO_2} = M/2$	(a) 4
B. $MnO_2 \rightarrow MnSO_4$	ii. $E_{MnO_2} = M/4$	(b) 2
C. $MnO_2 \rightarrow Mn$	iii. $E_{MnO_2} = M/1$	(c) 3
D. $KMnO_4 \rightarrow Mn_2O_3$	iv. $E_{MnO_4} = M/4$	(d) 8
E. $KMnO_4 \rightarrow MnO_2$	v. $E_{MnO_4} = M/3$	

ANSWERS

1. A–b; B–c; C–a; D–d

2. A–c; B–b; C–e; D–a; E–d

3. A–b; B–c; C–b,c,d; D–e; E–a

4. A–b; B–a, d; C–c, d; D–c; E–c

5. A–i–b; B–ii–a; C–ii–c; D–iii–d

6. A–iii–b; B–i–b; C–ii–a; D–iv–d; E–v–c