ALLEN CAREER INSTITUTE KOTA (RAJASTHAN)

path to success

# CONTENTS


| S.NO. | TOPIC | PAGE NO. |
|---|---|---|
| 01. | Redox | 01 - 44 |
| 02. | Atomic Structure | 45 - 119 |
| 03. | Gaseous State | 120 - 183 |

# REDOX

## Recap of Early Classes

In Previous classes we have studied about atoms, molecules, periodic classification of elements, metals, non metal and bonding between elements to form different compounds–ionic/covalent. Another aspect in the study of matter is interms of its quantitative mesurement. Our knowledge about chemcial reaction and equation is the basis of what we will study in this chapter called stoichiometry. We will discuss mole concept, equivalent concept and its application in this section. It is most significant tool for chemical counting purpose.

## Index


**1.0 OXIDATION & REDUCTION**

**2.0 OXIDATION NUMBER**

- 2.1 Rules governing oxidation number
- 2.2 Calculation of average oxidation number
- 2.3 Typical cases of oxidation number

**3.0 OXIDISING AND REDUCING AGENT**

**4.0 REDOX REACTION**

- 4.1 Disproportionations reactions
- 4.2 Balancing of Redox Reaction

**5.0 EQUIVALENT WEIGHT (E)**

- 5.1 Valency factor calculation For Acids
- 5.2 Valency factor calculation For Base
- 5.3 Valency factor calculation For Acid - base reaction
- 5.4 Valency factor calculation For Salts
- 5.5 Eq. wt. of oxidising / reducing agents in redox reaction

**6.0 NORMALITY**

**7.0 LAW OF EQUIVALENCE**

**8.0 APPLICATIONS OF THE LAW OF EQUIVALENCE**

- 8.1 Simple Titration
- 8.2 Back Titration
- 8.3 Double Titration
- 8.4 Standard redox titrations
- 8.5 Iodometric and Iodimetric Titration

**9.0 HYDROGEN PEROXIDE ($H_2O_2$)**

- 9.1 Volume strength of $H_2O_2$

**10.0 HARDNESS OF WATER**

**11.0 STRENGTH OF OLEUM**

**12.0 CALCULATION OF AVAILABLE CHLORINE FROM A SAMPLE OF BLEACHING POWDER**

**EXERCISE-1**

**EXERCISE-2**

**EXERCISE-3**

**EXERCISE-4**

**EXERCISE-5**

# REDOX

## 1.0 OXIDATION & REDUCTION

SL AL

| | ***Oxidation*** | | ***Reduction*** |
|---|---|---|---|
| (1) | Addition of oxygen<br>***e.g.*** $2Mg + O_2 \rightarrow 2MgO$ | (i) | Removal of oxygen<br>***e.g.*** $CuO + C \rightarrow Cu + CO$ |
| (2) | Removal of Hydrogen<br>***e.g.*** $H_2S + Cl_2 \rightarrow 2HCl + S$ | (ii) | Addition of Hydrogen<br>***e.g.*** $S + H_2 \rightarrow H_2S$ |
| (3) | Increase in positive charge<br>***e.g.*** $Fe^{2+} \rightarrow Fe^{3+} + e^-$ | (iii) | Decrease in positive charge<br>***e.g.*** $Fe^{3+} + e \rightarrow Fe^{2+}$ |
| (4) | Increase in oxidation number<br>(+2) (+4)<br>$SnCl_2 \rightarrow SnCl_4$ | (iv) | Decrease in oxidation number<br>(+7) (+2)<br>$MnO_4^- \rightarrow Mn^{2+}$ |
| (5) | Removal of electron<br>***e.g.*** $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$ | (v) | Addition of electron<br>***e.g.*** $Fe^{3+} + e^- \rightarrow Fe^{2+}$ |

## 2.0 OXIDATION NUMBER

SL AL

It is an imaginary or apparent charge gained by an element when it goes from its elemental free state to combined state in molecules.
It is calculated on basis of a arbitrary set of rules.
It is a relative charge in a particular bonded state.

### 2.1 Rules governing oxidation number

SL AL

The following rules are helpful in calculating oxidation number of the elements in their different compounds. It is remember that the basis of these rule is the electronegativity of the element.

**(a) Fluorine atom**

Fluorine is most electronegativity atom (known). It always has oxidation no. equal to –1 in all its compounds.

**(b) Oxygen atom**

In general and as well as in its oxides, oxygen atom has oxidation number equal to –2.

***In case of :*** (i) peroxide (e.g. $H_2O_2$, $Na_2O_2$) is –1
(ii) super oxide (e.g. $KO_2$) is $-\frac{1}{2}$
(iii) ozonide ($KO_3$) is $-\frac{1}{3}$
(iv) oxygen fluoride $OF_2$ is +2 & in $O_2F_2$ is +1

**(c) Hydrogen atom**

In general, H atom has oxidation number equal to +1. But in metallic hydrides (e.g. NaH, KH) it is –1.

**(d) Halogen atom**

In general, all halogen atom (Cl, Br, I) has oxidation number equal to –1.
But if halogen atom is attached with an more electronegative atom than halogen atom then it will show positive oxidation numbers.

e.g. $K\overset{+5}{Cl}O_3$ $H\overset{+5}{I}O_3$ $H\overset{+7}{Cl}O_4$ $K\overset{+5}{Br}O_3$

**(e) Metals**

(a) Alkali metal (Li, Na, K, Rb, .....) always have oxidation number +1.
(b) Alkaline earth metal (Be, Mg, Ca .....) always have oxidation number +2.
(c) Aluminium always have +3 oxidation number.

***Note :*** *(i) Metal may have negative or zero oxidation number.*
*(ii) Oxidation number of an element in free state or in allotropic forms is always zero.*

e.g. $\overset{0}{O_2}, \overset{0}{S_8}, \overset{0}{P_4}, \overset{0}{O_3}$

*(iii) Sum of the charges of elements in a molecule is zero.*
*(iv) Sum of the charges of all elements in an ions is equal to the charge on the ion.*
*(v) If the group no. of an element in periodic table is n then its oxidation number may vary from n to n – 8 (but it is mainly applicable in p-block elements)*

e.g. N-atom belongs to v group in the periodic table therefore as per rule its oxidation number may vary from –3 to +5 $(\overset{-3}{N}H_3, \overset{+2}{N}O, \overset{+3}{N_2}O_3, \overset{+4}{N}O_2, \overset{+5}{N_2}O_5)$

## 2.2 Calculation of average oxidation number

SL AL

In case there are more than one atom of an element having different oxidation state, then average oxidation number can be calculated as :

$$= \frac{n_1 \times \text{Oxidation number}_1 + n_2 \times \text{Oxidation number}_2}{n_1 + n_2}$$

***Ex.1*** Calculate oxidation number of underlined element $Na_2\underline{S_2}O_3$ :

***Sol.*** Let oxidation number of S-atom is x. Now work accordingly with the rules given before.

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

$x = +2$

***Ex.2*** $Na_2\underline{S_4}O_6$ :

***Sol.*** Let oxidation number of S-atom is x

$(+1) \times 2 + (x) \times 2 + (-2) \times 6 = 0$

$x = +2.5$

It's important to note here that $Na_2S_2O_3$ have two S-atom and there are four S-atom in $Na_2S_4O_6$ but none sulphur atom in both the compound have +2 or +2.5 oxidation number, it is the average charge (O. No.) Which reside on each sulphur atom therefore we should work to calculate the individual oxidation number of each sulphur atom in these compound.

## Illustrations

***Illustration 1.*** Calculate the O.S. of all the atoms in the following species :
(i) $ClO^-$, (ii) $NO_2^-$, (iii) $NO_3^-$ (iv) $CCl_4$ (v) $K_2CrO_4$ and (vi) $KMnO_4$

***Solution.*** (i) In $ClO^-$, the net charge on the species is –1 and therefore the sum of the oxidation statesof Cl and O must be equal to –1. Oxygen will have an O.S. of –2 and if the O.S. of Cl is assumed to be 'x' then x – 2 should be equal to –1. x is + 1

(ii) $NO_2^-$ : $(2 \times -2) + x = -1$ (where 'x' is O.S. of N)
$\therefore x = +3$

(iii) $NO_3^-$ : $x + (3 \times -2) = -1$ (where 'x' is O.S. of N)
$x = +5$

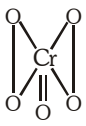
(iv) In $CCl_4$, Cl has an O.S. of –1
$x + 4 \times -1 = 0$
$\therefore x = +4$ (where 'x' is O.S. of C)

(v) $K_2CrO_4$ : K has O.S. of +1 and O has O.S. of –2 and let Cr has O.S. 'x' then,
$2 \times (+1) + x + 4 \times (-2) = 0$
$\therefore x = +6$

(vi) $KMnO_4$ : $+1 + x + (4 \times -2) = 0$
$\therefore x = +7$ (where x is O.S. of Mn).

## 2.3 Typical cases of Oxidation Number

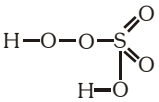
In order to determine the exact or individual oxidation number we need to take help from the structures of the molecules. Some special cases are discussed as follows :

(i) The structure of $CrO_5$ is 


From the structure it is evident that in $CrO_5$ there are two peroxide linkages and one double bond. The contribution of each peroxide linkage is –2. Let the O.N. of Cr is x.

$\therefore$ $x + (-2)2 + (-2) = 0$ or $x = 6$

$\therefore$ O.N. of Cr = +6 ***Ans.***

(ii) The strcuture of $H_2SO_5$ is 

From the structure, it is evident that in $H_2SO_5$. there are one peroxide linkage, two sulphur - oxygen double bond and one OH group. Let the O.N. of S = x.

$\therefore$ $+1 - 2 + x + (-2)\,2 + (-2) + 1 = 0$

or $x + 2 - 8 = 0$

or $x - 6 = 0$

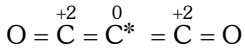
or $x = 6$

$\therefore$ O.N. of S in $H_2SO_5$ is +6 ***Ans***

(iii) ***Paradox of fractional oxidation number :***

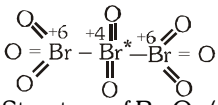
Fractional oxidation state is the average oxidation state of the element under examination and the structural parameters reveal that the element for whom fractional oxidation state is realised is actually present in different oxidation states. Structure of the species $C_3O_2$, $Br_3O_8$ and $S_4O_6^{2-}$ reveal the following bonding situations.

(a) The element marked with asterisk in each species is exhibiting the different oxidation state (oxidation number) from rest of the atoms of the same element in each of the species. This reveals that in $C_3O_2$, two carbon atoms are present in +2 oxidation state each whereas the third one is present in zero oxidation state and the average is 4/3. However the realistic picture is +2 for two terminal carbons and zero for the middle carbon.



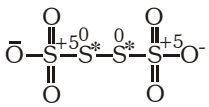
Structure of $C_3O_2$
(Carbon suboxide)

(b) Likewise in $Br_3O_8$, each of the two terminal bromine atoms are present in +6 oxidation state and the middle bromine is present in +4 oxidation state. Once again the average, that is different from reality is 16/3.



Structure of $Br_3O_8$ (tribromooctaoxide)

(c) In the same fashion, in the species $S_4O_6^{2-}$, is 2.5, whereas the reality being +5,0,0 and +5 oxidation number respectively for each sulphur.



Structure of $S_4O_6^{2-}$ (tetrathionate ion)

## 3.0 OXIDISING AND REDUCING AGENT

SL AL

- **Oxidising agent or Oxidant**

Oxidising agents are those compound which can oxidise others and reduced itself during the chemical reaction. Those reagents whose O.N. decrease or which gain electrons in a redox reaction are termed as oxidants e.g. $KMnO_4$, $K_2Cr_2O_7$, $HNO_3$, conc. $H_2SO_4$ etc, are powerful oxidising agents.

- **Reducing agent or Reductant**

Reducing agents are those compound which can reduce others and oxidise itself during the chemical reaction. Those reagents whose O.N. increase or which loses electrons in a redox reaction are termed as reductants. e.g. KI, $Na_2S_2O_3$ are powerful reducing agents.

***Note :*** *There are some compounds also which can work both oxidising agent and reducing agent. e.g.* $H_2O_2$, $NO_2^-$

## 4.0 REDOX REACTION

SL AL

A reaction in which oxidation and reduction simultaneously take place.

In all redox reactions the total increase in oxidation number must equal the total decrease in oxidation number.

e.g. $10\overset{+2}{Fe}SO_4 + 2K\overset{+7}{Mn}O_4 + 8H_2SO_4 \longrightarrow 5\overset{+3}{Fe_2}(SO_4)_3 + 2\overset{+2}{Mn}SO_4 + K_2SO_4 + 8H_2O$

***Some examples of redox reactions are :***

- $Sn^{2+} + 2Hg^{2+} \longrightarrow Hg^{2+} + Sn^{4+}$ (R, O)
- $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$ (O, R)
- $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$ (O, R)
- $3Cu + 2NO_3^- + 8H^+ \rightarrow 2NO + 3Cu^{2+} + 4H_2O$ (R, O)

### 4.1 Disproportionations reactions

SL AL

A redox reaction in which a same element present in a particular compound in a definite oxidation state is oxidized as well as reduced simultaneously is a disproportionation reaction.

Disproportionation reactions are a special type of redox reactions. One of the reactants in a disproportionation reaction always contains ***an element that can exist in at least three oxidation states.*** The element in the form of reacting substance is in the intermediate oxidation state and both higher and lower oxidation states of that element are formed in the reaction.

$2\overset{+1}{H_2}\overset{-1}{O_2}(aq) \longrightarrow 2\overset{+1}{H_2}\overset{-2}{O}(\ell) + \overset{0}{O_2}(g)$

$\overset{0}{S_8}(s) + 12OH^-(aq) \longrightarrow 4\overset{-2}{S^{2-}}(aq) + 2\overset{+2}{S_2}O_3^{2-}(aq) + 6H_2O(\ell)$

$\overset{0}{Cl_2}(g) + 2OH^-(aq) \longrightarrow \overset{+1}{ClO^-}(aq) + \overset{-1}{Cl^-}(aq) + H_2O(\ell)$

***Consider following reactions :***

(a) $2KClO_3 = 2KCl + 3O_2$

$KClO_3$ plays a role of oxidant and reductant both. Because same element is not oxidised and reduced. Here, Cl present in $KClO_3$ is reduced and O present in $KClO_3$ is oxidized. So ***its not a disproportion reaction*** although it looks like one.

(b) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

Nitrogen in this compound has –3 and +3 oxidation number so it is not a definite value, so its not a disproportion reaction. Its a example of ***comproportionation reaction*** which is a class of redox reaction in which a element from two different oxidation state gets converted into a single oxidation state.

(c) $4KClO_3 \longrightarrow 3KClO_4 + KCl$

Its a case of disproportionation reaction in which Cl is the atom disproportionating.

***Important disproportionation reaction :***

1. $H_2O_2 \longrightarrow H_2O + O_2$
2. $X_2 + OH^-$ (dil.) $\longrightarrow X^- + XO^-$
3. $X_2 + OH^-$ (conc.) $\longrightarrow X^- + XO_3^-$

***Note :*** *$F_2$ does not (can not) undergo disproportionation as it is the most electronegative element.*

$F_2 + NaOH\ (dil) \longrightarrow F^- + OF_2$

$F_2 + NaOH$ concentration $(dil) \longrightarrow F^- + O_2$

***Other diproportionation reactions :***

- $3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O$

  O.N.= 0 −1 +5

  R

  O

- $2Cu^+ \xrightarrow{\text{Disproportionates}} Cu + Cu^{2+}$

  R

  O

- $2HCHO + OH^- \rightarrow CH_3OH + HCOO^-$

  R

  O

- $4ClO_3^- \rightarrow 3ClO_4^- + Cl^-$

  O

  R

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

  R

  O

## 4.2 Balancing of Redox Reactions

SL AL

All balanced equations must satisfy two criteria

1. ***Atom balance (mass balance)***

   That is there should be the same number of atoms of each kind in reactant and products side.

2. ***Charge balance :***

   That is the sum of actual charges on both side of the equation must be equal

   There are two methods for balancing the redox equations

   (a) Oxidation - number change method

   (b) Ion electron method or half cell method

***(a) Oxidation number change method :*** This method was given by Jonson. In a balanced redox reaction, total increase in oxidation number must be equal to total decreases in oxidation number. This equivalence provides the basis for balancing redox reactions.

***The general procedure involves the following steps :***

(i) Select the atom in oxidising agent whose oxidation number decreases and indicate the gain of electrons.

(ii) Select the atom in reducing agent whose oxidation number increases and write the loss of electrons.

(iii) Now cross multiply i.e. multiply oxidising agent by the number of loss of electrons and reducing agent by number of gain of electrons.

(iv) Balance the number of atoms on both sides whose oxidation numbers change in the reaction.

(v) In order to balance oxygen atoms, add $H_2O$ molecules to the side deficient in oxygen. Then balance the number of H atoms by adding $H^+$ ions in the hydrogen.

**(b) *Ion electron method or half reaction method :***

By this method redox equation are balanced in two different medium

(a) Acidic medium (b) Basic medium

***Balancing in acidic medium***

Students are advised to follow the following steps to balance the redox reactions by ion electron method in acidic medium.

***Balancing in basic medium***

In this case except step VI all the steps are same. We can understand it by following example balance the redox reaction in basic medium

## Illustrations

***Illustration 2.*** Balance the following chemical reaction by oxidation number method and write their skeleton equation :

(i) Chloride ions reduce maganese dioxide to manganese (II) ions in acidic medium and get itself oxidized to chlorine gas.

(ii) The nitrate ions in acidic medium oxidize magnesium to $Mg^{2+}$ ions but itself gets reduced to nitrous oxide.

***Solution*** ***(i)*** The skeleton equation for the given process is

$$MnO_2 + Cl^- \longrightarrow Mn^{2+} + Cl_2 + H_2O$$

***Step (1) :*** $\overset{+4}{Mn}\overset{-2}{O_2} + Cl^- \longrightarrow Mn^{2+} + \overset{+4}{Cl_2} + \overset{+1}{H_2}\overset{-2}{O}$

O.N. decreases by 2 per Mn

***Step (2) :*** $\overset{+4}{MnO_2} + Cl^- \longrightarrow Mn^{2+} + Cl_2 + H_2O$

O.N. increases by 1 per Cl

***Step (3) :*** Equalize the increase/decrease in O.N. by multiplying

$MnO_2$ by 1 and $Cl^-$ by 2

$$MnO_2 + 2Cl^- \longrightarrow Mn^{2+} + Cl_2 + H_2O$$

***Step (4) :*** Balance other atoms except H and O. Here they are all balanced.

***Step (5) :*** Balance O atoms by adding $H_2O$ molecules to the side falling short of O atoms.

$$MnO_2 + 2Cl^- \longrightarrow Mn^{2+} + Cl_2 + H_2O + H_2O$$

***Step (6) :*** Balance H atoms by adding $H^+$ ions to the side falling short of H atoms.

$$MnO_2 + 2Cl^- + 4H^+ \longrightarrow Mn^{2+} + Cl_2 + 2H_2O$$

***(ii)*** The skeleton equation for the given process is

$$Mg + NO_3^- \longrightarrow Mg^{2+} + N_2O + H_2O$$

***Step (1) :*** $\overset{0}{Mg} + (\overset{+5}{N}\overset{-2}{O_3})^- \longrightarrow Mg^{2+} + \overset{+1}{N_2}\overset{-2}{O} + \overset{+1}{H_2}\overset{-2}{O}$

Multiply $NO_3^-$ by 2 to equalize N atoms

***Step (2) :*** O.N. increases by 2 per Mg atom

$\overset{0}{Mg} + 2NO_3^- \longrightarrow Mg^{2+} + \overset{+1}{N_2}O + H_2O$

4 2 = 8

O.N. decreases by 4 per N atom

***Step (3) :*** Equalize increase/decrease in O.N. by multiplying Mg by 4 and $2NO_3^-$ by 1.

$$4Mg + 2NO_3^- \longrightarrow Mg^{2+} + N_2O + H_2O$$

***Step (4) :*** Balance atoms other than O and H

$$4Mg + 2NO_3^- \longrightarrow 4Mg^{2+} + N_2O + H_2O$$

***Step (5) :*** Balance O atoms

$$4Mg + 2NO_3^- \longrightarrow 4Mg^{2+} + N_2O + H_2O + 4H_2O$$

***Step (6) :*** Balance H atoms as is done in acidic medium.

$$4Mg + 2NO_3^- + 10H^+ \longrightarrow 4Mg^{2+} + N_2O + 5H_2O$$

***Illustration 3.*** Balance the following redox reaction.

$$FeSO_4 + KMnO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + MnSO_4 + H_2O$$

***Solution*** ***Step-I*** assign the oxidation No. to each elements present in the reaction.

$$\overset{+2}{Fe}\,\overset{+6}{S}\,\overset{-2}{O_4} + \overset{+1}{K}\overset{+7}{Mn}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{+6}{S}\overset{-2}{O_4} \longrightarrow \overset{+3}{Fe_2}(\overset{+6}{S}\overset{-2}{O_4})_3 + \overset{+2}{Mn}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{-2}{O}$$

***Step-II*** Now convert the reaction in ionic form by eliminating the elements or species which are not going either oxidation or reduction

$$Fe^{2+} + \overset{+7}{Mn}O_4^- \longrightarrow Fe^{3+} + Mn^{2+}$$

***Step-III*** Now identify the oxidation / reduction occurring into the reaction.

undergoes reduction

$$Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$$

undergoes oxidation

***Step-IV*** Split the ionic reaction in two half one for oxidation and other for reduction

$$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} \;\Big|\; MnO_4^- \xrightarrow{\text{Reduction}} Mn^{2+}$$

***Step-V*** Balance the atom other than oxygen and hydrogen atom in both half reactions

$$Fe^{2+} \rightarrow Fe^{3+} \;\Big|\; MnO_4^- \rightarrow Mn^{2+}$$

Fe & Mn atom are balanced in both side.

***Step-VI*** Now balance O & H atom by $H_2O$ & $H^+$ respectively by the following way for one excess oxygen atom add one $H_2O$ on the other side and two $H^+$ on the same side.

$Fe^{2+} \longrightarrow Fe^{3+}$ (no oxygen atom) ...(i)

$8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$ ...(ii)

***Step VII*** Now see equation (i) & (ii) is balanced atomwise. Now balance both equations chargewise to balance the charge add electrons to the electrically positive side.

$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} + e^-$ ...(1)

$5e^- + 8H^+ + MnO_4^- \xrightarrow{\text{Reduction}} Mn^{2+} + 4H_2O$ ...(2)

***Step VIII*** The number of electrons gained and lost in each half-reaction are equalised by multiply suitable factor in both the half reaction and finally the half reactions are added to give the over all balanced reaction.

Here we multiply equation (i) by 5 and (ii) by one

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ ...(1) × 5

$5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$ ...(2) × 1

---

$5Fe^{2+} + 8H^+ + MnO_4^- \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

(Here at this stage you will get balanced redox reaction in ionic form)

***Step IX*** Now convert the ionic reaction in to molecular form by adding the elements or species which are removed instep (II).

Now by some manipulation you will get

$$5\ FeSO_4 + KMnO_4 + 4H_2SO_4 \rightarrow \frac{5}{2}\ Fe_2(SO_4)_3 + MnSO_4 + 4H_2O \text{ or}$$

$$10\ FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O + K_2SO_4$$

***Illustration 4.*** $ClO^- + CrO_2^- + OH^- \longrightarrow Cl^- + CrO_4^{2-} + H_2O$

***Solution*** By using up to step V we will get

$$\overset{+1}{ClO^-} \xrightarrow{\text{Reduction}} Cl^- \quad \Big| \quad \overset{+3}{CrO_2^-} \xrightarrow{\text{Oxidation}} \overset{+6}{CrO_4^{2-}}$$

Now student are advised to follow step VI to balance 'O' and 'H' atom

$$2H^+ + ClO^- \longrightarrow Cl^- + H_2O \quad \Big| \quad 2H_2O + CrO_2^- \longrightarrow CrO_4^{2-} + 4H^+$$

Now since we are doing balancing in basic medium therefore add as many as $OH^-$ on both side of equation as there are $H^+$ ions in the equation.

$2OH^- + 2H^+ + ClO^- \longrightarrow Cl^- + H_2O + 2OH^-$ $\quad 4OH^- + 2H_2O + CrO_2^- \rightarrow CrO_4^{2-} + 4H^+ + 4OH^-$

Finally you will get

$H_2O + ClO^- \longrightarrow Cl^- + 2OH^-$ ...(i)

$4OH^- + CrO_2^- \rightarrow CrO_4^{2-} + 2H_2O$ ...(ii)

Now see equation (i) and (ii) in which O and H atoms are balanced by $OH^-$ and $H_2O$

Now from step VIII

$2e^- + H_2O + ClO^- \rightarrow Cl^- + 2OH^-$ ....(i) × 3

$4OH^- + CrO_2^- \rightarrow CrO_4^{-2} + 2H_2O + 3e^-$ ...(ii) × 2

***Adding :*** $3ClO^- + 2CrO_2^- + 2OH^- \rightarrow 3Cl^- + 2CrO_4^{2-} + H_2O$

## BEGINNER'S BOX–1

### *Oxidation Number and Balancing of Redox Reactions*

**1.** Calculate the oxidation number of underlined elements in the following compounds :

(a) $K_4\underline{P_2}O_7$ (b) $\underline{Cr}O_2Cl_2$ (c) $Ca(\underline{Cl}O_2)_2$ (d) $\underline{Zn}O_2^{2-}$

(e) $\underline{Fe}_{0.93}O$

**2.** Write balanced net ionic equation for the following reactions in acidic solution.

(a) $S_4O_6^{2-}$ (aq) $+Al$ (s) $\longrightarrow H_2S$ (aq) $+ Al^{3+}$ (aq)

(b) $S_2O_3^{2-}$ (aq) $+ Cr_2O_7^{2-}$ (aq) $\longrightarrow S_4O_6^{2-}$ (aq) $+ Cr^{3+}$ (aq)

(c) $ClO_3^-$ (aq) $+ As_2S_3$ (s) $\longrightarrow Cl^-$ (aq) $+ H_2AsO_4^-$ (aq) $+ HSO_4^-$ (aq)

(d) $IO_3^-$ (aq) $+ Re$ (s) $\longrightarrow ReO_4^-$ (aq) $+ I^-$ (aq)

*(e) $HSO_4^-$ (aq) $+ As_4$ (s) $+ Pb_3O_4$ (s) $\longrightarrow PbSO_4$ (s) $+ H_2AsO_4^-$ (aq)

*(f) $HNO_2$ (aq) $\longrightarrow NO_3^- + NO$ (g)

**3.** Write balanced net ionic equations for the following reactions in basic solution :

(a) $C_4H_4O_6^{2-}$(aq) $+ ClO_3^-$ (aq) $\longrightarrow CO_3^{2-}$ (aq) $+ Cl^-$ (aq)

(b) Al (s) $+ BiONO_3$ (s) $\longrightarrow Bi$ (s) $+ NH_3$ (aq) $+ Al(OH)_4^-$(aq)

*(c) $H_2O_2$ (aq) $+ Cl_2O_7$ (aq) $\longrightarrow ClO_2^-$ (aq) $+ O_2$ (g)

*(d) $Tl_2O_3$ (s) $+ NH_2OH$ (aq) $\longrightarrow TlOH$ (s) $+ N_2$ (g)

(e) $Cu(NH_3)_4^{2+}$ (aq) $+ S_2O_4^{2-}$ (aq) $\longrightarrow SO_3^{2-}$ (aq) $+ Cu$ (s) $+ NH_3$ (aq)

(f) $Mn(OH)_2$ (s) $+ MnO_4^-$ (aq) $\longrightarrow MnO_2$ (s)

## 5.0 EQUIVALENT WEIGHT (E)

AL

$$\text{Eq. wt (E)} = \frac{\text{Molecular weight}}{\text{valency factor (v.f)}} = \frac{\text{Mol. wt.}}{\text{n} - \text{factor}}$$

$$\text{no of Equivalents} = \frac{\text{mass of a sample}}{\text{eq. wt. of that species}}$$

Equivalent mass is a pure number when expressed in gram, it is called gram equivalent mass.
The equivalent mass of substance may have different values under different conditions.

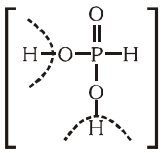
### 5.1 Valency factor calculation For Acids

AL

valence factor = number of replaceable $H^+$ ions

***Ex.1.*** HCl, $H_2SO_4$ $H_3PO_4$ $H_3PO_3$

{see there are only two replaceable $H^+$ ions}



***Sol.*** valence → 1 2 3 2

factor (assume 100% dissociation)

Eq.wt.→ $\frac{M}{1}$ $\frac{M}{2}$ $\frac{M}{3}$ $\frac{M}{2}$

### 5.2 Valency factor calculation For Base

AL

v.f. = number of replicable $OH^-$ ions

***Ex.2.*** NaOH, KOH

***Sol.*** v.f.→ 1 1

E.→ $\frac{M}{1}$ $\frac{M}{1}$

### 5.3 Valency factor calculation For Acid - base reaction

AL

In case of acid base reaction, the valence factor is the actual number of $H^+$ or $OH^-$ replaced in the reaction.
The acid or base may contain more number of replaceable $H^+$ or $OH^-$ than actually replaced in reaction.
v.f. for base is the number of $H^+$ ion form the acid replaced by per molecule of the base.

***Ex.1.*** $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

Base acid

***Sol.*** valency factor of base = 1

valency factor of acid = 2

Here two molecule of NaOH replaced $2H^+$ ion from the $H_2SO_4$ therefore per molecule of NaOH replaced only one $H^+$ ion of acid so v.f. = 1

v.f. for acid is number of $OH^-$ replaced from the base by per molecule of acid.

***Ex.2.*** $NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O$

Base acid

***Sol.*** valence factor of acid = 1

Here one of molecule of $H_2SO_4$ replaced one $OH^-$ from NaOH therefore v.f. for $H_2SO_4$ is = 1

$$E = \frac{\text{mol. wt. of } H_2SO_4}{1}$$

## 5.4 Valency factor calculation For Salts

AL

**(a)** In non reacting condition

v.f. = Total number of positive charge or negative charge present into the compound.

***Ex.1.*** $Na_2CO_3Fe_2(SO_4)_3(2Fe^{3+} + 3SO_4^{2-})\ FeSO_4.7H_2O$

***Sol.*** V.f. 2 $\quad 2 \times 3 = 6 \quad$ 2

E. $\frac{M}{2} \quad \frac{M}{6} \quad \frac{M}{2}$

**(b)** ***Salt in reacting condition :***

***Ex.2.*** $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

Base Acid

***Sol.*** It is a acid base reaction therefore v.f. for $Na_2CO_3$ is one while in non reaction condition it will be two.

## 5.5 Eq. wt. of oxidising / reducing agents in redox reaction

AL

The equivalent weight of an oxidising agent is that weight which accepts one mole electron in a chemical reaction.

**(a)** Equivalent wt. of an oxidant (get reduced) = $\frac{\text{Mol.wt.}}{\text{No. of electrons gained by one mole}}$

***Ex.1.*** In acidic medium

$6e^- + Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$

Eq. wt. of $K_2Cr_2O_7$ = $\frac{\text{Mol. wt of } K_2Cr_2O_7}{6} = \frac{\text{Mol. wt.}}{6}$

***Note :*** *[6 in denominator indicates that 6 electrons were gained by $Cr_2O_7^{2-}$ as it is clear from the given balanced equation]*

**(b)** Similarly equivalent wt. of a reductant (gets oxidised) = $\frac{\text{Mol. wt.}}{\text{No. of electrons lost by one mole}}$

***Ex.2.*** In acidic medium, $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$

Here, Total electrons lost = 2

So, eq. wt. = $\frac{\text{Mol. wt.}}{2}$

(c) In different condition a compound may have different equivalent weights. Because, it depends upon the number of electrons gained or lost by that compound in that reaction.

***Ex.3.*** (i) $\underset{(+7)}{MnO_4^-} \longrightarrow \underset{(+2)}{Mn^{2+}}$ (acidic medium)

Here 5 electrons are taken so eq. wt. = $\frac{\text{Mol.wt.of } KMnO_4}{5} = \frac{158}{5} = 31.6$

(ii) $\underset{(+7)}{MnO_4^-} \longrightarrow \underset{(+4)}{Mn^{+4}}$ (neutral medium)

Here, only 3 electrons are gained, so eq. wt. = $\frac{\text{Mol.wt.of } KMnO_4}{3} = \frac{158}{5} = 52.7$

(iii) $\underset{(+7)}{MnO_4^-} \longrightarrow \underset{(+6)}{MnO_4^{-2}}$ (alkaline medium)

Here, only one electron is gained, so eq. wt. = $\frac{\text{Mol.wt.of } KMnO_4}{1} = 158$

***Note :*** *It is important to note that $KMnO_4$ acts as an oxidant in every medium although with different strength which follows the order. acidic medium > neutral medium > alkaline medium*

***Ex.4.*** $2S_2O_3^{--} \longrightarrow S_4O_6^{--} + 2e^-$

(Reducing agent)

equivalent weight of $S_2O_3^{--}$ = $\frac{M}{1} = M$

- ***SOME OXIDIZING AGENTS/REDUCING AGENTS WITH EQ. WT.***

| ***Species*** | ***Changed to*** | ***Reaction exchanged or change in O.N.*** | ***Electrons*** | ***Eq. wt.*** |
|---|---|---|---|---|
| $MnO_4^-$(O.A.) | $Mn^{+2}$ in acidic medium | $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ | 5 | $E = \frac{M}{5}$ |
| $MnO_4^-$(O.A.) | $MnO_2$ in neutral medium | $MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$ | 3 | $E = \frac{M}{3}$ |
| $MnO_4^-$(O.A.) | $MnO_4^{2-}$ in basic medium | $MnO_4^- + e^- \longrightarrow MnO_4^{2-}$ | 1 | $E = \frac{M}{1}$ |
| $Cr_2O_7^{2-}$(O.A.) | $Cr^{3+}$ in acidic medium | $CrO_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ | 6 | $E = \frac{M}{6}$ |
| $MnO_2$(O.A.) | $Mn^{2+}$ in acidic medium | $MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$ | 2 | $E = \frac{M}{2}$ |
| $Cl_2$(O.A.) in bleaching powder | $Cl^-$ | $Cl_2 + 2e^- \longrightarrow 2Cl^-$ | 2 | $E = \frac{M}{2}$ |
| $CuSO_4$(O.A.) in iodometric titration | $Cu^+$ | $Cu^{2+} + e^- \longrightarrow Cu^+$ | 1 | $E = \frac{M}{1}$ |
| $S_2O_3^{2-}$ (R.A.) | $S_4O_6^{2-}$ | $2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$ (for two molecules) | 2 | $E = \frac{2M}{2} = M$ |
| $H_2O_2$(O.A.) | $H_2O$ | $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$ | 2 | $E = \frac{M}{2}$ |
| $H_2O_2$(R.A.) | $O_2$ | $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$ (O.N. of oxygen in $H_2O_2$ is –1 per atom) | 2 | $E = \frac{M}{2}$ |
| $Fe^{2+}$(R.A.) | $Fe^{3+}$ | $Fe^{2+} \longrightarrow Fe^{3+} + e^-$ | 1 | $E = \frac{M}{1}$ |

## Illustrations

***Illustration 5*** To find the n-factor in the following chemical changes.

(i) $KMnO_4 \xrightarrow{H^+} Mn^{2+}$ (ii) $KMnO_4 \xrightarrow{H_2O} Mn^{4+}$

(iii) $KMnO_4 \xrightarrow{OH^-} Mn^{6+}$ (iv) $K_2Cr_2O_7 \xrightarrow{H^+} Cr^{3+}$

(v) $C_2O_4^{2-} \rightarrow CO_2$ (vi) $FeSO_4 \rightarrow Fe_2O_3$

(vii) $Fe_2O_3 \rightarrow FeSO_4$

***Solution*** (i) In this reaction, $KMnO_4$ which is an oxidizing agent, itself gets reduced to $Mn^{2+}$ under acidic conditions.

$$n = |1 \times (+7) - 1 \times (+2)| = 5$$

(ii) In this reaction, $KMnO_4$ gets reduced to $Mn^{4+}$ under neutral or slightly (weakly) basic conditions.

$$n = |1 \times (+7) - 1 \times (+4)| = 3$$

(iii) In this reaction, $KMnO_4$ gets reduced to $Mn^{6+}$ under basic conditions.

$$n = |1 \times (+7) - 1 \times (+6)| = 1$$

(iv) In this reaction, $K_2Cr_2O_7$ which acts as an oxidizing agent reduced to $Cr^{3+}$ under acidic conditions. (It does not react under basic conditions.)

$$n = |2 \times (+6) - 2 \times (+3)| = 6$$

(v) In this reaction, $C_2O_4^{2-}$ (oxalate ion) gets oxidized to $CO_2$ when it is reacted with an oxidizing agent.

$$n = |2 \times (+3) - 2 \times (+4)| = 2$$

(vi) In this reaction, ferrous ions get oxidized to ferric ions.

$$n = |1 \times (+2) - 1 \times (+3)| = 1$$

(vi) In this reaction, ferric ions are getting reduced to ferrous ions.

$$n = |2 \times (+3) - 2 \times (+2)| = 2$$

***Illustration 6.*** Calculate the molar ratio in which the following two substances would react ?
$Ba_3(PO_4)_2$ and $AlCl_3$

***Solution*** n-factor of $Ba_3(PO_4)_2 = 3 \times (+2) = 6 = n_1$
While n-factor of $AlCl_3 = 1 \times (+3) = 3 = n_2$

$\frac{n_1}{n_2} = \frac{6}{3}$ If $\frac{n_1}{n_2} = \frac{x}{y}$

Molar ratio $= \frac{y}{x}$ (inverse of equivalent ratio)

$\therefore$ Molar ratio in which $Ba_3(PO_4)_2$ and $AlCl_3$ will react = 3 : 6 = 1 : 2

## BEGINNER'S BOX–2

### *Equivalent Weight*

**1.** Molecular weight of $KMnO_4$ in acidic medium and neutral medium will be respectively :
(A) 7 × equivalent wt. and 2 × equivalent wt. (B) 5 × equivalent wt. and 3 × equivalent wt.
(C) 4 × equivalent wt. and 5 × equivalent wt. (D) 2 × equivalent wt. and 4 × equivalent wt.

**2.** Equivalent wt. of $H_3PO_4$ in each of the reaction will be respectively :
$H_3PO_4 + OH^- \longrightarrow H_2PO_4^- + H_2O$
$H_3PO_4 + 2OH^- \longrightarrow HPO_4^{2-} + 2H_2O$
$H_3PO_4 + 3OH^- \longrightarrow PO_4^{3-} + 3H_2O$
(A) 98, 49, 32.67 (B) 49, 98, 32.67 (C) 98, 32.67, 49 (D) 32.67, 49, 98

**3.** In acidic medium, equivalent weight of $K_2Cr_2O_7$ (Mol. wt. = M) is –
(A) M/3 (B) M/4 (C) M/6 (D) M/2

**4.** In which of the following reaction is there a change in the oxidation number of nitrogen atoms :-
(A) $2\,NO_2 \rightarrow N_2O_4$ (B) $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
(C) $N_2O_5 + H_2O \rightarrow 2HNO_3$ (D) None

**5.** For the redox reaction :
$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$
the correct stoichiometric coefficients of $MnO_4^-$, $C_2O_4^{2-}$ and $H^+$ are respectively
(A) 2,5,16 (B) 16,5,2 (C) 5,16,2 (D) 2,16,5

## 6.0 NORMALITY

AL

Normality of solution is defined as the number of equivalent of solute present in one litre (1000 mL) solutions.
Let a solution is prepared by dissolving W g of solute of eq. wt. E in V mL water.

No. of equivalent of solute $= \frac{W}{E}$

V mL of solution have $\frac{W}{E}$ equivalent of solute

1000 mL solution have $\frac{W \times 1000}{E \times VmL}$

***Normality (N)*** $= \dfrac{W \times 1000}{E \times VmL}$

Normality (N) = molarity × Valence factor (n)

***or*** N × V (in mL) = M × V (in mL) × n
***or*** milli equivalents = millimoles × n

***Ex :*** Calculate the normality of a solution containing 50 mL of 5 M solution $K_2Cr_2O_7$ in acidic medium.

***Sol.*** Normality (N) = Molarity × Valence factor = 5 × 6 = 30 N

## Illustrations

***Illustration 7*** Calculate the normality of a solution containing 15.8 g of $KMnO_4$ in 50 mL acidic solution.

***Solution*** Normality (N) $= \dfrac{W \times 1000}{E \times VmL}$

where W = 15.8 g, V = 50 mL $E = \dfrac{\text{molar mass of } KMnO_4}{\text{Valence factor}} = 158/5 = 31.6$ ; So, N = 10

## 7.0 LAW OF EQUIVALENCE

AL

The law states that one equivalent of an element combine with one equivalent of the other, and in a chemical reaction equivalent and mill equivalent of reactants react in equal amount to give same no. of equivalent or milli equivalents of products separately.

***According :***

***(i)*** $aA + bB \rightarrow mM + nN$
m.eq of A = m.eq of B = m.eq of M = m.eq of N

***(ii)*** In a compound $M_xN_y$
m.eq of $M_xN_y$ = m.eq of M = m.eq of N

## Illustrations

***Illustration 8.*** Find the number of moles of $KMnO_4$ needed to oxidise one mole $Cu_2S$ in acidic medium.
The reaction is $KMnO_4 + Cu_2S \longrightarrow Mn^{2+} + Cu^{2+} + SO_2$

***Solution*** From law of equivalence
equivalents of $Cu_2S$ = equivalents of $KMnO_4$
moles of $Cu_2S$ × v.f = moles of $KMnO_4$ × v.f.
moles of $Cu_2S$ × 8 = 1 × 5 ⇒ moles of $Cu_2S$ = 5/8

***Illustration 9.*** The number of moles of oxalate ions oxidized by one mole of $MnO_4^-$ ion in acidic medium.

(A) $\frac{5}{2}$ (B) $\frac{2}{5}$ (C) $\frac{3}{5}$ (D) $\frac{5}{3}$

***Solution*** Equivalents of $C_2O_4^{2-}$ = equivalents of $MnO_4^-$
x (mole) × 2 = 1 × 5

$x = \frac{5}{2}$

***Illustration 10.*** What volume of 6 M HCl and 2 M HCl should be mixed to get two litre of 3 M HCl ?

***Solution*** Let, the volume of 6 M HCl required to obtain 2 L of 3M HCl = x L
∴ Volume of 2 M HCl required = (2 – x) L

$M_1V_1 + M_2V_2 = M_3V_3$
6M HCl 2M HCl 3M HCl
6 × (x) + 2 × (2 – x) = 3 × 2
⇒ 6x + 4 – 6x = 6 ⇒ 4x = 2
∴ x = 0.5 L
Hence, volume of 6 M HCl required = 0.5 L
Volume of 2M HCl required = 1.5 L

***Illustration 11.*** In a reaction vessel, 1.184 g of NaOH is required to be added for completing the reaction. How many millilitre of 0.15 M NaOH should be added for this requirement ?

***Solution*** Amount of NaOH present in 1000 mL of 0.15 M NaOH = 0.15 × 40 = 6 g

$\therefore$ 1 mL of this solution contain NaOH $= \frac{6}{1000} \times 10^{-3}$ g

$\therefore$ 1.184 g of NaOH will be present in $= \frac{1}{6 \times 10^{-3}} \times 1.184 = 197.33$ mL

***Illustration 12.*** What weight of $Na_2CO_3$ of 85% purity would be required to prepare 45.6 mL of 0.235N $H_2SO_4$?

***Solution*** Meq. of $Na_2CO_3$ = Meq. of $H_2SO_4$

$45.6 \times 0.235$

$\therefore \frac{W_{Na_2CO_3}}{E_{Na_2CO_3}} \times 1000 = 45.6 \times 0.235$

$\Rightarrow \frac{W_{Na_2CO_3}}{106/2} \times 1000 = 45.6 \times 0.235$

$\therefore W_{Na_2CO_3} = 0.5679$ g

For 85 g of pure $Na_2CO_3$, weighed sample = 100 g

$\therefore$ For 0.5679 g of pure $Na_2CO_3$, weighed sample $= \frac{100}{85} \times 0.5679 = 0.6681$ g

## 8.0 APPLICATIONS OF THE LAW OF EQUIVALENCE

### 8.1 Simple Titration

AL

In this, we can find the concentration of unknown solution by reacting it with solution of known concentration (standard solution). For example, let there be a solution of substance A of unknown concentration. We are given solution of another substance B whose concentration is known ($N_1$). We take a certain known volume of A in a flask ($V_2$) and then we add B to A slowly till all the A is consumed by B (this can be known with the help of indicators). Let us, assume that the volume of B consumed is $V_1$. According to the law of equivalence, the number of g equivalents of B at the end point.

$\therefore$ $N_1V_1 = N_2V_2$, where $N_2$ is the conc. of A.

From this we can calculate the value of $N_2$.

## Illustrations

***Illustration 13.*** 0.4 M $KMnO_4$ solution completely reacts with 0.05 M $FeSO_4$ solution under acidic conditions. The volume of $FeSO_4$ used is 50 mL. What volume of $KMnO_4$ was used ?

***Solution*** $0.4 \times 5 \times V = 0.05 \times 50$

V = 1.25 mL

***Illustration 14.*** 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 weight of $Na_2CO_3$ in the mixture. If another 20 mL of this solution is treated with excess of $BaCl_2$ what will be the weight of the precipitate ?

***Solution*** Let, weight of $Na_2CO_3$ = x g

Weight of $K_2CO_3$ = y g

$\therefore$ x + y = 1.20 g ....(i)

For neutralization reaction of 100 mL

Meq. of $Na_2CO_3$ + Meq. of $K_2CO_3$ = Meq. of HCl

$\Rightarrow \frac{x}{106} \times 2 \times 1000 + \frac{y}{138} \times 2 \times 1000 = \frac{40 \times 0.1 \times 100}{20}$

$\therefore$ 69 x + 53 y = 73.14 .....(ii)

From Eqs. (i) and (ii), we get

x = 0.5962 g

y = 0.604 g

Solution of $Na_2CO_3$ and $K_2CO_3$ gives ppt. of $BaCO_3$ with $BaCl_2$

(Meq. of $Na_2CO_3$ + Meq. of $K_2CO_3$) in 20 mL = Meq. of $BaCO_3$

$\Rightarrow$ Meq. of HCl for 20 mL mixture = Meq. of $BaCO_3$

$\Rightarrow$ Meq. of $BaCO_3$ = 40 × 0.1 = 4

$$\frac{W_{BaCO_3}}{M_{BaCO_3}} \times 1000 = 40 \times 0.1 = 4$$

$$\frac{W_{BaCO_3}}{197} \times 2 \times 1000 = 4$$

$\therefore$ $W_{BaCO_3}$ = 0.394 g

## 8.2 Back titration

AL

Back titration is used to calculate % purity of a sample. Let us assume that we are given an impure solid substance C weighing w gram and we are asked to calculate the percentage of pure C in the sample. We will assume that the impurities are inert. We are provided with two solutions A and B, where the concentration of B is known ($N_1$) and that of A is not known. This type of titration will work only if the following condition is satisfied, i.e. the nature of compounds A, B and C should be such that A and B can react with each other. A and C can react with each other but the product of A and C should not react with B.

Now, we take a certain volume of A in a flask ( the g equivalents of A taken should be ≥ g equivalents of C in the sample and this can be done by taking A in excess). Now, we perform a simple titration using B. Let us assume that the volume of B used is $V_1$. In another beaker, we again take the solution of A in the same volume as taken earlier. Now, C is added to this and after the reaction is completed, the solution is being titrated with B. Let us assume that the volume of B used up is $V_2$. Gram equivalents of B used in the first titration = $N_1V_1$.

$\therefore$ gm. equivalents of A initially = $N_1V_1$

gm. equivalents of B used in the second titration = $N_1V_2$

$\therefore$ gm. equivalents of A left in excess after reacting with C = $N_1V_2$

gm. equivalents of A that reacted with C = $N_1V_1 - N_1V_2$

If the n-factor of C is x, then the moles of pure C = $\frac{N_1V_1 - N_1V_2}{x}$

$\therefore$ The weight of C = $\frac{N_1V_1 - N_1V_2}{x} \times$ Molecular weight of C

$\therefore$ Percentage of C = $\frac{N_1V_1 - N_1V_2}{x} \times \frac{\text{Molecular wt. of C}}{w} \times 100$

## Illustrations

***Illustration 15.*** 20 g of a sample of $Ba(OH)_2$ is dissolved in 10 mL of 0.5 N HCl solution : The excess of HCl was titrated with 0.2 N NaOH. The volume of NaOH used was 10 cc. Calculate the percentage of $Ba(OH)_2$ in the sample.

***Solution***

| | | |
|---|---|---|
| Milli eq. of HCl initially | = | 10 × 0.5 = 5 |
| Milli eq. of NaOH consumed | = | Milli eq. of HCl in excess = 10 × 0.2 = 2 |
| $\therefore$ Milli eq. of HCl consumed | = | Milli eq. of $Ba(OH)_2$ = 5 – 2 = 3 |
| $\therefore$ Eq. of $Ba(OH)_2$ | = | $3/1000 = 3 \times 10^{-3}$ |
| Mass of $Ba(OH)_2$ | = | $3 \times 10^{-3} \times (171/2) = 0.2565$ g |
| % $Ba(OH)_2$ | = | (0.2565 / 20) × 100 = 1.28 % |

## 8.3 Double titration

AL

The method involves two indicators (Indicators are substances that change their colour when a reaction is complete) phenolphthalein and methyl orange. This is a titration of specific compounds. Let us consider a solid mixture of NaOH, $Na_2CO_3$ and inert impurities weighing w g. You are asked to find out the % composition of mixture. You are also given a reagent that can react with the sample say, HCl along with its concentration ($M_1$)

We first dissolve the mixture in water to make a solution and then we add two indicators in it, namely, phenolphthalein and methyl orange, Now, we titrate this solution with HCl.

NaOH is a strong base while $Na_2CO_3$ is a weak base. So, it is safe to assume that NaOH reacts completely and only then $Na_2CO_3$ reacts.

$NaOH + HCl \rightarrow NaCl + H_2O$

Once NaOH has reacted, it is the turn of $Na_2CO_3$ to react. It reacts with HCl in two steps :

$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$ and then,

$NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$

As can be seen, when we go on adding more and more of HCl, the pH of the solution keeps on falling. When $Na_2CO_3$ is converted to $NaHCO_3$, completely, the solution is weakly basic due to presence of $NaHCO_3$ (which is a weaker base as compared to $Na_2CO_3$). At this instant phenolphthalein changes colour since it requires this weakly basic solution to change its colour. Therefore, remember that ***phenolphthalein changes colour only when the weakly basic $NaHCO_3$ is present.*** As we keep adding HCl, the pH again falls and when all the $NaHCO_3$ reacts to form NaCl, $CO_2$ and $H_2O$, the solution becomes weakly acidic due to the presence of the weak acid $H_2CO_3$ ($CO_2 + H_2O$). At this instance, methyl orange changes colour since it requires this weakly acidic solution to do so. Therefore, remember ***methyl orange changes colour only when $H_2CO_3$ is present.***

Now, let us assume that the volume of HCl used up for the first and the second reaction, i.e., $NaOH + HCl \rightarrow NaCl + H_2O$ and $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$ be $V_1$ (this is the volume of HCl from the begining of the titation up to the point when phenolphthalein changes colour).

Let, the volume of HCl required for the last reacton, i.e. $NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$ be $V_2$ (this is the volume of HCl from the point where phenolphthalein had changed colour up to the point when methyl orange changes colour). Then,

Moles of HCl used for reacting with $NaHCO_3$ = Moles of $NaHCO_3$ reacted = $M_1V_2$

Moles of $NaHCO_3$ produced by the $Na_2CO_3 = M_1V_2$

Moles of $Na_2CO_3$ that gave $M_1V_2$ moles of $NaHCO_3 = M_1V_2$

Mass of $Na_2CO_3 = M_1V_2 \times 106$

$$\% \, Na_2CO_3 = \frac{M_1V_2 \times 106}{w} \times 100$$

Moles of HCl used for the first two reactions = $M_1V_1$

Moles of $Na_2CO_3 = M_1V_2$

Moles of HCl used for reacting with $Na_2CO_3 = M_1V_2$

Moles of HCl used for reacting with only NaOH = $M_1V_1 - M_1V_2$

$\therefore$ Moles of NaOH = $M_1V_1 - M_1V_2$

Mass of NaOH = $(M_1V_1 - M_1V_2) \times 40$

$$\% \, NaOH = \frac{(M_1V_1 - M_1V_2) \times 40}{w} \times 100$$

***Note :*** *Working range of few indicators*

| ***Indicator*** | ***pH range*** | ***Behaving as*** |
|---|---|---|
| *Phenolphthalein* | *8 – 10* | *Weak organic acid* |
| *Methyl orange* | *3 – 4.4* | *Weak organic base* |

*Thus, methyl orange with lower pH range can indicate complete neutralization of all types of bases. Extent of reaction for different bases with acid (HCl) using these two indicators is summarized below :*

| | ***Phenolphthalein*** | ***Methyl orange*** |
|---|---|---|
| *NaOH* | *100% reaction is indicated*<br>$NaOH + HCl \longrightarrow NaCl + H_2O$ | *100% reaction is indicated*<br>$NaOH + HCl \longrightarrow NaCl + H_2O$ |
| $Na_2CO_3$ | *50% reaction upto $NaHCO_3$ stage is indicated*<br>$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$ | *100% reaction is indicated*<br>$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$ |
| $NaHCO_3$ | *No reaction is indicated* | *100% reaction is indicated*<br>$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$ |

## Illustrations

***Illustration 16.*** 0.4 g of a mixture of NaOH and $Na_2CO_3$ and inert impurities was first titrated with phenolphthalein and N/10 HCl, 17.5 mL of HCl was required at the end point. After this methyl orange was added and 1.5 mL of same HCl was again required for next end point. Find out percentage of NaOH and $Na_2CO_3$ in the mixture.

***Solution*** Let $W_1$ g NaOH and $W_2$ g $Na_2CO_3$ was present in mixture. At phenolphthalein end point,

$$\left(\frac{W_1}{40}+\frac{1}{2}\times\frac{W_2}{53}\right)=\frac{1}{10}\times 17.5\times 10^{-3} \quad ...(1)$$

At second end point following reaction takes place

$$\text{Eq. of } NaHCO_3 = \text{Eq. of HCl used (in second titration)} = \frac{1}{2}\text{Eq. of } Na_2CO_3$$

$$\frac{1}{2}\times\frac{W_2}{53} = 1.5\times\frac{1}{10}\times 10^{-3}$$

$$W_2 = 0.01590 \text{ g}$$

Putting the value of $W_2$ in Eq. (1) we get

$$W_1 = 0.064 \text{ g}$$

$$\text{Percentage of NaOH} = \frac{0.064}{0.4}\times 100 = 16\%$$

$$\text{Percentage of } Na_2CO_3 = \frac{0.01590}{0.4}\times 100 = 3.975\ \%$$

## 8.4 Standard redox titrations

AL

| *Estimation of* | *By titrating with* | *Reactions* | *Relation between O.A. and R.A.* |
|---|---|---|---|
| $Fe^{2+}$ | $MnO_4^-$ | $Fe^{2+} \longrightarrow Fe^{3+} + e^-$<br>$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ | $5Fe^{2+} \equiv MnO_4^-$<br>Eq. wt. $Fe^{2+}$ = M/1<br>Eq. wt. $MnO_4^-$ = M/5 |
| $Fe^{2+}$ | $Cr_2O_7^{2-}$ | $Fe^{2+} \longrightarrow Fe^{3+} + e^-$<br>$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ | $6Fe^{2+} \equiv Cr_2O_7^{2-}$<br>Eq. wt. $Cr_2O_7^{2-}$ = M/6 |
| $C_2O_4^{2-}$ | $MnO_4^-$ | $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$<br>$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$ | $5C_2O_4^{2-} \equiv 2MnO_4^-$<br>Eq. wt. $C_2O_4^{2-}$ = M/2<br>Eq. wt. $MnO_4^-$ = M/5 |
| $H_2O_2$ | $MnO_4^-$ | $H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$<br>$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ | $5H_2O_2 \equiv 2MnO_4^-$<br>Eq. wt. $H_2O_2$ = M/2<br>Eq. wt. $MnO_4^-$ = M/5 |
| $As_2O_3$<br>$AsO_3^{3-}$ | $MnO_4^-$<br>$BrO_3^-$ | $As_2O_3 + 5H_2O \rightarrow 2AsO_4^{3-} + 10H^+ + 4e^-$<br>$AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-$<br>$BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$ | Eq. wt. $As_2O_3$ = M/4<br>Eq. wt. $AsO_3^{3-}$ = M/2<br>Eq. wt. $BrO_3^-$ = M/6 |

## Illustrations

***Illustration 17.*** 3.2 g of pyrolusite was treated with 50 mL of 0.5 M oxalic acid and some sulphuric acid. The oxalic acid left undecomposed was raised to 250 mL in a flask. 25 mL of this solution when treated with 0.02 M $KMnO_4$ required 32 mL of the solution : Find the % of $MnO_2$ in the sample and also the percentage of available oxygen.

***Solution*** Redox changes are $C_2O_4^{2-} \longrightarrow 2CO_2$ (n-factor = 2)

$MnO_4^- \longrightarrow Mn^{2+}$ (n-factor = 5)

$MnO_2 \longrightarrow Mn^{2+}$ (n-factor = 2)

Meq. of $MnO_2$ = Meq. of oxalic acid taken - Meq. of oxalic acid left

$= 50 \times 0.5 \times 2 - 32 \times 0.02 \times 5 \times 10$ (in 250 mL) $= 18$

$$\frac{W_{MnO_2}}{M_{MnO_2}} \times 2 \times 1000 = 18 \Rightarrow \frac{W_{MnO_2}}{87} \times 2 \times 1000 = 18,$$

$$\therefore \quad W_{MnO_2} = 0.7821 \text{ g}$$

$$\therefore \quad \% \text{ of } MnO_2 = \frac{0.7821}{3.2} \times 100 = 24.44 \%$$

Meq. of $MnO_2$ = Meq. of $O_2$

$$\frac{W_{O_2}}{16} \times 2 \times 1000 = 18, \quad \therefore \quad W_{O_2} = 0.144 \text{ g}$$

$$\% \text{ of available } O_2 = \frac{0.144}{3.2} \times 100 = 4.5$$

***Illustration 18**** A 20 g sample of only CuS and $Cu_2S$ was treated with 100 mL of 1.25 M $K_2Cr_2O_7$. The products obtained were $Cr^{3+}$, $Cu^{2+}$ and $SO_2$. The excess oxidant was reacted with 50 mL of $Fe^{2+}$ Solution : 25 mL of the same $Fe^{2+}$ solution required 0.875 M $KMnO_4$ under acidic condition, the volume of $KMnO_4$ used was 20 mL. Find the % of CuS and $Cu_2S$ in the sample.

***Solution*** Equivalents of dichromate initially $= \dfrac{1.25 \times 6 \times 100}{1000}$

$= 0.75$

Equivalents of $Fe^{2+}$ in 25 mL $= \dfrac{0.875 \times 5 \times 5 \times 20}{1000}$

$= 0.0875$

Equivalents of $Fe^{2+}$ in 50 mL $= 0.0875 \times 2 = 0.175$

Equivalents of excess dichromate $= 0.175$

$\therefore$ Equivalents of dichromate consumed by (CuS and $Cu_2S$) $= 0.75 - 0.175 = 0.575$

If x g is the mass of CuS, the mass of $Cu_2S$ is (10 – x) g

$$\frac{x}{95.5} \times 6 + \frac{(10-x)}{159} \times 8 = 0.575 \quad \therefore \quad x = 5.74 \text{ g}$$

$$\% \text{ CuS} = \frac{5.74}{20} \times 100 = 28.7 \%$$

$$\% \text{ } Cu_2S = 71.3 \%$$

***Illustration 19****. A 2.18 g sample contains a mixture of XO and $X_2O_3$. It reacts with 0.015 moles of $K_2Cr_2O_7$ to oxidize the sample completely to form $XO_4^-$ and $Cr^{3+}$. If 0.0187 mole of $XO_4^-$ is formed, what is the atomic mass of X?

***Solution*** $XO + K_2Cr_2O_7 \longrightarrow Cr^{3+} + XO_4^-$

$X_2O_3 + K_2Cr_2O_7 \longrightarrow Cr^{3+} + XO_4^-$

Let, wt. of XO in the mixture be x g

Equivalent of $K_2Cr_2O_7$ consumed by the mixture $= 0.015 \times 6$

$$\text{Equivalents of XO} = \frac{x}{x+16} \times 5$$

$$\text{Equivalents of } X_2O_3 = \frac{2.18 - x}{2x+48} \times 8$$

$$\therefore \quad \frac{x}{x+16} \times 5 + \frac{2.18 - x}{2x - 148} \times 8 = 0.015 \times 6$$

Since 1 mole of XO gives 1 mole $XO_4^-$ and 1 mole of $X_2O_3$ gives 2 moles of $XO_4^-$;

$$\therefore \quad \frac{x}{x+16} + \frac{2x(2.18 - x)}{2x+48} = 0.0187$$

On solving, x = 99

## 8.5 Iodometric and Iodimetric Titration

AL

The reduction of free iodine to iodide ions and oxidation of iodide ions to free iodine occurs in these titrations.

$I_2 + 2e^- \longrightarrow 2I^-$ (reduction)

$2I^- \longrightarrow I_2 + 2e^-$ (oxidation)

These are divided into two types :

***(a) Iodometic Titration :***

In iodometric titrations, an oxidizing agent is allowed to react in neutral medium or in acidic medium with excess of potassium iodide to liberate free iodine.

KI + oxidizing agent $\longrightarrow I_2$

Free iodine is titrated against a standard reducing agent usually with sodium thiosulphate. Halogen, dichromates, cupric ion, peroxides etc., can be estimated by this method.

$I_2 + 2NaS_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$

$K_4Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O + 3I_2$

***(b) Iodimetric Titration :***

These are the titrations in which free iodine is used as it is difficult to prepare the solution of iodine (volatile and less soluble in water), it is dissolved in KI solution :

$KI + I_2 \longrightarrow KI_3$ (Potassium triiodide)

This solution is first standardized before using with the standard solution of substance such as sulphite, thiosulphate, arsenite etc, are estimated.

In iodimetric and iodometric titration, starch solution is used as an indicator. Starch solution gives blue or violet colour with free iodine. At the end point, the blue or violet colour disappears when iodine is completely changed to iodide.

- ***SOME IODOMETRIC TITRATIONS (TITRATING SOLUTIONS IS $Na_2S_2O_3.5H_2O$)***

| ***Estimation of*** | ***Reaction*** | ***Relation between O.A. and R.A.*** |
|---|---|---|
| $I_2$ | $I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$<br>or<br>$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$ | $I_2 = 2I \equiv 2Na_2S_2O_3$<br>Eq. wt. of $Na_2S_2O_3$ = M/1 |
| $CuSO_4$ | $2CuSO_4 + 4KI \longrightarrow 2Cu_2I_2 + 2K_2SO_4 + I_2$<br>$Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$<br>(White ppt.)<br>$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$ | $2CuSO_4 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$<br>Eq. wt. of $CuSO_4$ = M/1 |
| $CaOCl_2$ | $Cl_2 + 2KI \longrightarrow 2KCl + I_2$<br>$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$<br>$MnO_2 + 4HCl\,(conc) \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$<br>$Cl_2 + 2KI \longrightarrow 2KCl + I_2$ | $CaOCl_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$<br>Eq. wt. of $CaOCl_2$ = M/2 |
| $MnO_2$<br>$2Na_2S_2O_3$ | or<br>$MnO_2 + 4H^+ + 2Cl^- \longrightarrow Mn^{2+} + 2H_2O + Cl_2$<br>$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$ | $MnO_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv$<br>Eq. wt. of $MnO_2$ = M/2 |
| $IO_3^-$ | $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$ | $IO_3^- \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$<br>Eq. wt. of $IO_3^-$ = M/6 |
| $H_2O_2$ | $H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$ | $H_2O_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$<br>Eq. wt. of $H_2O_2$ = M/2 |
| $Cl_2$ | $Cl_2 + 2I^- \longrightarrow 2CI^- + I_2$ | $Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$<br>Eq. wt. of $Cl_2$ = M/2 |
| $O_3$ | $O_3 + 6I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$ | $O_3 \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$<br>Eq. wt. of $O_3$ = M/6 |
| $Cr_2O_7^{2-}$ | $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$ | $Cr_2O_7^{2-} \equiv 3I_2 \equiv 6I$<br>Eq. wt. of $Cr_2O_7^{2-}$ |
| $MnO_4^-$ | $2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2MnO_4^- + 5I_2 + 8H_2O$ | $2MnO_4^- \equiv 5I_2 \equiv 10I$<br>Eq. wt. of $MnO_4^-$ = M/5 |
| $BrO_3^-$ | $BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3I_2 + 3H_2O$ | $BrO_3^- \equiv 3I_2 \equiv I_2$<br>Eq. wt. of $BrO_3^-$ = M/6 |
| As(V) | $H_3AsO_4 + 2I^- + 2H^+ \longrightarrow H_3AsO_3 + H_2O + I_2$ | $H_3AsO_4 \equiv I_2 \equiv 2I$<br>Eq. wt. of $H_3AsO_4$ = M/2 |

- ***SOME IODIMETRIC TITRATION (TITRATING SOLUTIONS IS $I_2$ IN KI)***

| *Estimation of* | *Reaction* | *Relation between O.A. and R.A.* |
|---|---|---|
| $H_2S$ (in acidic medium) | $H_2S + I_2 \longrightarrow S + 2I^- + 2H^+$ | $H_2S \equiv I_2 \equiv 2I$<br>Eq. wt. of $H_2S$ = M/2 |
| $SO_3^{2-}$ (in acidic medium) | $SO_3^{2-} + I_2 + H_2O \longrightarrow SO_3^{2-} + 2I^- + 2H^+$ | $SO_3^{2-} \equiv I_2 \equiv 2I$<br>Eq. wt. of $SO_3^{2-}$ = M/2 |
| $Sn^{2+}$ (in acidic medium) | $Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$ | $Sn^{2+} \equiv I_2 \equiv 2I$<br>Eq. wt. of $Sn^{2+}$ = M/2 |
| As(III) (at pH = 8) | $H_2AsO_3^- + I_2 + H_2O \longrightarrow HAsO_4^{2-} + 2I^- + 2H^+$ | $H_2AsO_3^- \equiv I_2 \equiv 2I$<br>Eq. wt. of $H_2AsO_3^-$ = M/2 |
| $N_2H_4$ | $N_2H_4 + 2I_2 \longrightarrow N_2 + 4H^+ + 4I^-$ | $N_2H_4 \equiv 2I_2 \equiv 4I$<br>Eq. wt. of $N_2H_4$ = M/4 |

## Illustrations

***Illustration 20*** 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 30 mL of M/10 $Na_2S_2O_3$ solution for titration. What is the weight percent of ozone in the mixture ?

Ultraviolet radiation of wavelength 300 mm 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?

***Solution*** $O_3 + 2\,KI + H_2O \rightarrow 2KOH + I_2 + O_2$

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

Millimoles of $O_3$ = Millimoles of $I_2$ = ½ Millimoles of $Na_2S_2O_3$

= ½ 30 × 1/10 = 1.5 millimoles = 0.0015 moles

Total moles of $O_3$ and $O_2$ in the mixture

PV = n RT

$1 \times 1 = n \times 0.0821 \times 273$

$\therefore$ n = 0.044

Moles of $O_2$ = 0.044 – 0.0015 = 0.0425

$W_{O_2} = 0.0425 \times 32$ g = 1.36 g

$W_{O_3} = 0.0015 \times 48$ g = 0.072 g

$\therefore$ % of $O_3 = \dfrac{0.072}{1.432} \times 100 = 5.028$ %

No. of photons required for decomposition of Ozone molecules

$= 0.0015 \times 6.023 \times 10^{23} = 0.90 \times 10^{21}$

***Illustration 21*** An aqueous solution containing 0.10 g $KIO_3$ (formula wt. = 214.0) was treated with an excess of KI Solution : The solution was acidified with HCl. The liberated $I_2$ consumed 55 mL of thiosulphate solution to decolourize the blue starch-iodine complex. Calculate molarity of the sodium thiosulphate solution :

***Solution*** Moles of $KIO_3 = \dfrac{0.1}{214} = 0.00047$

$\therefore$ Moles of $I_2$ liberated from $KIO_3 = \dfrac{0.00047}{2} = 0.000235$

Moles of KI reacting = 0.00047 × 5 = 0.00235($\because$ n-factor for $KIO_3$ and KI are 5 and 1 respectively)

Moles of $I_2$ produced from KI = $\frac{0.00235}{2}$ = 0.001175

Total moles of $I_2$ produced and reacted = 0.000235 + 0.001175 = 0.00141 equivalents of $I_2$ reacted = 0.00141 × 2 = 0.00282 = equivalents of thiosulphate Solution :

Molarity = $\frac{0.00282 \times 1000}{55}$ =0.0512 M (For thiosulphate n-factor = 1)

## BEGINNER'S BOX–3

### *Titration*

**1.** Which of the following relations is incorrect :-
(A) 3 N $Al_2(SO_4)_3$ = 0.5 M $Al_2(SO_4)_3$
(B) 3 M $H_2SO_4$ = 6 N $H_2SO_4$
(C) 1 M $H_3PO_4$ = 1/3 N $H_3PO_4$
(D) 1 M $Al_2(SO_4)_3$ = 6 N $Al_2(SO_4)_3$

**2.** A certain weight of pure $CaCO_3$ is made to react completely with 200 mL of an HCl solution to give 224 mL of $CO_2$ gas at STP. The normality of the HCl is :-
(A) 0.05 N (B) 0.1 N (C) 1.0 N (D) 0.2 N

**3.** The volume of 1.5 M$H_3PO_4$ solution required to neutralize exactly 90 mL of a 0.5 M Ba $(OH)_2$ solution is :-
(A) 10 mL (B) 30 mL (C) 20 mL (D) 60 mL

**4.** Volume $V_1$ mL of 0.1 M$K_2Cr_2O_7$ is needed for complete oxidation of 0.678 g $N_2H_4$ in acidic medium. The volume of 0.3 M $KMnO_4$ needed for same oxidation in acidic medium will be :-
(A) $\frac{2}{5}V_1$ (B) $\frac{5}{2}V_1$ (C) 113 $V_1$ (D) can't say

**5.** Given that 50.0 mL of 0.01 M $Na_2S_2O_3$ solution and $5 \times 10^{-4}$ mole of $Cl_2$ react according to equation,

$$Cl_2\,(g) + S_2O_3^{2-} \longrightarrow SO_4^{2-} + Cl^- + S$$

Answer the following :
(i) The balanced molecular equation is :
(A) $Cl_2 + H_2O + Na_2S_2O_3 \longrightarrow Na_2SO_4 + S + 2HCl$
(B) $Cl_2 + Na_2S_2O_3 \longrightarrow 2NaCl + Na_2SO_4$
(C) $Cl_2 + S_2O_3^{2-} \longrightarrow SO_4^{2-} + S + Cl^-$
(D) none of these

(ii) How many moles of $S_2O_3^{2-}$ are in the above sample :-
(A) 0.00050 (B) 0.0025 (C) 0.01 (D) 0.02

(iii) How many equivalents of oxidising agents are in this sample for the above reaction :-
(A) 0.001 (B) 0.080 (C) 0.020 (D) 0.010

(iv) What is the molarity of $Na_2SO_4$ in this solution :-
(A) 0.080 M (B) 0.040 M (C) 0.020 M (D) 0.010 M

**6.** 0.3 g of an oxalate salt was dissolved in 100 mL solution. The solution required 90 mL of N/20 $KMnO_4$ for complete oxidation. The % of oxalate ion in salt is :-
(A) 33% (B) 66% (C) 70% (D) 40%

**7.** How many millilitres of 0.1N $H_2SO_4$ solution will be required for complete reaction with a solution containing 0.125 g of pure $Na_2CO_3$ ?
(A) 23.6 ml (B) 25.6 ml (C) 26.3 ml (D) 32.6 ml

**8.** The mass of oxalic acid crystals ($H_2C_2O_4 \cdot 2H_2O$) required to prepare 50 ml of a 0.2 N solution is:
(A) 4.5 g (B) 6.3 g (C) 0.63 g (D) 0.45 g

**9.** Which of the following solutions will exactly oxidize 25 ml of an acid solution of 0.1 M iron (II) oxalate?
(A) 25 ml of 0.1 M $KMnO_4$
(B) 25 ml of 0.2 M $KMnO_4$
(C) 25 ml of 0.6 M $KMnO_4$
(D) 15 ml of 0.1 M $KMnO_4$

## 9.0 HYDROGEN PEROXIDE ($H_2O_2$)

AL

$H_2O_2$ can behave both like oxidising and reducing agents in both the medium (acidic and basic).

***Oxidising agent : ($H_2O_2$)***

***(a) Acidic medium :***

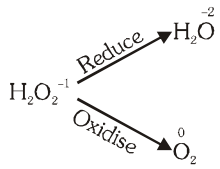
$$2e^- + 2H^+ + H_2O_2 \xrightarrow{\frac{3}{4}(R)} 2H_2O$$

v.f. = 2

***(b) Basic medium :***

$$2e^- + H_2O_2 \longrightarrow 2OH^-$$

v.f. = 2




***Reducing agent : ($H_2O_2$) :***

***(a) Acidic medium :***

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$

v.f. = 2

***(b) Basic medium :***

$$2OH^- + H_2O_2 \longrightarrow O_2 + 2H_2O + 2e^-$$

v.f. = 2

***Note :*** *Valency factor of $H_2O_2$ is always equal to 2.*

### 9.1 Volume strength of $H_2O_2$

Strength of $H_2O_2$ is represented as 10 V, 20 V, 30 V etc.

***20V $H_2O_2$*** means ***one litre*** of this sample of $H_2O_2$ on decomposition gives ***20 L of $O_2$*** gas at ***S.T.P.***

$$\text{Normality of } H_2O_2 \text{ (N)} = \frac{\text{Volume, strength of } H_2O_2}{5.6}$$

$$\because \quad M_{H_2O_2} = \frac{N_{H_2O_2}}{\text{v.f}} = \frac{N_{H_2O_2}}{2}$$

$$\text{Molarity of } H_2O_2 \text{ (M)} = \frac{\text{Volume, strength of } H_2O_2}{11.2}$$

***Strength (in g/L)*** : Denoted by S

Strength = molarity × mol. wt. = molarity × 34

Strength = Normality × Eq. weight. = Normality × 17

## Illustrations

***Illustration 22.*** 20 mL of $H_2O_2$ after acidification with dil $H_2SO_4$ required 30 mL of $\frac{N}{12}$ $KMnO_4$ for complete oxidation. The strength of $H_2O_2$ solution is [Molar mass of $H_2O_2$ = 34]

***Solution***

$$30 \times \frac{1}{12} = 20 \times N'$$

$$N' = \frac{30}{12 \times 20} = \frac{1}{8}$$

$$\therefore \quad \text{strength} = N' \times \text{equivalent mass} = \frac{1}{8} \times 17 = 2.12 \text{ g/L}$$

## 10.0 HARDNESS OF WATER

SL AL

Temporary hardness - due to bicarbonates of Ca & Mg

Permanent hardness - due to chloride & sulphates of Ca & Mg. There are some method by which we can softening the water

(a) by boiling : $2HCO_3^- \rightarrow H_2O + CO_2 + CO_3^{2-}$ ***or***

by slaked lime : $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O$

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$

(b) By Washing Soda : $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$

(c) By ion exchange resins : $Na_2R + Ca^{2+} \rightarrow CaR + 2Na^+$

***Parts per million (ppm):***

When the solute is present in very less amount then this concentration term is used. It is defined as the number of parts of the solute present in every 1 million parts of the solution. ppm can both be in terms of mass or in terms of moles. If nothing has been specified we take ppm to be in terms of mass. hence a 100 ppm solution means that 100 g of solute are present in every 1000000 g of solution.

$$ppm_A = \frac{\text{mass of A}}{\text{Total mass}} \times 10^6 = \text{mass fraction} \times 10^6$$

***Measurement of Hardness***

Hardness is measured in terms of ppm (parts per million) of $CaCO_3$ or equivalent to it.

## Illustrations

***Illustration 23.*** 0.00012% $MgSO_4$ and 0.000111% $CaCl_2$ is present in water. What is the measured hardness of water and millimoles of washing soda requires to purify 1000 litre water.

***Solution*** 0.00012% $MgSO_4$ = 1 mg $CaCO_3$ 1 L water

0.000111% $CaCl_2$ = 1 mg $CaCO_3$ 1 L water

hardness = 2 ppm and mm of $Na_2CO_3$ require is 20

## 11.0 STRENGTH OF OLEUM

SL AL

Oleum is $SO_3$ dissolved in 100% $H_2SO_4$. Sometimes, oleum is reported as more than 100% by weight, say y% (where y > 100). This means that (y – 100) grams of water, when added to 100 g of given oleum sample, will combine with all the free $SO_3$ in the oleum to give 100% sulphuric acid. Hence weight % of free $SO_3$ in oleum = 80(y – 100)/18

## 12.0 CALCULATION OF AVAILABLE CHLORINE FROM A SAMPLE OF BLEACHING POWDER

SL AL

The weight % of available $Cl_2$ from the given sample of bleaching powder on reaction with dil acids or $CO_2$ is called available chlorine.

$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$

$CaOCl_2 + 2HCl \rightarrow CaCl_2 + H_2O + Cl_2$

$CaOCl_2 + 2H_3CCOOH \rightarrow Ca(CH_3COO)_2 + H_2O + Cl_2$

$CaOCl_2 + CO_2 \rightarrow CaCO_3 + Cl_2$

- **Method of determination**

$$\text{Bleaching powder} + CH_3COOH + KI \xrightarrow{\text{or } KI_3} KI_3 \xrightarrow{\text{starch}} \text{Hypo end point (Blue} \rightarrow \text{colourless)}$$

$$\% \text{ of } Cl_2 = \frac{3.55 \times x \times V(mL)}{W(g)}$$

where x = molarity of hypo solution, v = mL of hypo solution used in titration.

## Illustrations

***Illustration 24.*** 3.55 g sample of bleaching powder suspended in $H_2O$ was treated with enough acetic acid and KI solution. Iodine thus liberated requires 80 mL of 0.2 M hypo for titration. Calculate the % of available chlorine. [Available Chlorine = mass of chlorine liberated / mass of bleaching powder × 100]

***Solution*** moles of iodine = moles of chlorine

$$= \frac{80 \times 0.2}{2} \times 10^{-3} = 8 \times 10^{-3}$$

$$\text{so required } \% = \frac{8 \times 71 \times 10^{-3}}{3.55} \times 100\% = 16\%$$

## BEGINNER'S BOX–4

### *$H_2O_2$,Oleum and Hardness of Water*

***1.*** A bottle labelled with "12 V $H_2O_2$" contain 700 mL solution. If a student mix 300 mL water in it what is the g/litre strength & normality and volume strength of final solution.

***2.*** 100 kg hard water contains 5 g $MgSO_4$. Find hardness.

***3.*** A solution of a 0.4 g sample of $H_2O_2$ reacted with 0.632 g of $KMnO_4$ in the presence of sulphuric acid. Calculate the percentage purity of the sample of $H_2O_2$.

***4*.*** 5 litre of a solution of $H_2O_2$ with x N strength is diluted to 5.5 litre. This 5.5 litre $H_2O_2$ solution gives 28 litre $O_2$ at NTP. Find the value of x.

***5.*** The volume strength of 1.5 N $H_2O_2$ solution is :

(A) 4.8 V (B) 8.4 V (C) 3 V (D) 8 V

***6*.*** Find the volume strength of $H_2O_2$ solution prepared by mixing of 250 ml of 3N $H_2O_2$ & 750 ml of 1N $H_2O_2$ solution :

(A) 1.5 V (B) 8.4 V (C) 5.6 V (D) 11.2 V

***7.*** Temporary hardness is due to bicarbonates of $Mg^{2+}$ and $Ca^{2+}$. It is removed by addition of CaO as follows:

$$Ca(HCO_3)_2 + CaO \longrightarrow 2CaCO_3 + H_2O$$

Mass of CaO required to precipitate 2 g $CaCO_3$ is :

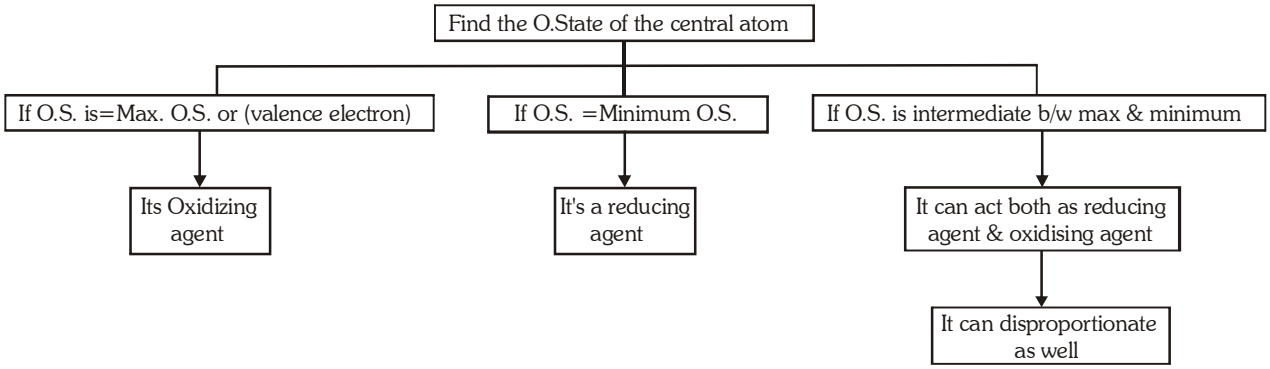
(A) 2 g (B) 0.56 g (C) 0.28 g (D) 1.12 g

***8*.*** 1 g of oleum sample is diluted with water. The solution required 54 mL of 0.4 N NaOH for complete neutralization. The % of free $SO_3$ in the sample is :

(A) 74 (B) 26 (C) 20 (D) none of these

## GOLDEN KEY POINTS

- ***How to Identify whether a Particular substance is an oxidising or reducing agent :***




- ***MOLARITY V/S NORMALITY***

| | ***Molarity (M)*** | | ***Normality (N)*** |
|---|---|---|---|
| ***1.*** | No. of moles of solute present in one litre of solution. | ***1.*** | No. of equivalents of solute present in one litre of solution. |
| ***2.*** | No. of moles $= \frac{W}{M}$ | ***2.*** | No. of equivalents $= \frac{W}{E}$ |
| ***3.*** | $\frac{W}{M} \times 1000$ = No. of millimoles | ***3.*** | $\frac{W}{E} \times 1000$ = No. of milliequivalance |
| ***4.*** | Molarity $\times$ V(in mL)=No. of millimoles | ***4.*** | Normality $\times$ V(in mL) = No. of milliequivalance |
| ***5.*** | Molarity $= \frac{\text{milli moles}}{\text{Volume of solution in mL}}$ | ***5.*** | Normality $= \frac{\text{milli equivalents}}{\text{Volume of solution in mL}}$ |

- Number of moles of molecules $= \frac{\text{wt. in g}}{\text{Mol. wt.}}$

  Number of moles of atoms $= \frac{\text{wt. in g}}{\text{Atomic mass}}$

  Number of moles of gases $= \frac{\text{Volume at STP}}{\text{Standard molar volume}}$

  Number of moles of particles, e.g. atoms, molecular ions etc. $= \frac{\text{Number of particles}}{\text{Avogadro No.}}$

  Moles of solute in solution = M $\times$ V(L)

- Equivalent wt. of element $= \frac{\text{Atomic wt.}}{\text{Valence}}$

  Equivalent wt. of compound $= \frac{\text{Mol. wt.}}{\text{Total charge on cation or anion}}$

  Equivalent wt. of acid $= \frac{\text{Mol wt.}}{\text{Basicity}}$

$$\text{Equivalent wt. of base} = \frac{\text{Mol wt.}}{\text{Acidity}}$$

$$\text{Equivalent wt. of an ion} = \frac{\text{Formula wt.}}{\text{Charge on ion}}$$

$$\text{Equivalent wt. of acid salt} = \frac{\text{Molecular wt.}}{\text{Replaceable H atom in acid salt}}$$

$$\text{Equivalent wt. of oxidizing or reducing agent} = \frac{\text{Mol. wt.}}{\text{Change in oxidation number per mole}}$$

$$\text{No. of equivalent} = N \times V(L) = \frac{\text{wt. in g}}{\text{Eq. wt.}}$$

- $$\text{Molarity (M)} = \frac{W_s \times 1000}{M_s \times V} = \frac{x \times d \times 10}{M_s}$$

where

$W_s$ = wt. of solute in g
$M_s$ = Mol. wt. of solute
x = % by mass of solute
d = density of solution in g/ml
V = volume of solution in ml

- $$\text{Normality (N)} = \frac{W_s \times 1000}{E_s \times V} = \frac{x \times d \times 1000}{E_s}$$

$W_s$ = wt. of solute in g.
$E_s$ = eqv. wt. of solute
V = volume of solution in ml
x = % by mass of solute
d = density of solution in g/ml

- $$\text{Moles} = M \times V(L) = \frac{\text{wt. of solute}}{\text{Mol.wt.}}$$

$$\text{Millimoles} = M \times V(ml) = \frac{\text{wt. of solute}}{\text{Mol.wt.}} \times 1000$$

$$\text{Equivalents of solute} = N \times V(L)$$

$$\text{Meq. of solute } \frac{\text{wt.}}{\text{Eq.wt.}} \times 1000$$

- ***Molarity equation :***

If a solution having molarity $M_1$ and volume $V_1$ is diluted to volume $V_2$ so that new molarity is $M_2$ then total number of moles remains the same.

$$M_1V_1 = M_2V_2$$

For a balanced equation involving $n_1$ moles of reactant 1 and $n_2$ moles of reactant 2.

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

Normality equation : According to the law of equivalence, the substances combine together in the ratio of their

equivalent masses $\frac{\text{wt. of A}}{\text{wt. of B}} = \frac{\text{Eq. wt. of A}}{\text{Eq. wt. of B}}$

$\Rightarrow \quad \frac{\text{wt. of A}}{\text{Eq. wt. of A}} = \frac{\text{wt. of B}}{\text{Eq. wt. of B}}$

Number of gram equivalents of A = Number of gram equivalents of B

Number of gram equivalents of A = $\frac{N_A \times V_A}{1000}$

Number of gram equivalents of B = $\frac{N_B V_B}{1000}$

$\Rightarrow \quad \frac{N_A V_A}{1000} = \frac{N_B V_B}{1000}$

$\Rightarrow \quad N_A \times V_B = N_B \times V_B$

The above equation is called normality equation.

- Normality (N) = Molarity (M) × n
  (where n = n-factor)
  For acid-base (neutralization reaction or redox reaction)
  $N_1V_1 = N_2V_2$ always true
  But $M_1V_1 = M_2V_2$ (may or may not be true )
  But $M_1n_1V_1 = M_2n_2V_2$ (always true where n-terms represent n-factor)

- Molality (m) = $\frac{\text{Moles of solute}}{\text{wt. of solvent (in kg)}}$

- Strength of solution (S) = N × Eq.wt.
  = M × mol. wt.

# SOME WORKED OUT ILLUSTRATIONS

***Illustration 1.***

What volume of 0.40 M $H_2SO_4$ is required to produce 34.0 g of $H_2S$ by the reaction,

$8\ KI + 5\ H_2SO_4 \rightarrow 4\ K_2SO_4 + 4\ I_2 + H_2S + 4\ H_2O$?

***Solution***

1 mole of $H_2S \equiv 5$ moles of $H_2SO_4$

34 g of $H_2S \equiv 5$ moles of $H_2SO_4$

$0.40 \times V_{H_2SO_4} = 5$

$$\therefore\ V_{H_2SO_4} = \frac{5}{0.40} = 12.5 \text{ litre}$$

***Illustration 2.***

To 50 L of 0.2 N NaOH, 2.5 L of 2N HCl and 15 L of 0.1 N $FeCl_3$ solutions are added. What weight of $Fe_2O_3$ can be obtained from the precipitate? Also report the normality of NaOH left in resultant solution :

***Solution***

Eq. of NaOH = 50 × 0.2 = 10

Eq. of HCl = 2.5 × 2 = 5

Eq. of NaOH left after reaction with HCl = 10 – 5 = 5

$FeCl_3 + NaOH \rightarrow Fe(OH)_3\downarrow \xrightarrow{\Delta} Fe_2O_3$

$FeCl_3$ reacts with NaOH to give $Fe(OH)_3$ which on ignition gives $Fe_2O_3$

∴ Eq. of NaOH used for $FeCl_3$ = Eq. of $Fe(OH)_3$

= Eq. of $Fe_2O_3$

= 15 × 0.1 = 1.5

∴ Eq. of NaOH left finally = 5 – 1.5 = 3.5

$$\text{Normality of NaOH in the resultant solution} = \frac{3.5}{67.5} = 0.051$$

$$\frac{W_{Fe_2O_3}}{M_{Fe_2O_3}} \times 6 = 1.5 \text{ (n-factor for } Fe_2O_3 = 6)$$

$$W_{Fe_2O_3} = \frac{1.5 \times 160}{6} = 40g$$

***Illustration 3*.***

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 30 mL of M/10 $Na_2S_2O_3$ solution for titration. What is the weight percent of ozone in the mixture ?

Ultraviolet radiation of wavelength 300 mm 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?

***Solution***

$O_3 + 2\ KI + H_2O \rightarrow 2KOH + I_2 + O_2$

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

Millimoles of $O_3$ = Millimoles of $I_2$ = ½ × Millimoles of $Na_2S_2O_3$

= ½ × 30 × 1/10 = 1.5 millimoles

= 0.0015 moles

Total moles of $O_3$ and $O_2$ in the mixture

PV = n RT

1 × 1 = n × 0.0821 × 273

∴ n = 0.044

Moles of $O_2$ = 0.044 – 0.0015 = 0.0425

$W_{O_2}$ = 0.0425 × 32 g = 1.36 g

$W_{O_3} = 0.0015 \times 48\ g = 0.072\ g$

$\therefore \quad \%\ of\ O_3 = \frac{0.072}{1.432} \times 100 = 5.028\ \%$

No. of photons required for decomposition of Ozone molecules $= 0.0015 \times 6.023 \times 10^{23} = 0.90 \times 10^{21}$

***Illustration 4.***

2.249 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 N.T.P. From this solution, $BaCrO_4$ was precipitated filtered and washed. The precipitate was dissolved in dil. $H_2SO_4$ 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 the percentage of CaO in the sample.

***Solution***

Let, weight of $BaCO_3$, $CaCO_3$ and CaO are x,y and z respectively.

$\therefore x + y + z = 2.249$

$BaCO_3 \longrightarrow BaCrO_4$

Redox change $\quad Cr^{6+} + 3e^- \longrightarrow Cr^{3+}$

$2I^- \longrightarrow I_2 + 2e^-$

Meq. of $BaCO_3$ = Meq. of $BaCrO_4$ = Meq. of $I_2$

$\therefore \quad \frac{x}{197/3} \times 1000 = 20 \times 0.05 \times \frac{100}{10}$

$\therefore \quad x = 0.657\ g \qquad ....(1)$

The equivalent weight of $BaCrO_4$ is M/3, therefore for $BaCO_3$, it should be M/3 also because mole ratio of $BaCO_3$ and $BaCrO_4$ is 1 : 1.

Applying POAC for C atom,

Moles of C in $BaCO_3$ + Moles of C in $CaCO_3$ = Moles of C in $CO_2$

$\therefore \quad \frac{x}{197} + \frac{y}{100} = \frac{168}{22400}$

$\Rightarrow \quad 200\,x + 294\,y = 295.5 \qquad ....(2)$

From equation (1) and (2)

$y = 0.416\ g$

$\therefore \quad 0.657 + 0.416 + z = 2.249$

$z = 1.176$

$\%\ of\ CaO = \frac{1.176}{2.249} = 52.29\ \%$

***Illustration 5.***

For estimating ozone in the air, a certain volume of air is passed through an alkaline KI solution when $O_2$ is evolved and iodide is oxidized to 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 L of air at 1 atm and 27°C were passed through an alkaline KI solution, and at the end, the iodine was entrapped in a solution which on titration as above required 1.5 mL of 0.02 N $Na_2S_2O_3$ solution. Calculate volume percentage of ozone in the sample.

***Solution***

The chemical reaction is, $H_2O + KI + O_3 \longrightarrow I_2 + O_2 + KOH$

Milliequivalents of iodine = Milliequivalents of KI = Milliequivalents of $O_3$ reacted

Milliequivalents of $Na_2S_2O_3 = 1.5 \times 0.02 = 3 \times 10^{-2}$

Millimoles of iodine $= \frac{3 \times 10^{-2}}{2} = 1.5 \times 10^{-2}$ [$\because$ n-factor for iodine = 2]

Millimoles of ozone $= 1.5 \times 10^{-2}$

Volume of ozone $= \frac{nRT}{P} = \frac{1.5 \times 10^{-5} \times 0.0821 \times 300}{1} = 36.945 \times 10^{-5}$ litre

Volume percent of ozone $= \frac{36.945 \times 10^{-5}}{10} \times 100 = 3.6945 \times 10^{-3}$

***Illustration 6.***

An aqueous solution containing 0.10 g $KIO_3$ (formula wt. = 214.0) was treated with an excess of KI Solution : The solution was acidified with HCl. The liberated $I_2$ consumed 55 mL of thiosulphate solution to decolourize the blue starch-iodine complex. Calculate molarity of the sodium thiosulphate solution :

***Solution***

Moles of $KIO_3 = \frac{0.1}{214} = 0.00047$

$\therefore$ Moles of $I_2$ liberated from $KIO_3 = \frac{0.00047}{2} = 0.000235$

Moles of KI reacting = 0.00047 × 5 = 0.00235 ($\because$ n-factor for $KIO_3$ and KI are 5 and 1 respectively)

Moles of $I_2$ produced from KI $= \frac{0.00235}{2} = 0.001175$

Total moles of $I_2$ produced and reacted = 0.000235 + 0.001175 = 0.00141 equivalents of $I_2$ reacted = 0.00141 × 2 = 0.00282 = equivalents of thiosulphate Solution :

Molarity $= \frac{0.00282 \times 1000}{55}$ =0.0512 M (For thiosulphate n-factor = 1)

***Illustration 7.***

Mg can reduce $NO_3^-$ to $NH_3$ in basic medium.

$NO_3^- + Mg\,(s) + H_2O \rightarrow Mg\,(OH)_2\,(s) + OH^-\,(aq.) + NH_3(g)$

A 25.0 mL sample of $NO_3^-$ solution was treated with Mg. The $NH_3$ (g) was passed into 100 mL of 0.15 N HCl. The excess of HCl required 32.10 mL of 0.10 N NaOH for neutralization. What was the molarity of $NO_3^-$ ions in the original sample ?

***Solution***

Meq. of $NH_3$ formed = Meq. of HCl used

= 100 × 0.15 – 32.10 × 0.10

= 11.79

Here, n-factor of $NH_3$ is 1 (acid - base reaction)

For redox change,

$\overset{+5}{N}O_3^- \xrightarrow{+8e^-} \overset{-3}{N}H_3$ (n - factor = 8)

$\therefore$ Meq. of $NH_3$ for n-factor 8 = 8 × 11.79

$\therefore$ Normality of $NO_3^- = \frac{94.32}{25} = 3.77$

Molarity of $NO_3^- = \frac{3.77}{8} = 0.47125$

***Illustration 8.***

30 mL of a solution containing 9.15 g/litre of an oxalate $K_xH_y\,(C_2O_4)_z.nH_2O$ are required for titrating 27 mL of 0.12 N NaOH and 36 mL of 0.12 N $KMnO_4$ separately. Calculate x,y,z and n. Assume all H atoms (except $H_2O$) are replaceable and x,y,z are in the simple ratio of g atoms.

***Solution.***

Let molecular weight of oxalate salt is M

(i) n - factor in acid - base reaction = 2

(ii) n - factor in redox titration = 2 × z

$(C_2O_4^{2-} \longrightarrow 2CO_2 + 2e)$

$\therefore$ Meq. of acid in 30 mL = Meq. of NaOH used

$30 \times \frac{9.15}{M} \times y = 27 \times 0.12$ ...(1)

Also, $30 \times \frac{9.15}{M} \times (2z) = 36 \times 0.12$ ...(2)

From equations (1) and (2) $\frac{y}{2z} = \frac{27}{36} \Rightarrow \frac{y}{z} = \frac{3}{2}$ ...(3)

Also, total cationic charge = total anionic charge

$\therefore x + y = 2z$ ...(4)

By equations (3) and (4)

x : y : z :: 1 : 3 : 2

These are in simplest ratio and molecular formula is $KH_3(C_2O_4)_2.nH_2O$

Molecular weight of salt = 39 + 3 + 176 + 18n = 218 + 18n

From equation (1), $M = \frac{30 \times 9.15 \times 3}{27 \times 0.12} = 254.16$

$\therefore$ 218 + 18n = 254.15

$\therefore$ n = 2

$\therefore$ ***Oxalate salt is $KH_3(C_2O_4)_2.2H_2O$***

***Illustration 9*.***

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 20 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 volume strength of $H_2O_2$.

***Solution***

Meq. of $MnO_2$ = Meq. of $Na_2C_2O_4$

$= 20 \times 0.2 \times 2 = 8$

($C_2O_4^{2-} \rightarrow 2CO_2$, n-factor = 2)

Millimoles of $MnO_2 = \frac{8}{2} = 4$

n-factor = 3

$MnO_4^- + Mn^{+2} \xrightarrow{H_2O} MnO_2$ brown (ppt.)

n-factor = 2

or $2MnO_4^- + 3Mn^{2+} \rightarrow 5MnO_2$ (Mole ratio is reciprocal of n-factor ratio)

$$\frac{\text{Millimoles of } MnO_4^-}{\text{Millimoles of } MnO_2} = \frac{2}{5}$$

Millimoles $MnO_4^- = \frac{2}{5} \times$ Millimoles of $MnO_2$

$= \frac{2}{5} \times 4 = \frac{8}{5}$

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

$$\frac{\text{Millimoles of } H_2O_2}{\text{Millimoles of } MnO_4^-} = \frac{5}{2}$$

$\therefore$ Millimoles of $H_2O_2 = \frac{5}{2} \times \frac{8}{5} = 4$

$N_{H_2O_2} \times 20 = 4 \times 2$ (n-factor for $H_2O_2$ = 2)

$\therefore$ $N_{H_2O_2} = 0.4$

Volume strength of $H_2O_2 = 5.6 \times N_{H_2O_2} = 5.6 \times 0.4 = 2.24$

***Illustration 10.***

1.0 g of moist sample of mixture of potassium chlorate ($KClO_3$) and potassium chloride (KCl) was dissolved in water and solution made upto 250 mL. This solution was treated with $SO_2$ to reduce all $ClO_3^-$ to $Cl^-$ and excess of $SO_2$ was removed by boiling. The total chloride was precipitated as silver chloride. The weight of precipitate was found to be 1.435 g. In another experiment, 25 mL of the original solution was heated with 30 ml 0.2 N $FeSO_4$ and unused $FeSO_4$ required 37.5 mL of 0.08 N $KMnO_4$ solutions.

Calculate the molar ratio of the $ClO_3^-$ to the given mixture.

Given that, $ClO_3^- + 6Fe^{2+} + 6H^+ \longrightarrow Cl^- + 6Fe^{3+} + 3H_2O$

$3SO_2 + ClO_3^- + 3H_2O \longrightarrow Cl^- + 3SO_4^{2-} + 6H^+$

***Solution***

$ClO_3^-$ is reduced to $Cl^-$ by $SO_2$ and $ClO_3^-$ is also reduced to $Cl^-$ by $Fe^{2+}$, hence AgCl is formed due to total $Cl^-$

Meq. of $Fe^{2+}$ initially taken = 30 × 0.2 = 6

Meq. of $Fe^{2+}$ unused = 37.5 × 0.08 = 3

∴ Meq. of $Fe^{2+}$ = 6.0 – 3.0 = 3.0

Thus, Meq. of $ClO_3^-$ in 25 mL = 3.0

Moles of $ClO_3^-$ in 25 mL = $\dfrac{3.0}{1000 \times 6}$ = 0.0005

$^{+5}ClO_3^- \longrightarrow {}^{-1}Cl^-$ (n-factor = 6)

O.N. 5 –1

Thus, moles of $ClO_3^-$ in 25 mL solution = 0.0005

$ClO_3^-$ is also reduced to $Cl^-$ by $SO_2$ in first experiment and precipitated as AgCl.

Thus, $Cl^-$ formed from $ClO_3^-$ = AgCl from $ClO_3^-$ = 1.435 g

$n_{KClO_3} = 0.005$

$n_{KCl} = 0.0052$

Thus, $ClO_3^-$ and $Cl^-$ are in molar ratio = ***1 : 1***

***Illustration 11.***

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 :

Step 1 : $IO_3^- + 3HSO_3^- \longrightarrow I^- + 3H^+ + 3SO_4^{2-}$

Step 2 : $5I^- + IO_3^- + 6H^+ \longrightarrow 3I_2 + 3H_4O$

One litre of chile salt peter solution containing 6.80 g $NaIO_3$, is treated with stoichiometric quantity of $NaHSO_3$. Now additional amount of same solution is added to the reaction mixture to bring about the second reaction. How many grams of $NaHSO_3$ are required in step 1 and what additional volume of chile salt peter must be added in step 2 to bring in complete conversion of $I^-$ to $I_2$ ?

***Solution***

Meq. of $NaHSO_3$ = Meq. of $NaIO_3$ = N × V = $\dfrac{6.8}{198} \times 6 \times 1000$

$I^{5+} + 6e^- \longrightarrow I^-$ (For $KIO_3$, n-factor = 6)

∴ Meq. of $NaHSO_3$ = 206.06

$$\frac{W_{NaHSO_3}}{M/2} \times 1000 = 206.06$$

$$\Rightarrow \quad W_{NaHSO_3} = \frac{206.06 \times 104}{2 \times 1000} = 10.715 \text{ g}$$

Also, Meq. of $I^-$ formed using n-factor 6 = 206.06

In step 2, n-factor $I^-$ is 1 and n-factor for $IO_3^-$ is 5

Meq. of $I^-$ formed using n-factor 1 = $\dfrac{206.06}{6}$

Meq. of $NaIO_3$ used in 2nd step = $\dfrac{206.06}{6}$

$$\Rightarrow \quad \frac{6.8}{198} \times 5 \times V = \frac{206.06}{6}$$

$$\therefore \quad V_{NaIO_3} = 199.99 \text{ mL}$$

# ANSWERS

## BEGINNER'S BOX-1

**1.** **(a)** +5 **(b)** +6 **(c)** +3 **(d)** +2 **(e)** 200/93 = 2.15

**2.** **(a)** $S_4O_6^{2-}(aq) + 6Al\,(s) + 20\,H^+ \longrightarrow 4\,H_2S\,(aq) + 6Al^{3+}\,(aq) + 6H_2O$

**(b)** $6S_2O_3^{2-}(aq) + Cr_2O_7^{2-}\,(aq) + 14\,H^+ \longrightarrow 3\,S_4O_6^{2-}\,(aq) + 2\,Cr^{3+}\,(aq) + 7H_2O$

**(c)** $14ClO_3^-(aq) + 3As_2S_3\,(s) + 18\,H_2O \longrightarrow 14\,Cl^-\,(aq) + 6H_2AsO_4^-\,(aq) + 9HSO_4^-\,(aq) + 15H^+$

**(d)** $7IO_3^-(aq) + 6Re\,(s) + 3H_2O \longrightarrow 6\,ReO_4^-\,(aq) + 7I^-\,(aq) + 6H^+$

**(e)** $30HSO_4^-(aq) + As_4\,(s) + 10\,Pb_3O_4(s) + 26H^+ \longrightarrow 30\,PbSO_4\,(s) + 4H_2AsO_4^-\,(aq) + 24H_2O$

**(f)** $3HNO_2\,(aq) \longrightarrow HNO_3 + 2NO\,(g) + H_2O$

**3.** **(a)** $3C_4H_4O_6^{2-}(aq) + 5ClO_3^-\,(aq) + 18\,OH^- \longrightarrow 12\,CO_3^{2-}\,(aq) + 5\,Cl^-\,(aq) + 15H_2O$

**(b)** $11Al\,(s) + 3BiONO_3\,(s) + 21H_2O + 11OH^- \longrightarrow 3Bi\,(s) + 3NH_3\,(aq) + 11Al\,(OH)_4^-(aq)$

**(c)** $4H_2O_2\,(aq) + Cl_2O_7\,(aq) + 2OH^- \longrightarrow 2ClO_2^-\,(aq) + 4O_2\,(g) + 5H_2O$

**(d)** $Tl_2O_3\,(s) + 4NH_2OH\,(aq) \longrightarrow 2TlOH\,(s) + 2N_2\,(g) + 5H_2O$

**(e)** $Cu(NH_3)_4^{2+}\,(aq) + S_2O_4^{2-}\,(aq) + 4OH^- \longrightarrow 2SO_3^{2-}\,(aq) + Cu\,(s) + 4NH_3\,(aq) + 2H_2O$

**(f)** $3Mn(OH)_2\,(s) + 2MnO_4^-\,(aq) \longrightarrow 5MnO_2\,(s) + 2H_2O + 2OH^-$

## BEGINNER'S BOX-2

**1.** (B) **2.** (A) **3.** (C) **4.** (D) **5.** (A)

## BEGINNER'S BOX-3

**1.** (C) **2.** (B) **3.** (C) **4.** (A) **5.** (i) (A), (ii) (A), (iii) (A), (iv) (D)

**6.** (B) **7.** (A) **8.** (C) **9.** (D)

## BEGINNER'S BOX-4

**1.** 25.5 g/L, 1.5 N, 8.4 V **2.** 41.66 ppm **3.** 85% **4.** x = 1

**5.** (B) **6.** (B) **7.** (B) **8.** (B)

## EXERCISE – 1 MCQ (SINGLE CHOICE CORRECT)

**1.** 50 mL of 0.1 M solution of a salt reacted with 25 mL of 0.1 M solution of sodium sulphite. The half reaction for the oxidation of sulphite ion is :-

$$SO_3^{2-}(aq) + H_2O(\ell) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$$

If the oxidation number of metal in the salt was 3, what would be the new oxidation number of metal :

(A) zero (B) 1 (C) 2 (D) 4

**2*.** An element A in a compound ABD has oxidation number $A^{n-}$. It is oxidised by $Cr_2O_7^{2-}$ in acid medium. In the experiment $1.68 \times 10^{-3}$ moles of $K_2Cr_2O_7$ were used for $3.26 \times 10^{-3}$ moles of ABD. The new oxidation number of A after oxidation is :-

(A) 3 (B) 3 – n (C) n – 3 (D) +n

**3.** The incorrect order of decreasing oxidation number of S in compounds is :-

(A) $H_2S_2O_7 > Na_2S_4O_6 > Na_2S_2O_3 > S_8$
(B) $H_2SO_5 > H_2SO_3 > SCl_2 > H_2S$
(C) $SO_3 > SO_2 > S_8 > H_2S$
(D) $H_2SO_4 > SO_2 > H_2S > H_2S_2O_8$

**4.** Which reaction does not represent autoredox or disproportionation :-

(A) $Cl_2 + OH^- \longrightarrow Cl^- + ClO_3^- + H_2O$
(B) $2H_2O_2 \longrightarrow H_2O + O_2$
(C) $2Cu^+ \longrightarrow Cu^{+2} + Cu$
(D) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$

**5.** Match List-I (Compounds) with List-II (Oxidation states of nitrogen) and select answer using the codes given below the lists :-

| ***List-I*** | ***List-II*** |
|---|---|
| (a) $NaN_3$ | 1. +5 |
| (b) $N_2H_2$ | 2. +2 |
| (c) NO | 3. –1/3 |
| (d) $N_2O_5$ | 4. –1 |

| ***Code:*** | (a) | (b) | (c) | (d) |
|---|---|---|---|---|
| (A) | 3 | 4 | 2 | 1 |
| (B) | 4 | 3 | 2 | 1 |
| (C) | 3 | 4 | 1 | 2 |
| (D) | 4 | 3 | 1 | 2 |

**6.** Which of the following is a redox reaction :-

(A) $2\,CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$
(B) $CuSO_4 + 4\,NH_3 \rightarrow [Cu(NH_3)_4]\,SO_4$
(C) $Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + NaI$
(D) $Cr_2O_7^{2-} + 2OH^- \rightarrow 2\,CrO_4^{2-} + H_2O$

**7.** In the reaction

$xHI + yHNO_3 \longrightarrow NO + I_2 + H_2O$

(A) x = 3, y = 2 (B) x = 2, y = 3 (C) x = 6, y = 2 (D) x = 6, y = 1

**8.** The mass of oxalic acid crystals ($H_2C_2O_4 . 2H_2O$) required to prepare 50 mL of a 0.2 N solution is :-

(A) 4.5 g (B) 6.3 g (C) 0.63 g (D) 0.45 g

**9.** 125 mL of 63% (w/v) $H_2C_2O_4 . 2H_2O$ is made to react with 125 mL of a 40% (w/v) NaOH solution. The resulting solution is :-

(A) neutral (B) acidic (C) strongly acidic (D) alkaline

**10.** If equal volumes of 0.1 M $KMnO_4$ and 0.1 M $K_2Cr_2O_7$ solutions are allowed to oxidise $Fe^{2+}$ to $Fe^{3+}$ in acidic medium, then $Fe^{2+}$ oxidised will be :-

(A) more by $KMnO_4$ (B) more by $K_2CrO_7$ (C) equal in both cases (D) can't be determined

**11*.** If 10 g of $V_2O_5$ is dissolved in acid and is reduced to $V^{2+}$ by zinc metal, how many mole $I_2$ could be reduced by the resulting solution if it is further oxidised to $VO^{2+}$ ions ?

[Assume no change in state of $Zn^{2+}$ ions] (V = 51, O = 16, I = 127) :

(A) 0.16 mole of $I_2$ (B) 0.22 mole of $I_2$ (C) 0.055 mole of $I_2$ (D) 0.44 mole of $I_2$

**12.** A 0.518 g sample of limestone is dissolved in HCl and then the calcium is precipitated as $CaC_2O_4$. After filtering and washing the precipitate, it requires 40.0 mL of 0.250 N $KMnO_4$ solution acidified with $H_2SO_4$ to titrate it as. The percentage of CaO in the sample is :-

$MnO_4^- + H^+ + C_2O_4^{2-} \longrightarrow Mn^{2+} + CO_2 + 2H_2O$

(A) 54.0 % (B) 27.1 % (C) 42 % (D) 84 %

**13*.** One gram of $Na_3AsO_4$ is boiled with excess of solid KI in presence of strong HCl. The iodine evolved is absorbed in KI solution and titrated against 0.2 N hyposolution. Assuming the reaction to be

$AsO_4^{3-} + 2H^+ + 2I^- \longrightarrow AsO_3^{3-} + H_2O + I_2$,

calculate the volume of thiosulphate hypo consumed. [Atomic weight of As = 75]

(A) 48.1 mL (B) 38.4 mL (C) 24.7 mL (D) 30.3 mL

**14.** 25 mL of 0.50 M $H_2O_2$ solution is added to 50 mL of 0.20 M $KMnO_4$ in acid solution. Which of the following statement are true :-

(A) 0.010 mole of oxygen is liberated (B) 0.005 mole of $KMnO_4$ are left

(C) 0.030 g atom of oxygen gas is evolved (D) 0.0025 mole $H_2O_2$ does not react with $KMnO_4$

**15*.** Hydrogen peroxide in aqueous solution decomposes on warming to give oxygen according to the equation

$2H_2O_2\,(aq) \longrightarrow 2H_2O\,(\ell) + O_2\,(g)$

Under conditions where 1 mole of gas occupies 24 $dm^3$. 100 $cm^3$ of XM solution of $H_2O_2$ produces 3 $dm^3$ of $O_2$. Thus X is :-

(A) 2.5 (B) 1 (C) 0.5 (D) 0.25

**16*.** Bottle (A) contain 320 mL of $H_2O_2$ solution & labeled with 10 V $H_2O_2$ & Bottle (B) contain 80 mL $H_2O_2$ having normality 5N. If bottle (A) & bottle (B) mixed & solution filled in bottle (C). Select the correct lable for bottle (C) in term of volume strength & in term of g / litre. :-

(A) 13.6 "V" & 41.285 g/L (B) 11.2 "V" & 0.68 g/L (C) 5.6 "V" & 0.68 g/L (D) 5.6 "V" & 41.285 g/L

**17.** An antifreeze mixture consists of 40% ethylene glycol ($C_2H_6O_2$) by weight in aqueous solution. If the density of this solution is 1.05 g/mL, what is the molar concentration :

(A) 6.77 M (B) 6.45 M (C) 0.017 M (D) 16.9 M

**18*.** A 150 mL of solution of $I_2$ is divided into two unequal parts. I part reacts with hypo solution in acidic medium. 15 mL of 0.4 M hypo was consumed. II part was added with 100 mL of 0.3 M NaOH solution. Residual base required 10 mL of 0.3 M $H_2SO_4$ solution for complete neutralization. What was the initial concentration of $I_2$ ?

(A) 0.08 M (B) 0.1 M (C) 0.2 M (D) none of these

## EXERCISE – 2 MCQ (ONE OR MORE CHOICE CORRECT)

**1.** Which of the following are disproportionation reaction ?

(A) $2RCHO \xrightarrow{Al(OEt)_3} RCOOCH_2R$

(B) $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$

(C) $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

(D) $PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$

**2.** A sample of $H_2O_2$ solution labelled as "28 volume" has density of 265 g/L. Mark the correct option(s) representing concentration of same solution in other units :

(A) $M_{H_2O_2} = 2.5$

(B) $\% \frac{w}{v} = 17$

(C) mole fraction of $H_2O_2 = 0.2$

(D) $m_{H_2O_2} = 13.88$

**3.** A sample of $H_2O_2$ solution labelled as 56 volume has density of 530 gm/L. Mark the correct option(s) representing concentration of same solution in other units. (Solution contains only $H_2O$ and $H_2O_2$)

(A) $M_{H_2O_2} = 6$

(B) $\% \frac{w}{v} = 17$

(C) Mole fraction of $H_2O_2 = 0.25$

(D) $m_{H_2O_2} = \frac{1000}{72}$

**4*.** 0.1 M solution of KI reacts with excess of $H_2SO_4$ and $KIO_3$ solutions, according to equation $5I^- + IO_3^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$ ; which of the following statement(s) is/are correct ?

(A) 200 ml of the KI solution react with 0.004 mole $KIO_3$.

(B) 100 ml of the KI solution reacts with 0.006 mole of $H_2SO_4$.

(C) 0.5 litre of the KI solution produced 0.005 mole of $I_2$.

(D) Equivalent weight of $KIO_3$ is equal to $\left(\frac{\text{Molecular Weight}}{5}\right)$.

**5*.** A mixture containing 0.84 gm of $NaHCO_3$, 4.0 gm of NaOH and 10.6 gm of $Na_2CO_3$ is dissolved in water and the resulting solution is titrated with 0.5 M HCl solution. Identify the option(s) which is/are correct.

(A) The volume of HCl used when phenolpthalein is used as an indicator is 400 ml

(B) The volume of HCl used when methyl orange is used as an indicator in a fresh solution is 620 ml.

(C) The volume of HCl further used when methyl orange is used as an indicator in a solution already titrated with phenolpthalein is 220 ml.

(D) The volume of HCl used when phenolpthalein is used as an indicator after titrating with methyl orange is 200 ml.

**6.** Which of the following samples of reducing agents is /are chemically equivalent to 25 ml of 0.2 N $KMnO_4$ to be reduced to $Mn^{2+}$ and water ?

(A) 25 ml of 0.2 M $FeSO_4$ to be oxidized to $Fe^{3+}$

(B) 50 ml of 0.1 M $H_3AsO_3$ to be oxidized to $H_3AsO_4$

(C) 25 ml of 0.1 M $H_2O_2$ to be oxidized to $H^+$ and $O_2$

(D) 25 ml of 0.1 M $SnCl_2$ to be oxidized to $Sn^{4+}$

**7*.** 25 ml of 0.5 M $H_2O_2$ solution is added to 50 ml of 0.2 M $KMnO_4$ in acid solution. Which of the following statement(s) is/are false ?

(A) 0.010 mole of oxygen gas is liberated

(B) 0.005 mole of $KMnO_4$ is left

(C) 0.030 g of oxygen gas is evolved

(D) 0.0025 mole $H_2O_2$ does not react with $KMnO_4$

**8.** Find the normality and the volume strength of the solution, which made by mixing of 5.6 V & 11.2 V $H_2O_2$ solutions. Volume of both is 1 litre each.

(A) 8.4 V (B) 1.5 N (C) 4.8 V (D) 1 N

## Match the column

**9*.**

| | Column-I (Reaction) | | Column-II (n–factor of underlined) |
|---|---|---|---|
| (A) | When $\underline{Bi_2S_3}$ converted into $Bi^{5+}$ and S | (p) | 18 |
| (B) | When $\underline{Al_2(Cr_2O_7)_3}$ reduced into $Cr^{3+}$ in acidic medium | (q) | 11 |
| (C) | When $\underline{FeS_2}$ converted into $Fe_2O_3$ and $SO_2$ | (r) | 2 |
| (D) | When $\underline{Mn(NO_3)_2}$ converted into $MnO_4^{2-}$ and NO | (s) | 10 |

**10.**

| | Column-I | | Column-II |
|---|---|---|---|
| (A) | $P_2H_4 \longrightarrow PH_3 + P_4H_2$ | (p) | $E = \frac{3M}{4}$ |
| (B) | $\underline{I_2} \longrightarrow I^- + IO_3^-$ | (q) | $E = \frac{3M}{5}$ |
| (C) | $MnO_4^- + Mn^{2+} + H_2O \longrightarrow \underline{Mn_3O_4} + H^+$ | (r) | $E = \frac{15M}{26}$ |
| (D) | $H_3PO_2 \longrightarrow PH_3 + H_3PO_3$ | (s) | $E = \frac{5M}{6}$ |

## Comprehension Based Questions

$$\text{Equivalent weight} = \frac{\text{Molecular weight / Atomic weight}}{\text{n – factor}}$$

n-factor is very important in redox as well as non-redox reactions. With the help of n-factor we can predicts the molar ratio of the reactant species taking part in reactions. The reaciprocal of n-factor's ratio of the reactants is the molar ratio of the reactants.

In general n-factor of acid/base is number of moles of $H^+$ /$OH^-$ furnished per mole of acid/base. n-factor of a reactant is no. of moles of electrons lost or gained per mole of reactant.

***Example 1 :***

1. In acidic medium : $KMnO_4$ (n = 5) $\longrightarrow Mn^{2+}$
2. In basic medium : $KMnO_4$ (n = 3) $\longrightarrow Mn^{2+}$
3. In neutral medium : $KMnO_4$ (n = 1) $\longrightarrow Mn^{6+}$

***Example 2 :*** $FeC_2O_4 \longrightarrow Fe^{3+} + 2CO_2$

Total no. of moles of $e^-$ lost by 1 mole of $FeC_2O_4 = 1 + 1 \times 2 \Rightarrow 3$

$\therefore$ n-factor of $FeC_2O_4 = 3$

**11.** n-factor of $Ba(MnO_4)_2$ in acidic medium is :

(A) 2 (B) 6 (C) 10 (D) none of these

**12.** For the reaction, $H_3PO_2 + NaOH \longrightarrow NaH_2PO_2 + H_2O$

What is the equivalent weight of $H_3PO_2$ ? (mol. wt. is M)

(A) M (B) M/2 (C) M/3 (D) none of these

**13.** In the reaction, $xVO + yFe_2O_3 \longrightarrow FeO + V_2O_5$. What is the value of x and y respectively ?

(A) 1, 1 (B) 2, 3 (C) 3, 2 (D) none of these

## EXERCISE – 3 SUBJECTIVE

**1.** In a quantitative determination of iron in an ore, an analyst converted 0.40 g, of the ore into its ferrous. This required 40.00 mL of 0.1 N solution of $KMnO_4$ for titration.

(i) How many milliequivalents of $KMnO_4$ does 40.00 mL of 0.1 N solution represent?

(ii) How many equivalents of iron were present in the sample of the ore taken for analysis?

(iii) How many grams of iron were present in the sample?

(iv) What is the percentage of iron in the ore?

(v) What is the molarity of $KMnO_4$ solution used?

(vi) How many moles of $KMnO_4$ were used for titration ? (Fe = 56)

**2.** The mixture of CuS (molar weight = $M_1$) and $Cu_2S$ (molecular weight = $M_2$) oxidised by $KMnO_4$ (molecular weight = $M_3$) in acidic medium, the product obtained are $Cu^{2+}$, $SO_2$. Find the equivalent weight of CuS, $Cu_2S$ and $KMnO_4$ respectively.

**3.** Consider the reaction $H^+ + IO^-_4 + I^- \rightarrow I_2 + H_2O$. Find the ratio of coefficients of $IO_4^-$ , $I^-$ and $I_2$.

**4.** A dilute solution of $H_2SO_4$ is made by adding 5 mL of 3N $H_2SO_4$ to 245 mL of water. Find the normality and molarity of the solution.

**5.** What volume at NTP of gaseous ammonia will be required to be passed into 30 cc of N – $H_2SO_4$ solution to bring down the acid strength of the latter to 0.2 N.

**6.** How many mL of 0.1 N HCl are required to react completely with 1 g mixture of $Na_2CO_3$ and $NaHCO_3$ containing equimolar amounts of two?

**7.** 0.5 g of fuming $H_2SO_4$ (oleum) is diluted with water. The solution requires 26.7 mL of 0.4N NaOH for complete neutralization. Find the % of free $SO_3$ in the sample of oleum.

**8.** $H_3PO_4$ is a tri basic acid and one of its salt is $NaH_2PO_4$. What volume of 1 M NaOH solution should be added to 12 g of $NaH_2PO_4$ to convert it into $Na_3PO_4$?

**9.** 1.5 g of chalk were treated with 10 mL of 4N – HCl. The chalk was dissolved and the solution made to 100 mL, 25 mL of this solution required 18.75 mL of 0.2 N – NaOH solution for complete neutralisation. Calculate the percentage of pure $CaCO_3$ in the sample of chalk?

**10*.** A solution contains $Na_2CO_3$ and $NaHCO_3$. 20 mL of this solution required 4 mL of 1N – HCl for titration with Ph indicator. The titration was repeated with the same volume of the solution but with MeOH. 10.5 mL of 1 – N HCl was required this time. Calculate the amount of $Na_2CO_3$ & $NaHCO_3$.

**11.** A solution contains a mix of $Na_2CO_3$ and NaOH. Using Ph as indicator 25 mL of mixture required 19.5 mL of 0.995 N HCl for the end point. With MeOH, 25 mL of the solution required 25 mL of the same HCl for the end point. Calculate g/L of each substance in the mixture.

**12.** 200 mL of a solution of mixture of NaOH and $Na_2CO_3$ was first titrated with Ph and $\frac{N}{10}$ HCl. 17.5 mL of HCl was required for end point. After this MeOH was added and 2.5 mL of same HCl was again required for next end point. Find out amounts of NaOH and $Na_2CO_3$ in the mix.

**13.** A 1.0 g sample of $H_2O_2$ solution containing x% $H_2O_2$ by mass requires x $cm^3$ of a $KMnO_4$ solution for complete oxidation under acidic conditions. Calculate the normality of $KMnO_4$ solution.

**14.** One litre hard water contains 1 mg $CaCl_2$ and 1 mg $MgSO_4$. Find hardness.

**15.** Calculate the hardness of water sample which contains 0.001 mol $MgSO_4$ per litre of water.

**16.** Calculate the amount of lime $Ca(OH)_2$ required to remove the hardness in 60 litre of pond water containing 1.62 mg of calcium bicarbonate per 100 mL of water.

## EXERCISE – 4 RECAP OF AIEEE/JEE (MAIN)

**1.** $MnO_4^-$ is good oxidising agent in different medium changing to - ***[AIEEE-02]***

$MnO_4^- \longrightarrow Mn^{2+}$

$\longrightarrow MnO_4^{2-}$

$\longrightarrow MnO_2$

$\longrightarrow Mn_2O_3$

Changes in oxidation number respectively are -

(A) 1, 3, 4, 5 (B) 5, 4, 3, 2 (C) 5, 1, 3, 4 (D) 2, 6, 4, 3

**2.** Oxidation number of Cl in $CaOCl_2$ (bleaching powder is ) ***[AIEEE-02]***

(A) Zero, since it contains $Cl_2$ (B) –1, since it contains $Cl^-$

(C) +1, since it contains $ClO^-$ (D) +1 and –1 since it contains $ClO^-$ and $Cl^-$

**3*.** Which of the following is a redox ***[AIEEE-02]***

(A) $2NaAg(CN)_2 + Zn \longrightarrow Na_2Zn(CN)_4 + 2Ag$ (B) $BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$

(C) $N_2O_5 + H_2O \longrightarrow 2HNO_3$ (D) $AgNO_3 + KI \longrightarrow AgI + KNO_3$

**4.** In the coordination compound, $K_4[Ni(CN)_6]$, the oxidation state of nickel is– ***[AIEEE-03]***

(A) +1 (B) +2 (C) –1 (D) 0

**5.** The oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ is - ***[AIEEE-05]***

(A) +2 (B) +3 (C) 0 (D) +1

**6*.** The oxidation state of chromium in the final product formed by the reaction between Kl and acidified potassium dichromate solution is - ***[AIEEE-05]***

(A) +6 (B) +4 (C) +3 (D) +2

**7.** Which of the following chemical reaction depicts the oxidizing behaviour of $H_2SO_4$ ? ***[AIEEE-06]***

(A) $Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$ (B) $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

(C) $2PCl_5 + H_2SO_4 \rightarrow 2POCl_3 + 2HCl + SO_2Cl_2$ (D) $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$

**8*.** Amount of oxalic acid present in a solution can be determined by its titration with $KMnO_4$ solution in the presence of $H_2SO_4$. The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl ***[AIEEE-2008]***

(A) gets oxidized by oxalic acid to chlorine

(B) furnishes $H^+$ ions in addition to those from oxalic acid

(C) reduces permanganate to $Mn^{2+}$

(D) oxidises oxalic acid to carbon dioxide and water

**9.** The mass of potassium dichromate crystals required to oxidise 750 $cm^3$ of 0.6 M Mohr's salt solution is: (Given molar mass : potassium dichromate = 294, Mohr's salt = 392) :- ***[AIEEE-2011]***

(A) 0.49 g (B) 0.45 g (C) 22.05 g (D) 2.2 g

**10.** Consider the following reaction : $xMnO_4^- + yC_2O_4^{2-} + zH^+ \rightarrow xMn^{2+} + 2yCO_2 + \frac{z}{2} H_2O$

The values of x, y and z in the reaction are, respectively : ***[JEE Mains-2013]***

(A) 5, 2 and 16 (B) 2, 5 and 8 (C) 2, 5 and 16 (D) 5, 2 and 8

**11.** 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 Mains-2013]***

(A) 7.01 % (B) 4.08 % (C) 6.05 % (D) 5.08 %

**12.** For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl method and the evolved ammonia was absorbed in 60 mL of $\frac{M}{10}$ sulphuric acid. The unreacted acid required 20 mL of $\frac{M}{10}$ sodium hydroxide for complete neutralizaton. The percentage of nitrogen in the compound is : ***[JEE Mains-2014]***

(A) 3% (B) 5% (C) 6% (D) 10%

**13.** In which of the following reaction $H_2O_2$ acts as a reducing agent ? ***[JEE Mains-2014]***

(a) $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (b) $H_2O_2 - 2e^- \rightarrow O_2 + 2H^+$

(c) $H_2O_2 + 2e^- \rightarrow 2OH^-$ (d) $H_2O_2 + 2OH^- - 2e^- \rightarrow O_2 + 2H_2O$

(A) (a), (c) (B) (b), (d) (C) (a), (b) (D) (c), (d)

**14.** Which of the following reactions is an example of a redox reaction ? ***[JEE Mains-2017]***

(A) $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$ (B) $XeF_2 + PF_5 \rightarrow [XeF]^+PF_6^-$

(C) $XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$ (D) $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$

**15.** In the reaction of oxalate with permaganate in acidic medium, the number of electrons involved in producing one molecule of $CO_2$ is ***[JEE-MAIN-2019]***

(A) 10 (B) 2 (C) 1 (D) 5

**16.** 25 ml of the given HCl solution requires 30 mL of 0.1 M sodium carbonate solution. What is the volume of this HCl solution required to titrate 30 mL of 0.2 M aqueous NaOH solution? ***[JEE-MAIN-2019]***

(A) 25 mL (B) 50 mL (C) 12.5 mL (D) 75 mL

**17.** The volume strength of 1M $H_2O_2$ is : ***[JEE-MAIN-2019]***

(Molar mass of $H_2O_2$ = 34 g/mol)

(A) 16.8 (B) 11.35 (C) 22.4 (D) 5.6

**18.** The correct order of the oxidation states of nitrogen in NO, $N_2O$, $NO_2$ and $N_2O_3$ is :

(A) $NO_2 < N_2O_3 < NO < N_2O$ (B) $NO_2 < NO < N_2O_3 < N_2O$

(C) $N_2O < N_2O_3 < NO < NO_2$ (D) $N_2O < NO < N_2O_3 < NO_2$

**19.** Chlorine on reaction with hot and concentrated sodium hydroxide gives : ***[JEE-MAIN-2019]***

(A) $Cl^-$ and $C1O_2$ (B) $Cl^-$ and $ClO_3^-$ (C) $Cl^-$ and $ClO^-$ (D) $ClO_3^-$ and $C1O_2$

**20.** 50 mL of 0.5 M oxalic acid is needed to neutralize 25 mL of sodium hydroxide solution. The amount of NaOH in 50 mL of the given sodium hydroxide solution is : ***[JEE-MAIN-2019]***

(A) 40 g (B) 20 g (C) 80 g (D) 4 g

**21.** In order to oxidise a mixture one mole of each of $FeC_2O_4$, $Fe_2(C_2O_4)_3$, $FeSO_4$ and $Fe_2(SO_4)_3$ in acidic medium, the number of moles of $KMnO_4$ required is - ***[JEE-MAIN-2019]***

(A) 3 (B) 2 (C) 1 (D) 1.5

**22.** 100 mL of a water sample contains 0.81 g of calcium bicarbonate and 0.73 of magnesium bicarbonate. The hardness of this water sample expressed in terms of equivalents of $CaCO_3$ is: ***[JEE-MAIN-2019]***

(molar mass of calcium bicarbonate is 162 g $mol^{-1}$ and magnesium bicarbonate is 146 $gmol^{-1}$)

(A) 1,000 ppm (B) 10,000 ppm (C) 100 ppm (D) 5,000 ppm

**23.** The strength of 11.2 volume solution of $H_2O_2$ is : [Given that molar mass of H = 1 g $mol^{-1}$ and O = 16 g $mol^{-1}$] ***[JEE-MAIN-2019]***

(A) 13.6% (B) 3.4% (C) 34% (D) 1.7%

**24.** An example of a disproportionation reaction is : ***[JEE-MAIN-2019]***

(A) $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$

(B) $2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

(C) $2CuBr \rightarrow CuBr_2 + Cu$

(D) $2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$

## EXERCISE – 5 RECAP OF IIT-JEE/JEE (ADVANCED)

**1.** Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is : ***[JEE 2007]***

(A) 3 (B) 4 (C) 5 (D) 6

**2.** The reagent (s) used for softening the temporary hardness of water is (are) : ***[JEE 2010]***

(A) $Ca_3(PO_4)_2$ (B) $Ca(OH)_2$ (C) $Na_2CO_3$ (D) NaOCl

**3.** A student performs a titration with different burettes and finds titre values of 25.2 mL, 25.25 mL, and 25.0 mL. The number of significant figures in the average titre value is : ***[JEE 2010]***

**4.** Among the following, the number of elements showing only one non-zero oxidation state is : ***[JEE 2010]***

O, Cl, F, N, P, Sn, Tl, Na, Ti

**5.** The difference in the oxidation numbers of the two types of sulphur atoms in $Na_2S_4O_6$ is. ***[JEE 2011]***

**6.** 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 ***[JEE 2011]***

**7.** Reduction of the metal centre in aqueous permanganate ion involves ***[JEE 2011]***

(A) 3 electron in neutral medium (B) 5 electrons in neutral medium

(C) 3 electrons in alkaline medium (D) 5 electrons in acidic medium

**8.** For the reaction :

$$I^- + ClO_3^- + H_2SO_4 \rightarrow Cl^- + HSO_4^- + I_2$$ ***[JEE 2014]***

The correct statement(s) in the balanced equation is/are

(A) Stoichiometric coefficient of $HSO_4^-$ is 6 (B) Iodide is oxidized

(C) Sulphur is reduced (D) $H_2O$ is one of the products.

**9*.** In neutral or faintly alkaline solution, 8 moles of permanganate anion quantitatively oxidize thiosulphate anions to produce X moles of a sulphur containing product. The magnitude of X is ***[JEE 2016]***

**10.** The order of the oxidation state of the phosphorus atom in $H_3PO_2$, $H_3PO_4$, $H_3PO_3$ and $H_4P_2O_6$ is ***[JEE 2017]***

(A) $H_3PO_4 > H_4P_2O_6 > H_3PO_3 > H_3PO_2$ (B) $H_3PO_3 > H_3PO_2 > H_3PO_4 > H_4P_2O_6$

(C) $H_3PO_2 > H_3PO_3 > H_4P_2O_6 > H_3PO_4$ (D) $H_3PO_4 > H_3PO_2 > H_3PO_3 > H_4P_2O_6$

**11.** To measure the quantity of $MnCl_2$ dissolved in an aqueous solution, it was completely converted to $KMnO_4$ using the reaction,

$MnCl_2 + K_2S_2O_8 + H_2O$ ® $KMnO_4 + H_2SO_4 + HCl$ (equation not balanced).

Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 g) was added in portions till the colour of the permanganate ion disappeard. The quantity of $MnCl_2$ (in mg) present in the initial solution is _____.

(Atomic weights in g $mol^{-1}$ : Mn = 55, Cl = 35.5) ***[JEE 2018]***

# ANSWERS

## EXERCISE-1

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | C | B | D | D | A | C | C | C | A | B |
| Que. | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | | |
| Ans. | A | A | A | B | A | A | A | B | | |

## EXERCISE-2

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Ans. | AB | ACD | BD | ABD | ABC | ACD | ACD | AB |

- ***Match the Column***

**9.** (A) $\rightarrow$ s ; (B) $\rightarrow$ p ; (C) $\rightarrow$ q ; (D) $\rightarrow$ r

**10.** (A) $\rightarrow$ s ; (B) $\rightarrow$ q ; (C) $\rightarrow$ r ; (D) $\rightarrow$ p

- ***Comprehension Based Questions***

**11.** (C) **12.** (A) **13.** (B)

## EXERCISE-3

**1.** (i) 4.0, (ii) 0.0040, (iii) 0.224, (iv) 56.00%, (v) 0.02 M, (vi) 0.0008 mole

**2.** $\frac{M_1}{6}, \frac{M_2}{8}, \frac{M_2}{5}$ **3.** 1 : 7 : 4 **4.** 0.06 N and 0.03 M

**5.** 537.6 mL **6.** V = 157.89 mL **7.** 20.72 %

**8.** 200 mL **9.** 83.33 **10*.** 0.424 g ; 0.21g

**11.** 23.2 g, 22.28 g **12.** 0.06 g ; 0.0265 g **13.** 0.588 N

**14.** 1.734 ppm **15.** 100 ppm **16.** 0.444 g

## EXERCISE-4

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | C | D | A | B | B | C | D | C | C | C |
| Que. | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Ans. | B | D | B | A | C | A | B | D | B | D |
| Que. | 21 | 22 | 23 | 24 | | | | | | |
| Ans. | B | B | B | C | | | | | | |

## EXERCISE-5

**1.** (D) **2.** (B) **3.** (3) **4.** (2) **5.** (5)

**6.** (5) **7.** AD or ACD **8.** (ABD) **9.** (6) **10.** (A)

**11.** (126)

# ATOMIC STRUCTURE

## Recap of Early Classes

In earlier classes we have studied basic mole concept. We have also learnt that an atom consists of certain fundamental particles – protons, neutrons and electrons. The existence of atoms has been proposed since the time of early Indian and Greek philosophers (400 B.C.) who were of the view that atoms are the fundamental building blocks of matter. According to them, the continued subdivisions of matter would ultimately yield atoms which subdivisions of matter would not be further divisile. This chapter aims of understand varies theories experiments which late to the development of structure of atom.

## Index


**1.0 INTRODUCTION TO ATOM**
**2.0 DALTONS ATOMIC THEORY**
**3.0 EVIDENCE FOR THE ELECTRICAL NATURE OF THE ATOM**
- 3.1 Cathode rays-discovery of electron Discharge tube experiment
- 3.2 Canal rays (or anode rays) – discov ery of proton
- 3.3 Comparison of Positive (Canal) Rays and Cathode Rays

**4.0 DISCOVERY OF NEUTRON**
**5.0 THOMSON'S MODEL OF ATOM [1904]**
**6.0 RUTHERFORD'S $\alpha-$ SCATTERING EXPERIMENT**
- 6.1 Applications of Rutherford Model

**7.0 WAVE THEORY**
- 7.1 Wave characteristics
- 7.2 Electromagnetic waves (EM waves) or Radiant Energy/Electromagnetic radiation

**8.0 PLANCK'S QUANTUM THEORY**
**9.0 BOHR'S ATOMIC MODEL**
- 9.1 Radii of various orbits of hydrogen atom
- 9.2 Calculation of energy of an electron
- 9.3 Calculation of velocity
- 9.4 Terms associated with Bohr's model as per energy considerations

**10.0 SPECTRUM**
- 10.1 Emissions spectrum
- 10.2 Absorption spectrum
- 10.3 Hydrogen line spectrum or Hydrogen spectrum

**11.0 THE DUAL NATURE OF MATTER (THE WAVE NATURE OF ELECTRON)**
**12.0 HEISENBERG UNCERTAINTY PRINCIPLE**
**13.0 WAVE MECHANICAL MODEL OF ATOM**
- 13.1 Concept of Orbitals
- 13.2 The wave function
- 13.3 Schrodinger Equation in Cartesien Coordinates
- 13.4 Schrodinger Equation in Polar Coordinates
- 13.5 Quantum Number
- 13.6 Radial probability distribution function (rpdf), $4\pi r^2\psi^2(r)$
- 13.7 Angular Probability distrubtion function
- 13.8 Electron-density distribution in 1s, 2s and 3s-orbitals

**14.0 ENERGY LEVEL DIAGRAM**
- 14.1 Energy level diagram of Hydrogen atom
- 14.2 Energy level diagram of multi-electron atoms
- 14.3 Bohr Bury (n + *l*) rule (for multi-electronic atoms)

**15.0 RULES FOR FILLING OF ORBITALS IN AN ATOM**
- 15.1 Aufbau Principle
- 15.2 Pauli's Exclusion principle
- 15.3 Hund's Maximum Multiplicity Rule
- 15.4 Electronic configuration of atoms of various elements
- 15.5 Exception of Aufbau principle
- 15.6 Electronic configuration of ions

**16.0 MAGNETIC PROPERTIES**
**17.0 PHOTOELECTRIC EFFECT**
**18.0 BLACK BODY RADIATION & EXPLANATION BY PLANCK'S QUANTUM THEORY**
**EXERCISE-1**
**EXERCISE-2**
**EXERCISE-3**
**EXERCISE-4**
**EXERCISE-5**

# ATOMIC STRUCTURE

## 1.0 INTRODUCTION TO ATOM

The ideas of classical mechanics developed by ***Galileo, Kepler and Newton***, when applied to atomic and molecular systems were found to be inadequate. Need was felt for a theory to describe, correlate and predict the behaviour of the sub-atomic particles. The quantum theory, proposed by ***Max Planck*** and applied by ***Einstein and Bohr*** to explain different aspects of behaviour of matter, is an important milestone in the formulation of the modern concept of atom.

In this chapter, we will study how black body radiation, photoelectric effect and atomic spectra of hydrogen can be explained on the basis of theories proposed by Max Planck, Einstein and Bohr. They based their theories on the postulate that all interactions between matter and radiation occur in terms of definite packets of energy, known as quanta. Their idea, when extended further, led to the evolution of wave mechanics, which shows the dual nature of matter and energy.

## 2.0 DALTONS ATOMIC THEORY

SL

This theory is based on law of mass conservation and law of definite proportions.

***The salient feature's of this theory are :***

***(i)*** Each element is composed of extremely small particles called atoms.

***(ii)*** Atoms of a particular element are like but differ from atom's of other element.

***(iii)*** Atom of each element is an ultimate particle and it has a characteristic mass but is structureless.

***(iv)*** Atom's are indestructible i.e. they can neither be created nor be destroyed.

***(v)*** Atom of element's take part in chemical reaction to form molecule.

## 3.0 EVIDENCE FOR THE ELECTRICAL NATURE OF THE ATOM

SL

The earliest evidence for the electrical nature of matter came from experiments on frictional electricity when it was found that substances like glass or ebonite when rubbed with silk or fur generated electricity. Although these observations paved the way for a detailed understanding of electromagnetic phenomena, they did not directly contribute to the understanding of the electrical nature of atoms and molecules.

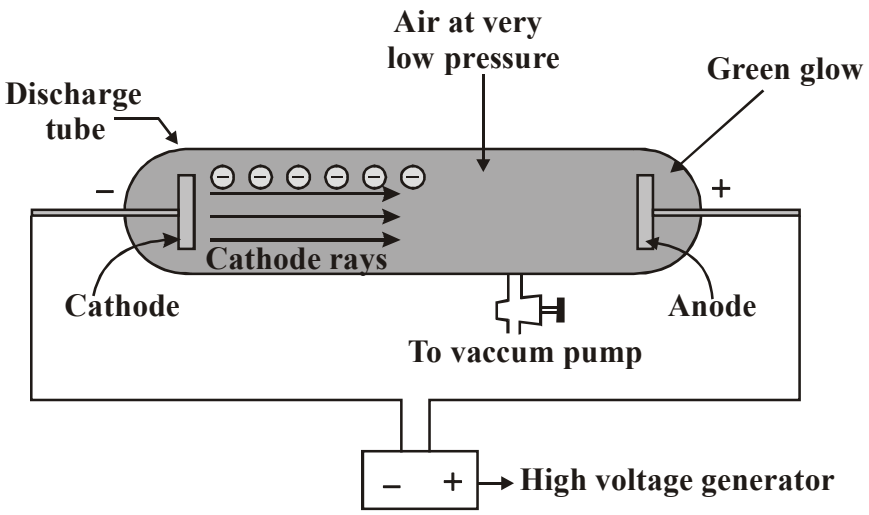
### 3.1 CATHODE RAYS-DISCOVERY OF ELECTRON-DISCHARGE TUBE EXPERIMENT

SL

Gases are bad conductors of elctricity. However under reduced pressure and at high potential difference gases conduct electric current.

***(i)*** ***Discharge tube :*** Discharge tube is a glass tube fitted with two electrodes placed opposite to each other. The tube is sealed and contains a vacuum pump. The function of vacuum pump is to reduced or change the pressure inside the tube. The two electrodes are connected to a high voltage battery.

***(ii)*** ***Experiment :***




A high voltage electric current pass through gases under reduced pressure led to ***Julius Plucker's discovery (1859)*** of cathode rays.

**(iii) *Observation :*** Under different pressures different observations were noted ;

**(a) *At 1 cm Hg pressure :*** When pressure inside the tube is reduced to 1 cm of Hg, at a potential difference of a few thousand volts causes a spark to pass like a flash of light.

**(b) *At 1 mm Hg :*** At 1 mm Hg, the tube is mostly filled with a glow extending from the positive electrode. This is known as "positive column".

**(c) *At 0.001 mm Hg :*** At 0.001 m Hg, the glow disappears and the walls of the glass tube begin to glow with a brilliant green light.

**(iv) *Result :*** These observations indicate that some radiation or rays are emitted from cathode. These rays are known as "Cathode Rays". The cathode rays stream from the negative electode , which is called the cathode.

**(v) *Application :*** If anode has holes (perforated) and tube behind anode is coated with ZnS (phosphorescent material) which glows when hit by cathode rays.Similarly televisions picture tubes are also cathode ray tubes in which pictures result due to fluoroscence on television screen coated with phosphorescent or fluoroscent materials.

**(vi) *Properties :*** Cathode rays are fast moving beams of electrons which have following properties :

- They are negatively charged known from their deflection in external electrical or magnetic field.
- Start from cathode and end at anode.
- By changing electrode material or gas in the tube there is no effect on nature of cathode rays which means that "electrons are basic constituents of all atoms".
- Their velocities change with the applied voltage.
- They penetrate through the metals and other substances and also produce flourescence.
- An obstacle placed in the path of cathode rays is heated up and thus cathode rays possess heating effect.
- Cathode rays on striking solid objects of high melting point produce X-rays.
- They affect the photographic plate.
- They can ionise gases.
- Their e/m is constant.
- No cathode rays were produced when tube was completely evacuated.
- Like ordinary light, cathode rays come out at right angles to the surface of cathode and travel in a straight line normal to the cathode. It casts sharp shadows, if any opaque solid object is placed in their path.
- They rotate a light paddle wheel if placed in their path and thus shows mechanical effect i.e. they have momentum and energy and therefore, mass. The cathode rays are material particles.

**(vii) *Conclusion :*** Different scientists tried different discharge tubes with different electrodes and different gases but results of all the experiments gave same value for charge to mass ratio. This shows that there is something common in all materials. Experiment shows that these particles could be produced from any kind of material. Cathode rays consist of particles which are known as electrons and electron is a fundamental particle in all matter.

**(viii) *Charge to mass (e/m) ratio calculation :*** In ***1897, J.J. Thomson*** measured the ratio of electrical charge (e) to the mass of electron ($m_e$) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons.

$$\frac{e}{m_e} = 1.758820 \times 10^{11}\ C\ kg^{-1}$$

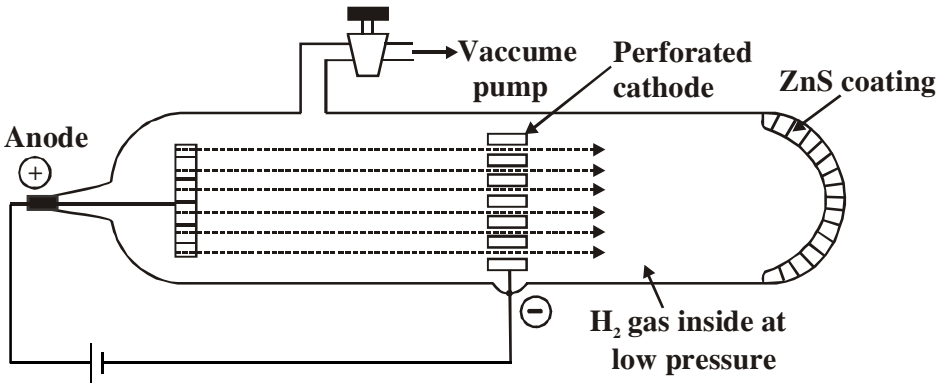
**(ix) *Mass on the Electron : R.A. Millikan (1868-1953)*** devised a method known as oil drop experiment ($1906^{-14}$), to determine the charge on the electrons. He found that the charge on the electron to be $-1.6 \times 10^{-19}$ C. The present accepted value of electrical charge is $-1.6022 \times 10^{-19}$ C. The mass of the electron ($m_e$) was determined by combining these results with Thomson's value of $e/m_e$ ratio.

$$m_e = \frac{e}{e/m_e} = 9.1094 \times 10^{-31}\ kg$$

## 3.2 Canal rays (or anode rays) – discovery of proton

SL

Atoms are electrically neutral. Hence after the discovery of the negatively charged constituent (electron) of an atom, attempts were made to discover the positively charged counterpart of electrons. By using a discharge tube containing a perforated cathode. ***Goldstein (1886)*** found that some rays passed through these holes in a direction opposite to that of the cathode rays.




***(i) Positive Rays or Canal Rays :*** These are called the positive rays or canal rays. ***J.J. Thomson (1910)*** measured their charge by mass ratio from which he was able to deduce that these contain positive ions.

***(ii) Properties***

- They are positively charged.
- The positive charge is either equal to or whole number multiple of the charge on an electron.
- When hydrogen gas was filled in the discharge tube the positive charge on the positive rays was equal to the negative charge on an electron, and the mass was slightly less than the hydrogen atom.
- Unlike cathode rays the properties of positive rays are characteristics of the gas in the tube.
- The deflection of positive rays under the influence of an electric or magnetic field is smaller than that of the cathode rays for the same strength of field. This shows that the positive rays have a greater mass than that of electrons.
- The mass of the positive rays depends on the atomic weights or molecular weights of the gases in the discharge tube. The charge/mass ratio also varies because the change in positive charge on the rays. It may be either equal to or integral multiple of the charge on an electron. Also masses were different for different gases.
- The lightest of all particles identified in positive rays from different elements was one with a mass very slightly less than that of hydrogen atom (or nearly equal to H-atom).

The lightest positively charged particle is called a proton (P or P+). Positive rays are atomic or molecular cations from which some electrons have been removed. The removed electrons constitute the cathode rays and the positive cations form the positive or canal rays.

| ***Element*** | | ***Positive Rays*** | ***Cathode Rays*** | ***charge / mass*** |
|---|---|---|---|---|
| H | → | $H^+$ | $e^-$ | e/1 amu |
| O | → | $O^+$ | $e^-$ | e/16 amu |
| $O_2$ | → | $O_2^+$ | $e^-$ | e/32 amu |
| $O_2$ | → | $O_2^{2+}$ | $2\ e^-$ | e/16 amu |

The mass of a proton is very slightly less than that of a H-atom. This shows that protons are sub-atomic particles. Protons are fundamental constituent of matter because positive rays are produced by all substances and for all gases (e/m) ratio is integral divisor of (e/m) ratio of H(g).

"A sub-atomic particle, which is a fundamental constituent of all matter having a mass slightly less than that of H-atom and which carries a positive charge equal in magnitude to the charge on an electron, is called a proton". A proton is denoted by p or $p^+$ or $^1_1p$.

## 3.3 Comparison of Positive (Canal) Rays and Cathode Rays

SL

| ***Properties*** | ***Cathode Rays*** | ***Canal Rays*** |
|---|---|---|
| Sign of Charge | Negative | Positive |
| Mag. of Charge | Always –1 | Mostly +1, but also +2, +3… |
| Mass | Definite value | Variable, depends on ions |
| e/m | Definite value | Variable, depends on ions |

## 4.0 DISCOVERY OF NEUTRON

SL

After the discovery of electron and proton ***Rutherford (1920)*** had predicted the existence of a neutral fundamental particle. In ***1932, Chadwick*** bombarded the element Beryllium with α-particles and noticed the emission of a radiation having the following characteristics.

***(i)*** The radiation was highly penetrating.

***(ii)*** The radiation was unaffected by magnetic and electric fields which shows that it is electrically neutral.

***(iii)*** It was found to have approximately the same mass as the protons.

The name 'neutron' was given to this sub-atomic particle. It is denoted by n or $_0n^1$. Bombardment of beryllium by α-particles results in the formation of carbon and neutrons are emitted.

$$_4Be^9 + {}_2He^4 \longrightarrow {}_6C^{12} + {}_0n^1$$

Mass of a neutron is 1.008930 amu ($1.6753 \times 10^{-24}$g or $1.6753 \times 10^{-27}$ kg)

***A sub-atomic particle, which is a fundamental constituent of matter having mass approximately equal to the hydrogen atom and which is electrically neutral, is called a neutron.***

Properties of fundamental particles :

| Particles | Symbol | Mass | Charge | Discoverer |
|---|---|---|---|---|
| Electron | $_{-1}e^0$ or β | $9.1096 \times 10^{-31}$ kg<br>0.000548 amu | $-1.602 \times 10^{-19}$ Coulombs<br>$-4.803 \times 10^{-10}$ esu | J.J. Thompson<br>Stoney Lorentz 1887 |
| Proton | $_1H^1$ | $1.6726 \times 10^{-27}$ kg<br>1.00757 amu | $+1.602 \times 10^{-19}$ Coulombs<br>$+4.803 \times 10^{-10}$ esu | Goldstein<br>Rutherford1907 |
| Neutron | $_0n^1$ | $1.6749 \times 10^{-27}$ kg<br>1.00893 amu<br>1 amu $\approx 1.66 \times 10^{-27}$ kg | neutral<br>0 | James Chadwick<br>1932 |

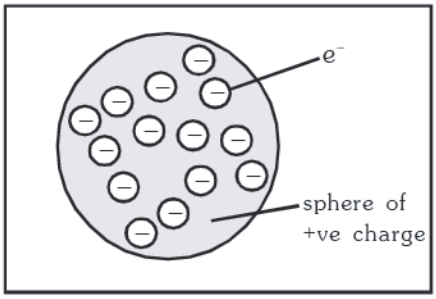
## 5.0 THOMSON'S MODEL OF ATOM [1904]

SL

***(i)*** Thomson was the first to propose a detailed model of the atom.

***(ii)*** Thomson proposed that an atom consists of a uniform sphere of positive charge in which the electrons are present at some places.

***(iii)*** This model of atom is known as '***Plum-Pudding model***'.




- **Drawbacks**

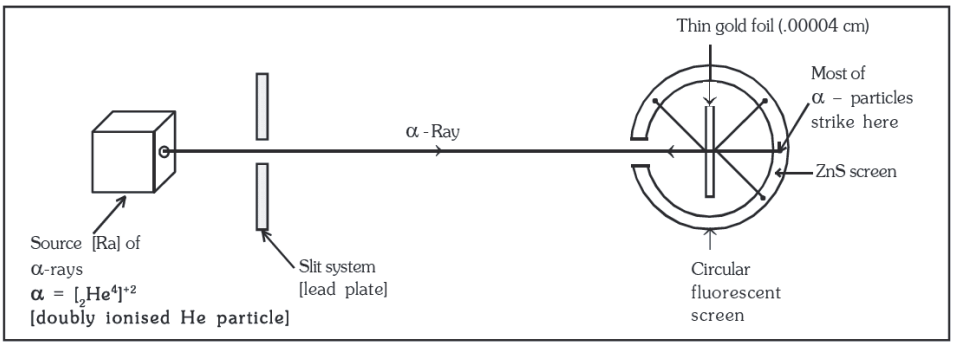
***(i)*** An important drawback of this model is that the mass of the atoms is considered to be evenly spread over that atom.

***(ii)*** It is a static model. It does not reflect the movement of electron.

## 6.0 RUTHERFORD'S α– SCATTERING EXPERIMENT

SL AL

***α-scattering experiment***

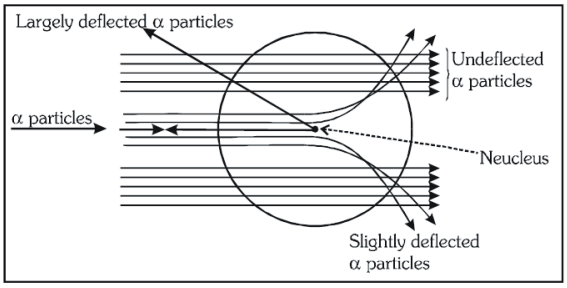



- **Ruther ford observed that**

  ***(i)*** Most of the α-particles (nearly 99.9%) went straight without suffering any deflection.

  ***(ii)*** A few of them got deflected through small angles.

  ***(iii)*** A very few α-particles (about one in 20,000) did not pass through the foil at all but suffered large deflections (more than 90°) or even come back in the direction from which they have come i.e. a deflection of 180°.




- **Following conclusions were drawn from the above observations**

  ***(i)*** Since most of the α-particle went straight through the metal foil undeflected, it means that there must be very large empty space within the atom.

  ***(ii)*** Since few of the α-particles were deflected from their original path through moderate angles; it was concluded that whole of the +ve charge is concentrated and the space occupied by this positive charge is very small in the atom.Whenever α-particles come closer to this point, they suffer a force of repulsion and deviate from their paths.The positively charged heavy mass which occupies only a small volume in an atom is called ***nucleus***.It is supposed to be present at the centre of the atom.

  ***(iii)*** A very few of the α-particles suffered strong deflections on even returned on their path indicating that the nucleus is rigid and α-particles recoil due to direct collision with the heavy positively charged mass.

***Note:*** *The relation between number of deflected particles and deflection angle $\theta$ is*

$$\mu = \frac{1}{\sin^4 \frac{\theta}{2}} \quad [\theta \text{ increases } \mu \text{ decreases}]$$

*where $\mu$ = deflected particles*

*$\theta$ = deflection angle*

*As atomic number increases, the number of protons increases which increases the repulsion and so deflection angle $\theta$ increases.*

## 6.1 Applications of Rutherford Model

SL AL

On the basis of scattering experiments, Rutherford proposed the model of an atom, which is known as nuclear atomic model. According to this model -

***(i)*** An atom consists of a heavy positively charged nucleus where all the protons are present.

***(ii)*** The volume of the nucleus is very small and is only a minute fraction of the total volume of the atom.Nucleus has a radius of the order of $10^{-13}$ cm and the atom has a radius of the order of $10^{-8}$ cm

$$\frac{r_A}{r_N} = \frac{\text{radius of the atom}}{\text{radius of the nucleus}} = \frac{10^{-8}}{10^{-13}} = 10^5, \quad \boldsymbol{r_A = 10^5\, r_N}$$

Thus radius (size) of the atom is $10^5$ times the radius of the nucleus.
The radius of a nucleus is proportional to the cube root of the no. of nucleons within it.

$R \propto A^{1/3} \Rightarrow R = R_0 A^{1/3}$ cm

***Where*** $R_0 = 1.33 \times 10^{-13}$(a constant) and, A = mass number (p + n)
R = radius of the nucleus.
$R = 1.33 \times 10^{-13} A^{1/3}$ cm

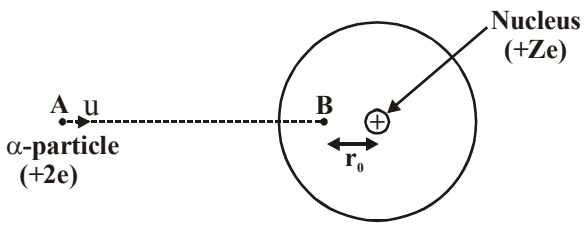
***(iii)*** There is an empty space around the nucleus called extra nuclear part. In this part electrons are present.The no. of electrons in an atom is always equal to no. of protons present in the nucleus. As the nuclear part of atom is responsible for the mass of the atom, the extra nuclear part is responsible for its volume. The volume of the atom is about $10^{15}$ times the volume of the nucleus.

$$\frac{\text{vol. of the atom}}{\text{vol. of the nucleus}} = \frac{\left(\frac{4}{3}\pi r_A^3\right)}{\left(\frac{4}{3}\pi r_N^3\right)} = \frac{\left(10^{-8}\right)^3}{\left(10^{-13}\right)^3} = 10^{15}$$

***(iv)*** Electrons revolve round the nucleus in closed orbits with high speeds.

This model was similar to the solar system, the nucleus representing the sun and revolving electrons as planets.

***Distance of closest approach and estimating nuclear dimension from α-particle scattering experiment:***
An α-particle traveling directly towards the centre of the nucleus slows down as it approaches the nucleus. At a certain distance say $r_0$ from the nucleus, the α-particle comes to rest and its initial kinetic energy is completely converted into electrostatic potential energy. The distance $r_0$ called the distance of closest approach.




At point B, K.E. of α-particle is completely converted to electrostatic potential energy (P.E.) of the system.

$$\text{P.E. of system at B} = \frac{1}{4\pi\varepsilon_0} \times \frac{(2e)(Ze)}{r_0}$$

$$\text{K.E. of } \alpha\text{-particle} = \frac{1}{2} \times m_\alpha \times u^2$$

$$\text{Equating both we get , } r_0 = \frac{2Ze^2}{4\pi\varepsilon_0 \times \frac{1}{2} \times m_\alpha u^2} = \frac{2Ze^2}{4\pi\varepsilon_0 \times \text{K.E.}}$$

***Ex.*** An $\alpha$-particle having K.E. = 7.7 MeV is scattered by gold (Z = 79) nucleus through 180°. Find distance of closest approach.

***Sol.*** K.E. = 7.7 M eV

$= 7.7 \times 10^6 \times 1.6 \times 10^{-19}$ J

$= 1.23 \times 10^{-12}$ J

$$\frac{1}{4\pi\varepsilon_0} = 9\times10^9 \text{Nm}^2\text{C}^{-2}$$

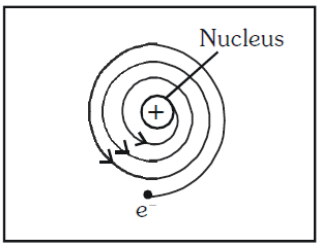
Using we get : $\dfrac{9\times10^9\times2\times79\times(1.6\times10^{-19})^2}{1.23\times10^{-12}}$

$r_0 = 3 \times 10^{-14}$ m

From the above example it is clear that nuclear dimension cannot be greater than $3 \times 10^{-14}$ m.

- **Drawbacks of Rutherford model**

***(i)*** This theory could ***not*** explain the stability of an atom. According to Maxwell electron loses it's energy continuously in the form of electromagnetic radiations. As a result of this, the e- should loss energy at every turn and move closer and closer to the nucleus following a spiral path. The ultimate result will be that it will fall into the nucleus, thereby making the atom unstable.




***(ii)*** If the electrons loss energy continuously, the observed spectrum should be continuous but the actual observed spectrum consists of well defined lines of definite frequencies (discontinuous). Hence, the loss of energy by electron is ***not*** continuous in an atom.

## BEGINNER'S BOX–1

### *Earlier Model of Atom*

**1.** The mass to charge ratio for $A^+$ iobns is $1.97 \times 10^{-7}$ kg $C^{-1}$. Calculate the mass of A atom.

**2.** 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 ?

**3.** With what velocity should an $\alpha$–particles travel towards the nucleus of a Cu atom so as to arrive at a distance of $10^{-13}$ m.

## 7.0 WAVE THEORY

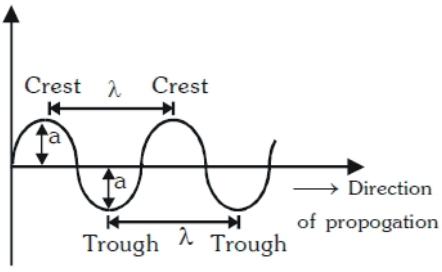
SL AL

A wave is difined as a periodic disturbance in space or in a medium that involves elastic displacement of material particles or a periodic change in some physical quantities such as T, P, V etc. Thus, wave motion represents propagation of a periodic disturbance carying energy. The wave travels at right angles to the vibratory motion of the object.

### 7.1 Wave characteristics

SL AL

A wave is characterized by following six characterstics. The upper most point of the wave is called crest and the lower most point is called trough. Some of the terms employed in dealing with the waves are described below.




- **Wavelength $\lambda$ (Lambda)**

***(i)*** It is defined as the distance between two nearest crest or nearest trough.

***(ii)*** It is measured in terms of a A° (Angstrom), pm (Picometre), nm (nanometer), cm(centimetre), m (metre)

***1Å = $10^{-10}$ m, 1 pm = $10^{-12}$ m, 1nm = $10^{-9}$ m, 1cm = $10^{-2}$m***

- **Frequency (ν) (nu)→**
  ***(i)*** Frequency of a wave is defined as the number of waves which pass through a point in 1 sec.
  ***(ii)*** It is measured in terms of Hertz (Hz), $sec^{-1}$, or cycle per second (cps)
  1 Hertz = 1 $sec^{-1}$ = 1 cps.

- **Time period (T)**
  Time taken by a wave to pass through one point.
  $$T = \frac{1}{\nu} \text{ sec.}$$

- **Velocity → (c)**
  Velocity of a wave is defined as distance covered by a wave in 1 sec.
  $C = \lambda / T = \lambda\nu \quad \Rightarrow \quad \nu = C/\lambda$
  Since C is constants $\quad \nu \propto 1/\lambda$
  i.e. frequency is inversely proportional to λ

- **Wave number → ( $\bar{\nu}$ ) ( nu bar) →**
  It is the reciprocal of the wave length that is number of waves present in 1cm
  1 m = 100 cm
  $$\bar{\nu} = \frac{1}{\lambda} \qquad \frac{1}{cm} = \frac{100}{m}$$
  $(1cm^{-1} = 100\ m^{-1})$
  It is measured in terms of $cm^{-1}$, $m^{-1}$ etc,

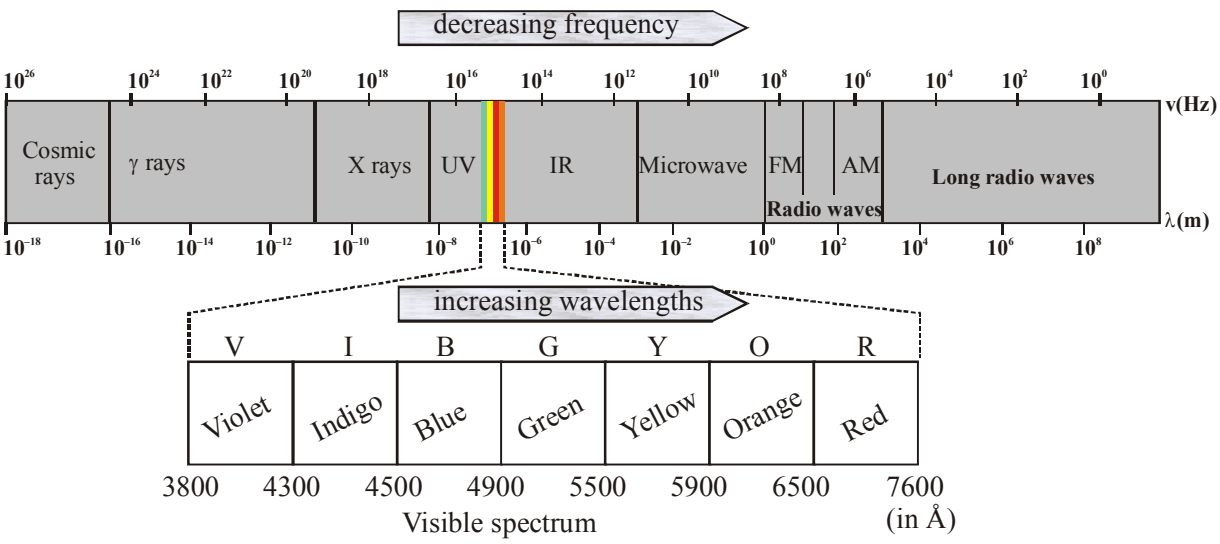
- **Amplitude → (a)**
  The amplitude of a wave is defined as the height of crust or depth of trough.
  $$\nu = \frac{C}{\lambda} = C\bar{\nu} \quad \left(\bar{\nu} = \frac{1}{\lambda}\right)$$

## 7.2 Electromagnetic waves (EM waves) or Radiant Energy/Electromagnetic radiation

SL AL

- It is the energy transmitted from one body to another in the form of waves and these waves travel in the space with the same speed as light ( $3 \times 10^8$ m/s) and these waves are known as Electromagnetic waves or radiant energy.
- The radiant Energy do not need any medium for propogation.

***Ex :*** Radio waves, micro waves, Infra red rays, visible rays, ultraviolet rays, x–rays, gama rays and cosmic rays.



## Illustrations

***Illustration 1.*** The vividh Bharti station of All India Radio broadcast on a frequency of 1368 Kilo Hertz. Calculate the wave length of the Electromagnetic waves emited by the transmitter.

***Solution*** As we know velocity of light (C)

$C = 3 \times 10^8$ m/sec.

Given ν (frequency)

$= 1368$ kHz

$= 1368 \times 10^3$ Hz

$= 1368 \times 10^3\ sec^{-1}$

$$\because \lambda = \frac{C}{\nu} \qquad \therefore \lambda = \frac{3\times10^8 m\, sec^{-1}}{1368\times10^3\ sec^{-1}} \qquad \Rightarrow \lambda = 219.3\ m$$

***Illustration 2.*** Calculate $\bar{\nu}$ in $cm^{-1}$ and ν of yellow radiations have wavelength of 5800 Å

***Solution.*** As we known $\bar{\nu} = \frac{1}{\lambda}$

$$\bar{\nu} = \frac{1}{5800Å}$$

$$\bar{\nu} = \frac{1}{5800\times10^{-8} cm} \quad \{\because\ 1Å = 10^{-8}\ cm\}$$

$$= \frac{10^8}{5800}\ cm^{-1} = 17241.4\ cm^{-1}$$

$$\nu = c\bar{\nu}$$

$$= 3 \times 10^{10}\ cm\ sec^{-1} \times 1.7 \times 10^4\ cm^{-1}$$

$$= 3 \times 1.7 \times 10^{14}$$

$$= 5.1 \times 10^{14}\ sec^{-1}$$

***Illustration 3.*** How long would it take a radio wave of frequency $6 \times 10^3\ sec^{-1}$ to travel from mars to the earth, a distance of $8 \times 10^7$ km ?

***Solution.*** Distance to be travelled from mars to earth

$= 8 \times 10^7$ km

$= 8 \times 10^{10}$ m

$\because$ Velocity of EM waves

$= 3 \times 10^8$ m/sec

$$\therefore \text{Time} = \frac{\text{Distance}}{\text{Velocity}} = \frac{8\times10^{10} m}{3\times10^8 m/sec^{-1}} = 2.66 \times 10^2\ sec.$$

***Illustration 4.*** What will be the frequency of photon of wavelength 2225 Å traveling in vacuum ?

***Solution.*** Velocity of light in vacuum $= 3 \times 10^8$ m $sec^{-1}$

Wavelength $= 2225 \times 10^{-10}$ meter

$$\text{Frequency} = \frac{\text{Velocity}}{\text{Wavelength}} = \frac{3\times10^8 meter/sec}{2225\times10^{-10} meter} = \frac{3000}{2225}\times10^{15}\ sec^{-1} = 1.349 \times 10^{15}\ sec^{-1}$$

## 8.0 PLANCK'S QUANTUM THEORY

SL AL

The electromagnetic theory of radiations given by Maxwell regarded radiant energy as a continuous flow of energy in the form of waves. This theory, no doubt , explained certain phenomena associated with light. But at the same time , it failed to account for a few more phenomena.

***These are listed as follows :***

(a) The nature of radiations which are emitted by a black body also known as ***black body radiations.***

***(b)*** The ejection of electrons from the surface of certain metals when light radiations strike the surface. This is known as ***photoelectric effect.***

***(c)*** The spectral lines emitted by excited atomic gases. These are known as line spectrum and help in the identification of the elements.

***Features of planck's quantum theory :***

***(i)*** The radiant energy emitted or absorbed by a body not continuously but discontinuously in the form of small discrete packets of energy and these packets are called quantum.

***(ii)*** In case of light, the smallest packet of energy is called as '***photon***' but in general case the smallest packet of energy called as quantum.

***(iii)*** The energy of each quantum is directly proportional to frequency of the radiation i.e.

$$E \propto \nu \Rightarrow \quad E = h\nu \quad \text{or} \quad E = \frac{hc}{\lambda} \quad \left\{\because \nu = \frac{c}{\lambda}\right\}$$

Proportionality constant or Plank's constant (h)

$h = 6.626 \times 10^{-37}$ kJ sec.

***or*** $6.626 \times 10^{-34}$ J sec (1erg = $10^{-7}$J)

***or*** $6.626 \times 10^{-27}$ erg sec.

***(iv)*** Total amount of energy transmitted from one body to another will be some integral multiple of energy of a quantum.

$E = nh\nu$

Where n is an integer and n = number of quantum

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

## Illustrations

***Illustration 5.*** Calculate the energy of a photon of sodium light of wave length $5.862 \times 10^{-16}$ m in Joules.

***Solution.*** $\lambda = 5.862 \times 10^{-16}$ m

$c = 3 \times 10^{8}$ m sec$^{-1}$

$$E = nh\nu \quad \text{or} \quad \frac{nhc}{\lambda} \quad \{\because n = 1\}$$

$$\therefore E = \frac{hc}{\lambda}$$

$$E = \frac{1 \times 6.6 \times 10^{-34}\,\text{Joule} \times 3 \times 10^{8}\,\text{m sec}^{-1}}{5.862 \times 10^{-16}\,\text{m}}$$

$$= \frac{6.6 \times 3}{5.862} \times 10^{-10}\,\text{Joules} \quad = \quad 3.38 \times 10^{-10}\,\text{Joules.}$$

***Illustration 6.*** Calculate the frequency & energy of a photon of wave length 4000 Å

***Solution.*** ***(a) Calculation of frequency :***

$\lambda = 4000$ Å

$\lambda = 4000 \times 10^{-10}$ m

$$\because \quad \nu = \frac{C}{\lambda}$$

$$\therefore \quad \nu = \frac{3 \times 10^{8}\,\text{m/sec}}{4 \times 10^{-7}\,\text{m}}$$

$= 0.75 \times 10^{15}$ sec$^{-1}$ $= 7.5 \times 10^{14}$ sec$^{-1}$

***(b) Calculation of energy :***

$E = h\nu$

$= 6.626 \times 10^{-34}$ Joule $\times$ $7.5 \times 10^{14}$ sec$^{-1}$

$= 4.96 \times 10^{-19}$ Joule

***Illustration 7.*** Calculate the $\lambda$ and frequency of a photon having an energy of 2 electron volt

***Solution.*** $\because$ 1ev = $1.602 \times 10^{-19}$ J

$\therefore$ 2ev = $3.204 \times 10^{-19}$ J = E

***(a) Calculation of wavelength ($\lambda$) :***

$$E = \frac{hc}{\lambda} \text{ or } \lambda = \frac{hc}{E}$$

$$= \frac{6.626 \times 10^{-34} \text{Js} \times 3 \times 10^{8} \text{m sec}^{-1}}{3.204 \times 10^{-19} \text{J}}$$

$= 6.204 \times 10^{-7}$ m

***(b) Calculation of frequency ($\nu$) :***

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^{8} \text{m sec}^{-1}}{6.204 \times 10^{-7} \text{m}}$$

$= 0.48 \times 10^{15}$ sec$^{-1}$

$= 4.8 \times 10^{14}$ sec$^{-1}$

***Illustration 8.*** Which has a higher energy ?

***(a)*** A photon of violet light with wave length 4000 Å

***or***

***(b)*** A photon of red light with wave length 7000 Å

***Solution.*** ***(a) Violet light :***

$$E_{violet} = \frac{hc}{\lambda}$$

$$= \frac{6.626 \times 10^{-34} \text{J sec} \times 3 \times 10^{8} \text{m sec}^{-1}}{4000 \times 10^{-10} \text{m}} = 4.97 \times 10^{-19} \text{ Joule}$$

***(b) Red light :***

$$E_{red} = \frac{hc}{\lambda}$$

$$= \frac{6.626 \times 10^{-34} \text{J sec} \times 3 \times 10^{8} \text{m sec}^{-1}}{7000 \times 10^{-10} \text{m}} = 2.8 \times 10^{-19} \text{ Joule}$$

So, $E_{violet} > E_{red}$

***Illustration 9.*** How many photons of lights having a wave length of 5000 Å are necessary to provide 1 Joule of energy.

***Solution.*** $\because$ $E = \frac{nhc}{\lambda}$

$\therefore$ $n = \frac{E \times \lambda}{hc}$

$$= \frac{1\text{Joule} \times 5000 \times 10^{-10} \text{m}}{6.626 \times 10^{-34} \text{Joule sec} \times 3 \times 10^{8} \text{m sec}^{-1}} = 2.5 \times 10^{18} \text{ photons}$$

## BEGINNER'S BOX–2

### *Plancks Quantum Theory*

**1.** The dissociation energy of $H_2$ is 150 kJ mol$^{-1}$. If $H_2$ is exposed to light energy of wavelength 500 nm, what % of light energy will be converted into kinetic energy ?

**2.** Assume that $10^{-17}$ J of light energy is needed by the interior of the human eye to see an object. How many photons of green light ($\lambda$ = 495 nm) are needed to generate this minimum energy.

**3.** A photon of 300 nm is absorbed by a gas and then re-emits two photons. One re-remitted photon has wave-length 500 nm. Calculate energy of other photon re-emitted out.

**4.** Find out the number of photons emitted by a 60 watt bulb in one minute if wavelength of an emitted photon is 620 nm.

**5.** For a wave, frequency is 10 Hz and wavelength is 2.5 m. How much distance it will travel in 40 seconds.

## 9.0 BOHR'S ATOMIC MODEL

SL AL

- **Some Important formulae**

  ***(i)*** Coulombic force $= \frac{kq_1q_2}{r^2}$

  ***(ii)*** Centrifugal force $= \frac{mv^2}{r}$

  ***(iii)*** Angular momentum = mvr

  It is a quantum mechanical model. This model was based on quantum theory of radiation and Classical law of physics.

- **The important postulates on which Bohr's Model is based are the following**

  ***1st Postulate:***
  - Atoms has a nucleus where all protons and neutrons are present.
  - The size of nucleus is very small and it is present at the centre of the atom.

  ***2nd Postulate :***
  - Negatively charged electron are revolving around the nucleus in the same way as the planets are revolving around the sun.
  - The path of electron is circular.
  - The attraction force (Coulombic or electrostatic force) between nucleus and electron is equal to the centrifugal force on electron.
    i.e. Attraction force towards nucleus = centrifugal force away from nucleus.

  ***3rd Postulate :***

  - Electrons can revolve only in those orbits whose angular momentum (mvr) is integral multiple of $\frac{h}{2\pi}$.

  i.e. $mvr = \frac{nh}{2\pi}$

  n = Whole number = 1, 2, 3..... $\left[\frac{h}{2\pi} = \hbar\right]$

  Where h = Plank's constant,

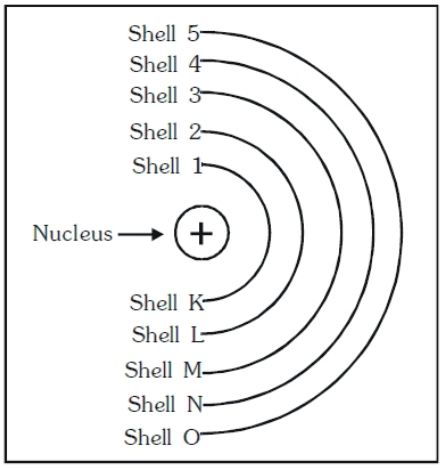
  $\pi$ = Constant

  - Angular momentum can have values such as $\frac{h}{2\pi}, 2\frac{h}{2\pi}, 3\frac{h}{2\pi}, 4\frac{h}{2\pi}, 5\frac{h}{2\pi}$ .....but can not have fractional values such as $1.5\frac{h}{2\pi}, 1.2\frac{h}{2\pi}, .5\frac{h}{2\pi}$ .....

  ***4th Postulate :***
  - The orbits in which electron can revolve are known as ***stationary Orbits*** because in these orbits energy of electron is always constant.

  ***5th Postulate :***
  - Each stationary orbit is associated with definite amount of energy therefore these orbits are also called as energy levels and are numbered as 1, 2, 3, 4, 5, .... or K, L, M, N, O, ..... from the nucleus outwards.

  ***6th Postulate :***
  - The emission or absorbtion of energy in the form of photon can only occur when electron jumps from one stationary state to another & it is $\Delta E = E_{final\ state} - E_{initial\ state}$
  - Energy is absorbed when electron jumps from inner to outer orbit and is emitted when electron moves from outer to inner orbit.



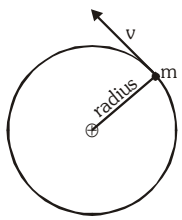

## 9.1 Radii of various orbits of hydrogen atom

SL AL

Consider, an electron of mass 'm' and charge 'e' revolving around a nucleus of charge Ze (where, Z = atomic number and e is the charge of the proton) with a tangential velocity v. r is the radius of the orbit in which electron is revolving.

By Coulomb's law, the electrostatic force of attraction between the moving electron and nucleus is Coulombic

$$\text{force} = \frac{KZe^2}{r^2}$$




$K = \frac{1}{4\pi \epsilon_0}$ (where $\epsilon_0$ is permittivity of free space)

$K = 9 \times 10^9\ Nm^2C^{-2}$

In C.G.S. units, value of K = 1 dyne $cm^2$ $(esu)^{-2}$

The centrifugal force acting on the electron is $\frac{mv^2}{r}$

Since the electrostatic force balance the centrifugal force, for the stable electron orbit.

$$\frac{mv^2}{r} = \frac{KZe^2}{r^2} \qquad \textbf{...(1)}$$

(or) $$v^2 = \frac{KZe^2}{mr} \qquad \textbf{...(2)}$$

According to Bohr's postulate of angular momentum quantization, we have

$$mvr = \frac{nh}{2\pi}$$

$$v = \frac{nh}{2\pi mr}$$

$$v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \qquad \textbf{...(3)}$$

***Equating (2) and (3)***

$$\frac{KZe^2}{mr} = \frac{n^2h^2}{4\pi^2m^2r^2}$$

Solving for r we get $r = \frac{n^2h^2}{4\pi^2mKZe^2}$

where n = 1, 2, 3, ....., ∞

Hence, only certain orbits whose radii are given by the above equation are available for the electron. The greater the value of n, i.e., farther the energy level from the nucleus the greater is the radius.
The radius of the smallest orbit (n = 1) for hydrogen atom (Z = 1) is $r_0$.

$$r_0 = \frac{n^2h^2}{4\pi^2me^2K} = \frac{1^2 \times \left(6.626 \times 10^{-34}\right)^2}{4 \times (3.14)^2 \times 9 \times 10^{-31} \times \left(1.6 \times 10^{-19}\right)^2 \times 9 \times 10^9} = 5.29 \times 10^{-11} \text{ m} = 0.529 \text{ Å}$$

Radius of $n^{th}$ orbit for an atom with atomic number Z is simply written as

$$r_n = 0.529 \times \frac{n^2}{Z} \text{Å}$$

## 9.2 Calculation of energy of an electron

SL AL

The total energy (E) of the electron is the sum of kinetic energy and potential energy.
Kinetic energy of the electron = ½ $mv^2$

$$\text{Potential energy} = \int \text{columbic force.dr} = \int \frac{KZe^2}{r^2}.dr = \frac{-KZe^2}{r}$$

$$\text{Total energy} = 1/2\ mv^2 - \frac{-KZe^2}{r} \qquad \textbf{...(4)}$$

From equation (1) we know that

$$\frac{mv^2}{r} = \frac{KZe^2}{r^2}$$

$$\because \tfrac{1}{2}\ mv^2 = \frac{KZe^2}{r^2}$$

***Substituting this in equation (4)***

$$\text{Total energy (E)} = \frac{KZe^2}{2r} - \frac{KZe^2}{r} = -\frac{KZe^2}{2r}$$

Substituting for r, gives us

$$E = \frac{2\pi^2mZ^2e^4K^2}{n^2h^2} \text{ where } n = 1, 2, 3, .....$$

This expression shows that only certain energies are allowed to the electron. Since this energy expression consist of so many fundamental constant, we are giving you the following simplified expressions.

$$E = -21.8 \times 10^{-12} \times \frac{Z^2}{n^2} \text{ erg per atom}$$

$$= -21.8 \times 10^{-19} \times \frac{Z^2}{n^2} \text{ J per atom} = -13.6 \times \frac{Z^2}{n^2} \text{ eV per atom}$$

(1 eV = $3.83 \times 10^{-23}$ Kcal)
1 eV = $1.602 \times 10^{-12}$ erg
(1 eV = $1.602 \times 10^{-19}$ J)

$$[E = -313.6 \times \frac{Z^2}{n^2} \text{ Kcal/mole (1 cal = 4.18 J)}]$$

The energies are negative since the energy of the electron in the atom is less than the energy of a free electron, i.e. the electron is at infinite distance from the nucleus which is taken as zero. The lowest energy level of the atom corresponds to n = 1, and as the quantum number increases, E becomes less negative.
When n = ∞, E = 0, which corresponds to an ionized atom, i.e. the electron and nucleus are infinitely separated.

$H \longrightarrow H^+ + e^-$ (ionization)

$$\text{Total Energy} = -\text{Kinetic energy} = \frac{\text{Potential Energy}}{2}$$

## 9.3 Calculation of velocity

SL AL

We know that

$$mvr = \frac{nh}{2\pi};\ v = \frac{nh}{2\pi mr}$$

By substituting for r we are getting

$$v = \frac{2\pi KZe^2}{nh}$$

where excepting n and Z all are constants

$$v = 2.18 \times 10^8 \frac{Z}{n} \text{ cm/sec.}$$

## 9.4 Terms associated with Bohr's model as per energy considerations

SL AL

***Ground state :***

lowest energy state of any atom or ion is called ground state of the atom.

Ground state energy of H–atom = – 13.6 ev

Ground state energy of $He^+$ Ion = – 54.4 ev

***Excited State :***

States of atom other than the ground state are called excited states :

| | |
|---|---|
| n = 2 | first exited state |
| n = 3 | second exited state |
| n = 4 | third exited state |
| n = n + 1 | $n^{th}$ exited state |

***Ionisation energy (IE) :***

Minimum energy required to move an electron from ground state to $n = \infty$ is called ionisation energy of the atom or ion.

Ionisation energy of H–atom = 13.6 ev

Ionisation energy of $He^+$ ion = 54.4 ev

Ionisation energy of $Li^{+2}$ ion = 122.4 ev

***Ionisation Potential (I.P.) :***

Potential difference through which a free electron must be accelerated from rest, such that its kinetic energy becomes equal to ionisation energy of the atom is called ionisation potential of the atom.

I.P. of H atom = 13.6 v

I.P. of $He^+$ Ion= 54.4 v

***Excitation Energy :***

Energy required to move an electron from ground state of the atom to any other state of the atom is called excitation energy of that state. excitation energy of $2^{nd}$ state = excitation energy of $1^{st}$ excited state = $1^{st}$ excitation energy = 10.2 ev.

***Excitation Potential :***

Potential difference through which an electron must be accelerated from rest to so that its kinetic energy become equal to excitation energy of any state is called excitation potential of that state.

excitation potntial of third state = excitation potntial of second exicited state = second excitation potential = 12.09 v.

***Binding Energy 'or' Seperation Energy :***

Energy required to move an electron from any state to $n = \infty$ is called binding energy of that state.

Binding energy of ground state = I.E. of atom or Ion.

## Illustrations

***Illustration 10.*** Calculate the radius of $1^{st}$,$2^{nd}$,$3^{rd}$,$4^{th}$ Bohr's Orbit of hydrogen.

***Solution.*** Radius of Bohr's orbit

$$r = 0.529 \times \frac{n^2}{Z}$$

***(a) Radius of $1^{st}$ orbit :***

$$r = 0.529 \times \frac{1^2}{1} = 0.529 \text{ Å}$$

***(b) Radius of $2^{nd}$ orbit :***

$$r = 0.529 \times \frac{2^2}{1} = 0.529 \times 4 = 2.116 \text{ Å}$$

***(c) Radius of $3^{rd}$ orbit :***

$$r = 0.529 \times \frac{3^2}{1} = 0.529 \times 9 = 4.761 \text{ Å}$$

***(d) Radius of $4^{th}$ orbit :***

$$r = 0.529 \times \frac{4^2}{1} = 0.529 \times 16 = 8.464 \text{ Å}$$

***Illustration 11.*** Calculate the radius ratio of $2^{nd}$ orbit of hydrogen and $3^{rd}$ orbit of $Li^{+2}$

***Solution.*** Atomic number of H = 1

Atomic number of $Li^{2+}$ = 3

$2^{nd}$ orbit radius of hydrogen

$$(r_2)_H = 0.529 \times \frac{2^2}{1}$$

$3^{rd}$ orbit radius of $Li^{+2}$

$$(r_3)Li^{+2} = 0.529 \times \frac{3^2}{3}$$

$$\because \frac{(r_2)_H}{(r_3)_{Li^{+2}}} = \frac{0.529 \times \frac{2^2}{1}}{0.529 \times \frac{3^2}{3}} = \frac{4}{3} \Rightarrow \therefore (r_2)_H : (r_3)_{Li^{+2}} = 4 : 3$$

***Illustration 12.*** The ratio of the radius of two Bohr's orbit of $Li^{+2}$ is 1:9. what Would be their nomenclature.

***(1)*** K & L ***(2)*** L & M ***(3)*** K & M ***(4)*** K & N

***Solution.***

$$\frac{r_x}{r_y} = \frac{1}{9} = \frac{0.529 \times \frac{n_x^2}{3}}{0.529 \times \frac{n_y^2}{3}} \Rightarrow \sqrt{\frac{n_x^2}{n_y^2}} \Rightarrow \sqrt{\frac{1}{9}}$$

$$\frac{n_x}{n_y} = \frac{1}{3} = \frac{\text{K Shell}}{\text{M Shell}}$$

***Illustration 13.*** Calculate the radius ratio of $2^{nd}$ excited state of H & $1^{st}$ excited state of $Li^{+2}$.

***Solution.*** $2^{nd}$ excited state, means $e^-$ is present in $3^{rd}$ shell of hydrogen

$$r_3 = 0.529 \times \frac{(3)^2}{1} = 0.529 \times 9$$

$1^{st}$ excited state, means $e^-$ exist in $2^{nd}$ shell of $Li^{+2}$

$$r_2 = 0.529 \times \frac{(2)^2}{3}$$

$$= 0.529 \times \frac{4}{3} \Rightarrow \frac{(r_3)_H}{(r_2)_{Li^{+2}}} = \frac{0.529 \times \frac{9}{1}}{0.529 \times \frac{4}{3}}$$

$$= \frac{\text{radius of } 2^{nd} \text{ excited state of hydrogen}}{\text{radius of } 1^{st} \text{ excited state of } Li^{+2}} \Rightarrow \frac{(r_3)_H}{(r_2)_{Li^{+2}}} = \frac{27}{4}$$

***Illustration 14.*** Calculate the energy of $Li^{+2}$ atom for $2^{nd}$ excited state.

***Solution.*** $E = -13.6 \times \frac{Z^2}{n^2}$

$\because$ Z = 3 and $e^-$ exist in $2^{nd}$ excited state, means $e^-$ present in $3^{rd}$ shell i.e. n = 3

$$\therefore \quad E = -13.6 \times \frac{(3)^2}{(3)^2} = -13.6 \text{ eV/atom}$$

***Illustration 15.*** Calculate the ratio of energies of $He^+$ for $1^{St}$ & $2^{nd}$ excited state .

***Solution.*** $(He^+)$ $1^{st}$ Excited state : $(He^+)_2$ $2^{nd}$ Excited state

i.e. $(He^+)2^{nd}$ shell : $(He^+)3^{rd}$ shell

$$-13.6 \times \frac{(2)^2}{(2)^2} \quad : \quad -13.6 \times \frac{(2)^2}{(3)^2}$$

$$\frac{4}{4} \quad : \quad \frac{4}{9}$$

$$\frac{1}{4} \quad : \quad \frac{1}{9}$$

$$\mathbf{9} \quad : \quad \mathbf{4}$$

***Illustration 16.*** If the P.E. of an electron is –6.8 eV in hydrogen atom then find out K.E., E of orbit where electron exist & radius of orbit.

***Solution.*** ***(1)*** P.E. = –2K.E.

–6.8 = –2K.E.

$\frac{6.8}{2}$ = K.E. K.E. = 3.4 eV

***(2)*** E. = – K.E.

= – 3.4 eV

***(3)*** Orbit = $2^{nd}$

$$\because \quad E = -13.6 \times \frac{Z^2}{n^2}$$

$$\therefore \quad 3.4 = -13.6 \times \frac{1^2}{n^2}$$

$$\Rightarrow n^2 = \frac{-13.6}{-3.4} = 4$$

i.e. n = 2

**(4)** $r = 0.529 \times \frac{n^2}{Z}$ Å

$r = 0.529 \times \frac{(2)^2}{1}$ Å

$= 0.529 \times 4$Å

$= 2.16$ Å

***Illustration 17.*** The ionization energy for the hydrogen atom is 13.6 ev then calculate the required energy in ev to excite it from the ground state to 1st excited state.

***Solution.*** Ionization energy = 13.6 eV

i.e. 1st energy state = – 13.6 eV

Energy of 1st excited state

i.e. 2nd orbit = –3.4 eV

so, $E_2 - E_1$ = – 3.4 + 13.6 = 10.2 eV

***Illustration 18.*** If the total energy of an electron is –1.51 ev in hydrogen atom then find out K.E, P.E, orbit radius and velocity of the electron in that orbit.

***Solution.*** Given E = –1.5 eV

***(i)*** E = – KE

K.E = – E $\{\because Z = 1\}$

= 1.51 eV

***(ii)*** PE = – 2 × 1.51

= – 3.02 eV

***(iii)*** Orbit = 3rd

$\because E = -13.6 \times \frac{Z^2}{n^2}$ ev $\Rightarrow -1.51 = -13.6 \times \frac{1^2}{n^2}$

$n^2 = \frac{-13.6}{-1.51} = 9$

$\therefore n = 3$

***(iv)*** $r = 0.529 \times \frac{3 \times 3}{1}$ Å

$= 0.529 \times 9 = 4.761$ Å

$v = 2.188 \times 10^8 \times \frac{1}{3}$ cm/sec $= \frac{2.188 \times 10^8}{3} = 0.729 \times 10^8$ cm / sec

***Illustration 19.*** Calculate the velocity of an electron placed in the 3rd orbit of the $Li^{2+}$ ion. Also calculate the number of revolutions per second that it makes around the nucleus.

***Solution.*** Radius of 2nd orbit $= r_1 x \frac{(n)^2}{Z} \times 10^{-8}$ cm

$= 0.529 \times 10^{-8} \times \frac{(3)^2}{3} = 1.587 \times 10^{-8}$ cm

Velocity of electron in 2nd orbit,

$v = 2.18 \times 10^8 \frac{Z}{n}$ cm/sec $= \frac{2.18 \times 10^8 \times 3}{3} = 2.18 \times 10^8$ cm/sec

No. of revolutions/sec $= \frac{1}{2\pi r / v} = \frac{v}{2\pi r} = \frac{2.18 \times 10^8 \text{ cm/sec}}{2 \times 3.14 \times 1.587 \times 10^{-8} \text{ cm}} = 0.2187 \times 10^{16}$

$= 2.187 \times 10^{15}$ rev/sec

## BEGINNER'S BOX–3

### *Bohr's Atomic model*

**1.** If the radius of the first Bohr orbit of the H atom is r, then for the $Li^{2+}$ ion it will be :
(A) 3r (B) 9r (C) r/3 (D) r/9

**2.** The energy levels for ${}_ZA^{+(z-1)}$ can be given by:
(A) $E_n$ for $A^{(+z-1)}$ = $Z^2$ x $E_n$ for H
(B) $E_n$ for $A^{(+z-1)}$ = Z x $E_n$ for H
(C) $E_n$ for $A^{(+z-1)}$ = $1/Z^2$ x $E_n$ for H
(D) $E_n$ for $A^{(+z-1)}$ = 1/Z x $E_n$ for H

**3.** The radii of two of the first four Bohr's orbits of the hydrogen atom are in the ratio 1 : 4. The energy difference between them may be:
(A) Either 12.09 eV or 3.4 eV
(B) Either 2.55eV or 10.2 eV
(C) Either 13.6 eV or 3.4 eV
(D) Either 3.4eV or 0.85 eV

**4*.** The potential energy of the electron present in the ground state of $Li^{2+}$ ion is represented by:
(A) $+\frac{3e^2}{4\pi \epsilon_0 r}$ (B) $-\frac{3e}{4\pi \epsilon_0 r}$ (C) $-\frac{3e^2}{4\pi \epsilon_0 r^2}$ (D) $-\frac{3e^2}{4\pi \epsilon_0 r}$

**5.** In a certain electronic transition in the hydrogen atom from an initial state i to a final state f, the difference in the orbit radius $(r_i - r_f)$ is seven times the Bohr radius. Identify the transition.
(A) $4 \rightarrow 1$ (B) $4 \rightarrow 2$ (C) $4 \rightarrow 3$ (D) $3 \rightarrow 1$

**6*.** The velocity of electron in the ground state of H atom is $2.185 \times 10^8$ cm/sec. The velocity of electron in the second orbit of $Li^{2+}$ ion in cm/sec would be
(A) $3.276 \times 10^8$ (B) $2.185 \times 10^8$ (C) $4.91 \times 10^8$ (D) $1.638 \times 10^8$

**7.** If the angular momentum of an electron in a Bohr orbit is $\frac{2h}{\pi}$, then the value of potential energy of electron present in $He^+$ ion is :
(A) – 13.6 eV (B) – 3.4 eV (C) – 6.8 eV (D) – 27.2 eV.

**8.** For which of the following species, Bohr model is not valid :
(A) $He^+$ (B) H (C) $Li^{2+}$ (D) $H^+$

**9.** The ratio of radius of two different orbits in a H-atom is 4 : 9, then the ratio of the frequency of revolution of electron in these orbits is :
(A) 2 : 3 (B) 27 : 8 (C) 3 : 2 (D) 8 : 27

**10.** The ratio of the difference in energy between the first and second Bohr orbit to that between the second and third Bohr orbit in a H-like species is
(A) $\frac{1}{2}$ (B) $\frac{1}{3}$ (C) $\frac{4}{9}$ (D) $\frac{27}{5}$

**11.** When an electron is brought close to the nucleus of the atom from an infinite distance, the energy of the electron–nucleus system changes such that it
(A) increases to a smaller negative value
(B) increases to a greater positive value
(C) decreases to a smaller positive value
(D) decreases to a greater negative value

## 10.0 SPECTRUM

SL AL

- **Electromagnetic spectrum or EM spectrum**

The arrangement obtained by arranging various types of EM waves in ordes of their increasing frequency or decreasing wave length is called as EM SPECTRUM

| low ν<br>low E<br>longer λ | RW | MW | IR | Visible Rays | U.V | X-ray | γ | Cosmic | high ν<br>high E<br>Shorter λ |
|---|---|---|---|---|---|---|---|---|---|

When a radiation is passed through a spectroscope (Prism) for the dispersion of the radiation, the pattern (photograph) obtained on the screen (photographic plate) is called as spectrum of the given radiation

***Classification of Spectrum***

- (1) Emission
  - (a) Continuous
  - (b) line
  - (c) band
- (2) Absorption
  - (a) line
  - (b) band

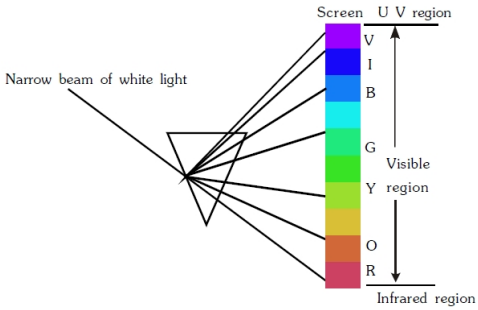
## 10.1 Emissions spectrum

SL AL

When the radiation emitted from incandescence source (eg. from the candle, sun, tubelight, burner, bulb, or by passing electric discharge through a gas at low pressure, by heating some substance at high temp) is passed directly through the prism and then received on the screen then the obtained spectrum is called as emission spectrum.

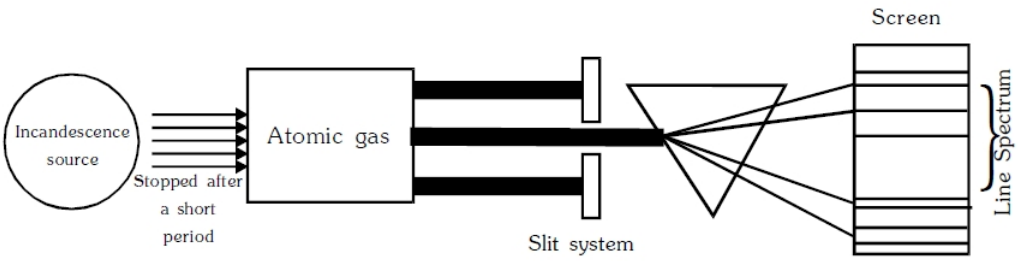
***(a) Emission continuous spectrum or continuous spectrum :***

When a narrow beam of white light is passed through a prism, it is dispersed into 7 colours from violet to Red.

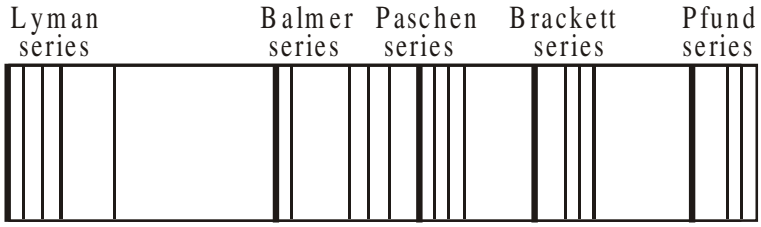



***(b) Emission line spectrum :***

When an atomic gas is raised to incandescence source or subjected to electrical excitation, it first absorbs energy & then gives it out as radiation. On examining these radiation through a spectroscope a spectrum is obtained which have well defined lines,each corresponding to a definite wave length & these lines are separated from each other by dark space. This type of Emission spectrum is called as Emission line spectrum.



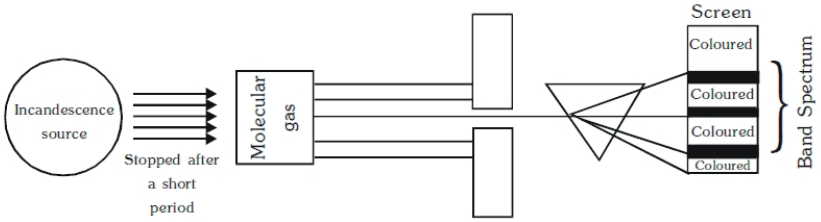

***Ex. Emission atomic spectrum of Hydrogen :***




***(c) Emission band spectrum :***

If molecular form of the gas is used, it first absorbs energy for not only electron transition but for rotational, vibrational and translational then emits radiations.

On examining these radiations through a spectroscope a spectrum is obtained on the screen, which are group of closely packed lines called Bands, therefore this type of Emission spectrum is called as emission band spectrum. Bands are separated from each other by dark space.



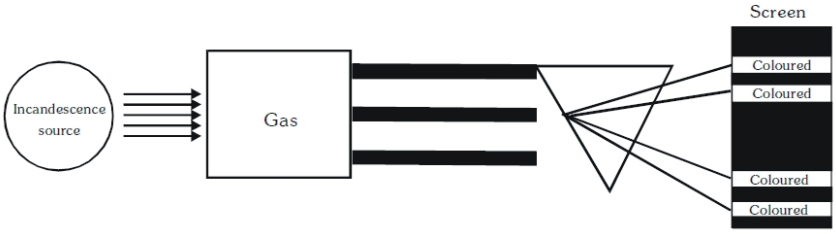

***Note:*** *Since band spectrum are caused by molecules therefore band spectrum are also called as molecular spectrum.*

## 10.2 Absorption spectrum

SL AL

When white light is first passed through a solution or vapours of chemical substance or gas and then analyzed by spectroscope, it is observed that some dark lines are obtained in otherwise continuous spectrum.
This type of spectrum is called as Absorption spectrum.

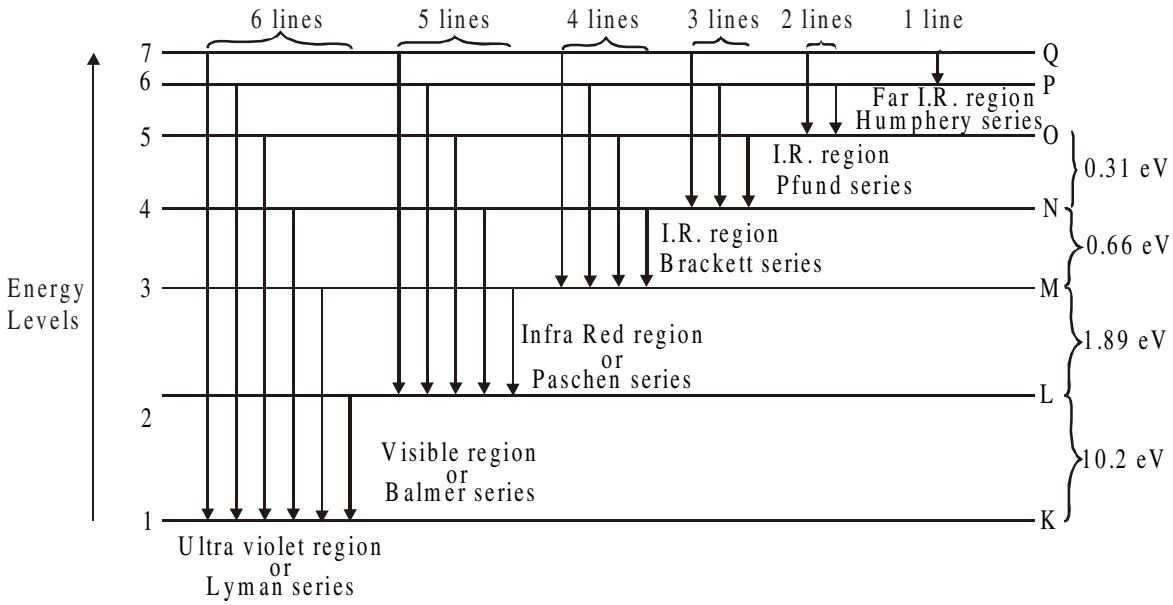
- If white light is passed through atomic gas then the obtained spectrum is called as Absorption line spectrum.
- If white light is passed through molecular gas then the obtained spectrum is called as Absorption band spectrum.




## 10.3 Hydrogen line spectrum or Hydrogen spectrum

SL AL

When an electric excitation is applied on atomic hydrogen gas at Low pressure,a bluish light is emitted. when a ray of this light is passed through a prism, a spectrum of several isolated sharp line is obtained.The wavelength of various lines show that spectrum lines lie in Visible, Ultraviolet and Infra red region. These lines are grouped into different series.



| Series | Discovered by | regions | $n_2 \rightarrow n_1$ | Number of lines |
|---|---|---|---|---|
| lyman | lyman | U.V. region | $n_2 = 2,3,4 \ldots / n_1 = 1$ | $n_2 - 1$ |
| Balmer | Balmer | Visible region | $n_2 = 3,4,5 \ldots / n_1 = 2$ | $n_2 - 2$ |
| Paschen | Paschen | Infra red (I.R.) | $n_2 = 4,5,6 \ldots / n_1 = 3$ | $n_2 - 3$ |
| Bracket | Bracket | I.R. region | $n_2 = 5,6,7 \ldots / n_1 = 4$ | $n_2 - 4$ |
| Pfund | Pfund | I.R. region | $n_2 = 6,7,8 \ldots / n_1 = 5$ | $n_2 - 5$ |
| Humphery | Humphery | far I.R. region | $n_2 = 7,8,9 \ldots / n_1 = 6$ | $n_2 - 6$ |

***KEY POINTS :***

- First line / Starting line / Initial line ( $\lambda_{max.}$ and $\nu_{min}$ )
- Last line / limiting line / Series limit ( $\lambda_{min}$ and $\nu_{max.}$ )
- First line of any series = $\alpha$ line
  Second line of any series = $\beta$ line
  Third line of any series = $\gamma$ line
- Total no. of emission lines between $n_2$ & $n_1$ = $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$, $(n_2 > n_1)$
- For transition from any orbit 'n' to n = 1 , total no. of emission lines = $\frac{n(n-1)}{2}$
- $\frac{1}{\lambda} = \bar{\nu} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \times Z^2$ where $R_H$ represents Rydberg's constant

  value of R = $109677\ cm^{-1} = 10967700 m^{-1}$
  $\simeq 109700\ cm^{-1} \simeq 10970000\ m^{-1}$

  $\frac{1}{R} = 912 Å$

## Illustrations

***Illustration 20.*** In a hydrogen spectrum if electron moves from 7 to 1 orbit by transition in multi steps then find out the total number of lines in the spectrum.

***Solution.***

| | | |
|---|---|---|
| Lyman | = | $(n_1 - 1) = 7 - 1 = 6$ |
| Balmer | = | $(n_2 - 2) = 7 - 2 = 5$ |
| Paschen | = | $(n_2 - 3) = 7 - 3 = 4$ |
| Bracket | = | $(n_2 - 4) = 7 - 4 = 3$ |
| Pfund | = | $(n_2 - 5) = 7 - 5 = 2$ |
| Humphrey | = | $(n_2 - 6) = 7 - 6 = 1$ |
| Total | = | 21 |

Total number of lines can be calculated as follows :

Total number of lines = $\frac{(n_2\text{-}n_1)[(n_2\text{-}n_1)+1]}{2} = \frac{(7\text{-}1)(6+1)}{2} = \frac{42}{2} = 21$

***Illustration 21.*** In a hydrogen spectrum if electron moves from $6^{th}$ to $2^{nd}$ by transition in multi steps then find out the number of lines in spectrum

***Solution.*** Total number of line = 4 + 3 + 2 + 1 + 0
= 10

Total number of lines = $\frac{(n_2 - n_1)[(n_2 - n_1) + 1]}{2} = \frac{(6-2)(4+1)}{2} \Rightarrow \frac{4 \times 5}{2} = 10$

***Illustration 22.*** In a hydrogen spectrum if electron moves from $6^{th}$ to $3^{rd}$ orbit by transition in multi steps then find out the following steps :

***(a)*** Total number of lines in spectrum
***(b)*** Total number of lines in U.V. region
***(c)*** Total number of lines in visible region
***(d)*** Total number of lines in IR region

**Solution.** **(a)** ***Calculation of total number of lines :***

$$= \frac{(n_2 - n_1)[(n_2 - n_1)+1]}{2} = \frac{(6-3)[(6-3)+1]}{2} = \frac{3\times 4}{2} = 6$$

**(b)** Calculation of number lines present in U.V. region.
$e^-$ moves from 6th to 3rd orbit in multisteps.
For U.V. region, $e^-$ should be comes into 1st shell. So the number of lines in U.V. region zero.

**(c)** Calculation of total number of lines in visible region.
For visible region, $e^-$ should be comes into 2nd shell, so the number of lines in visible region zero.

**(d)** Calculation of total number of lines in I.R. region.
In I.R. region, Paschen, Bracket and Pfund series are present.

Number of lines in Paschen series $= n_2 - 3 = 6 - 3 = 3$

Number of lines in Bracket series $= n_2 - 4 = 6 - 4 = 2$

Number of lines in Pfund series $= n_2 - 5 = 6 - 5 = 1$

So total number of lines $= 3 + 2 + 1 = 6$

***Illustration 23.*** In Balmer series of H atom/spectrum, which electronic transitions represents 3rd line ?

**Solution.** In Balmer series

3rd to 2nd → 1line
4th to 2nd → 2 line
5th to 2nd → 3 line
Infinite to 2nd → Last line or limiting line

***So, Ans is***

5th to 2nd line → 3rd line

***Illustration 24.*** In H atom if $e^-$ moves, from $n^{th}$ orbit to 1st orbit by transition in multi steps, if there are total number of lines in spectrum are 10 then find out the value of n.

**Solution.** Total number of lines $= \frac{(n_2 - n_1)[(n_2 - n_1)+1]}{2}$

So, $10 = \frac{(n_2 - n_1)(n_2)}{2}$

$n_2^2 - n_2 - 20 = 0$
$n_2^2 - 5n_2 + 4n_2 - 20 = 0$
$n_2(n_2 - 5) + 4(n_2 - 5) = 0$
$(n_2 + 4)(n_2 - 5) = 0$
$n_2 = 5$

***Illustration 25.*** Calculate the wavelength of 1st line of Balmer series in Hydrogen spectrum.

**Solution.** For first line of Balmer series

$n_1 = 2, n_2 = 3$

$$\frac{1}{\lambda} = R(1)^2\left[\frac{1}{4} - \frac{1}{9}\right] \Rightarrow \frac{1}{\lambda} = R\left[\frac{9-4}{36}\right] \Rightarrow \frac{1}{\lambda} = R\left[\frac{5}{36}\right]$$

$$= \lambda = \frac{36}{5R} \Rightarrow \lambda = \frac{36}{5}\times\frac{1}{R} = \frac{36}{5}\times 912 \text{ Å}$$

$= 6566.4$ Å

**Illustration 26.** Calculate the frequency of the last line of the lyman series in hydrogen spectrum.

**Solution.** For last line of Lyman series $n_1 = 1$, $n_2 = \infty$

$$\frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\frac{1}{\lambda} = R\left(\frac{1}{1} - 0\right)$$

$$\frac{1}{\lambda} = R$$

$$\frac{1}{\lambda} = 109700 \text{ cm}^{-1}$$

$$\upsilon = \frac{C}{\lambda}$$

$$= C \times \frac{1}{\lambda}$$

$$= C \times R$$

$$= 3 \times 10^8 \text{ m sec}^{-1} \times 109700 \text{ cm}^{-1}$$

$$= 3 \times 10^{10} \text{ cm sec}^{-1} \times 109700 \text{ cm}^{-1}$$

$$= 3.29 \times 10^{15} \text{ sec}^{-1}$$

**Illustration 27.** What will be the shortest and longest wavelength of absorption lines of hydrogen gas containing atoms in ground state ? Give Z = 1, R = 109737.5

**Solution.**

$$\frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

For shortest wavelength $\Delta E$ should be maximum for that $n_1 = 1$, $n_2 = \infty$

$$\frac{1}{\lambda} = 109737.5 \text{cm}^{-1} \times 1\left[\frac{1}{1^2} - \frac{1}{\infty}\right] = 109737.5 \text{ cm}^{-1}$$

$\lambda = 911 \times 10^{-8}$ cm

For largest wavelength $\Delta E$ should be minimum so $n_1 = 1$, $n_2 = 2$

$$\frac{1}{\lambda} = 109737.5 \text{ cm}^{-1} \times \left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$

$\lambda = 1215$ Å

**Illustration 28*.** A series of lines in the spectrum of atomic hydrogen lies at wavelengths 656.46, 482.7, 434.17, 410.29 nm. What is the wavelength of next line in this series.

**Solution.** The give series of lines are in the visible region and thus appears to be Balmer series

Therefore, $n_1 = 2$ and $n_2 =$? for next line

If $\lambda = 410.29 \times 10^{-7}$ cm and $n_1 = 2$

$n_2$ may be calculated for the last line

$$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{410.29 \times 10^{-7}} = 109737\left[\frac{1}{2^2} - \frac{1}{n_2^2}\right] \quad n_2 = 6$$

Thus next line will be obtained during the jump of electron from 7th to 2nd shell, i.e.

$$\frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{7^2}\right] = 109737\left[\frac{1}{4} - \frac{1}{49}\right]$$

$\lambda = 397.2 \times 10^{-7}$ cm = 397.2 nm

***Illustration 29*.*** The wave number of $1^{St}$ line of Balmer series of hydrogen spectrum is 15200 $cm^{-1}$ . The wave number of $1^{St}$ line of Balmer series of $Li^{+2}$ spectrum will be ?

***Solution.*** Wave number of $1^{st}$ line of Balmer series of hydrogen spectrum.

$$\bar{v} = \frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

or $$\bar{v} = Z^2 \times R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{for H, Z = 1}$$

$$\bar{v} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 15200\ cm^{-1}$$

Wave number of $1^{st}$ line of Balmer series of $Li^{+2}$ ion is.

$$\bar{v} = Z^2 \times R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \{\because Z = 3 \text{ for } Li^{+2}\}$$

$$\therefore \quad \bar{v} = 3^2 \times 15200 = 9 \times 15200 = 136800\ cm^{-1}$$

***Illustration 30*.*** Calculate the ratio of maximum $\lambda$ of Lyman & Balmer series ?

***Solution.*** $E \ \alpha \ v \propto \frac{1}{\lambda}$

$$\frac{\text{Maximum } \lambda \text{ of Lyman series}}{\text{Maximum } \lambda \text{ of Balmer series}} = \frac{1^{st} \text{ line of Lyman series}}{1^{st} \text{line of Balmer series}}$$

$$\frac{\text{Lyman}}{\text{Balmer}} = \frac{\frac{1}{\lambda_L}}{\frac{1}{\lambda_B}} \Rightarrow \frac{R\left[\frac{1}{1^2} - \frac{1}{2^2}\right]}{R\left[\frac{1}{2^2} - \frac{1}{3^2}\right]}$$

$$= \frac{R\left[\frac{1}{1} - \frac{1}{4}\right]}{R\left[\frac{1}{4} - \frac{1}{9}\right]} = \frac{R\left[\frac{3}{4}\right]}{R\left[\frac{5}{36}\right]}$$

$$\frac{\lambda_B}{\lambda_L} = \frac{27}{5} \Rightarrow \frac{\lambda_L}{\lambda_B} = \frac{5}{27}$$

***Illustration 31.*** A certain electronic transition from an excited state to ground state of the Hydrogen atom in one or more steps gives rise of 5 lines in the ultra violet region of the spectrum.How many lines does this transition produce in the infra red region of the spectrum?

***Solution.*** ***(Lyman Series) ultra violet region :*** 5 Lines i.e. $e^-$ is coming from $6^{th}$ to $1^{st}$ Orbit

$n_2 - 1 = 5 \qquad n_2 = 6$

Infrared region line

***(i)*** Paschen series = (6 – 3) = 3

***(ii)*** Bracket = (6 – 4) = 2

***(iii)*** Pfund = (6 – 5) = 1

***Total Number of lines are = 6***

- **Limitation of the Bohr's model**

  ***(i)*** Bohr's theory does not explain the spectrum of multi electron atom.

  ***(ii)*** Why the Angular momentum of the revolving electron is equal to $\frac{nh}{2\pi}$, has not been explained by Bohr's theory.

  ***(iii)*** Bohr interrelate quantum theory of radiation and classical law of physics with out any theoritical explanation.This was the biggest drawback of this model.

  ***(iv)*** Bohr's theory does not explain the fine structure of the spectral lines. Fine structure of the spectral line is obtained when spectrum is viewed by spectroscope of more resolution power.

  ***(v)*** Bohr theory does not explain the spiliting of spectral lines in the presence of magnetic field ***(Zemman's effect)*** or electric field ***(Stark's effect)***

## BEGINNER'S BOX–4

***Bohr's Atomic model & Spectrum***

***1.*** Wavelength of radiations emitted when an electron jumps from a state A to C is 2000 Å and it is 6000 Å when the electron jumps from state B to state C. Wavelength of the radiations emitted when an electron jumps from state A to B will be

(A) 2000 Å (B) 3000 Å (C) 4000 Å (D) 6000 Å

***2.*** Wave number of a spectral line for a given transition is x $cm^{-1}$ for $He^+$, then its value for $Be^{3+}$ (isoelectronic of $He^+$) for same transition is :

(A) x $cm^{-1}$ (B) 4x $cm^{-1}$ (C) $\frac{x}{4}$ $cm^{-1}$ (D) 2x $cm^{-1}$

***3.*** The ionization energy of a hydrogen like Bohr atom is 4 Rydberg. What is the radius of the first orbit of this atom? (Bohr radius of hydrogen = $5 \times 10^{-11}$ m; 1 Rydberg = $2.2 \times 10^{-18}$ J)

***4.*** The hydrogen atoms in the ground state is excited by means of monochromatic radiations of wavelength $\lambda$ Å. The resulting spectrum consists of maximum 15 different lines. What is the value of $\lambda$. $R_H = 109737$ $cm^{-1}$.

## 11.0 THE DUAL NATURE OF MATTER (THE WAVE NATURE OF ELECTRON)

SL AL

***(i)*** In 1924. a French physicist, Louis De Broglie suggested that if the nature of light is both that of a particle and of a wave, then this dual behavior should be true for the matter also.

***(ii)*** According to De Broglie, the wavelength $\lambda$ of an electron is inversely proportional to its momentum p.

$$\lambda \propto \frac{1}{p} \quad \text{or} \quad \lambda \propto \frac{1}{mv}$$

$\lambda = \frac{h}{p}$ Here h = Planck's constant

p = momentum of electron

$\therefore$ Momentum (p) = Mass (m) $\times$ Velocity (c)

- $\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2m(K.E.)}}$

From the de-Broglie equation it follows that wavelength of a particle decrease with increase in velocity of the particle. Moreover, lighter particles would have longer wavelength than heavier particles, provided velocity is equal.

- If a charged particle Q is accelerated through potential difference V from rest then de-broglie wavelength is

  $$\lambda = \frac{h}{\sqrt{2mQV}}$$

- de-Broglie concept is more significant for microscopic or sub-microscopic particles whose wavelength can be measured.
- The circumference of the $n^{th}$ orbit is equal to n times the wavelength of the electron.

  $2\pi r_n = n\lambda$

- Wavelength of electron is always calculated using De-broglie calculation.

## Illustrations

***Illustration 32.*** Two particles X and Y are in motion. If the wavelength associated with particle X is $4 \times 10^{-8}$ m, calculate the wavelength associated with particle Y if its momentum is half of X.

***Solution.*** According to de Broglie equation

$$\lambda_x = \frac{h}{p_x} \text{ and } \lambda_y = \frac{h}{p_y}$$

$$\frac{\lambda_x}{\lambda_y} = \frac{p_y}{p_x}$$

But $p_y = ½\ p_x$ (given)

$$\frac{\lambda_x}{\lambda_y} = \frac{1/2p_x}{p_x} = ½$$

$\lambda_y = 2\lambda_x = 2 \times 4 \times 10^{-8}\text{m} = 8 \times 10^{-8}\text{m}$

***Illustration 33.*** Calculate the de Broglie wavelength of a ball of mass 0.1 kg moving with a speed of 30 $ms^{-1}$.

***Solution.*** $\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{0.1 \times 30}$

$\lambda = 2.2 \times 10^{-34}$ m

This is apparent that this wavelength is too small for ordinary observation.

Although the de Broglie equation is applicable to all material objects but it has significance only in case of microscopic particles.

Since, we come across macroscopic objects in our everyday life, de Broglie relationship has no significance in everyday life.

## 12.0 HEISENBERG UNCERTAINTY PRINCIPLE

SL AL

- Bohr's theory considers an electron as a material particle. Its position and momentum can be determined with accuracy. But, when an electron is considered in the form of wave as suggested by de-Broglie, it is not possible to ascertain simultaneously the exact position and velocity of the electron more precisely at a given instant since the wave is extending throughout a region of space.
- In 1927, Werner Heisenberg presented a principle known as Heisenberg uncertainty principle which states as : "It is impossible to measure simultaneously the exact position and exact momentum of a body as small as an electron."
- The uncertainty of measurement of position, $\Delta x$, and the uncertainty of momentum $\Delta p$ or $m\Delta v$, are related by Heisenberg's relationship as : ( $p = mv$, $\Delta p = m\Delta v$)

$$\Delta x \,.\, \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \,.\, m\Delta v \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x.\Delta v \geq \frac{h}{4\pi m}$$

where h is Planck's constant.

$\Delta x\, \Delta v$ = uncertainty product

For an electron of mass m ($9.10 \times 10^{-28}$ g), the product of uncertainty is quite large.

$$\Delta x \,.\, \Delta v \geq \frac{6.624 \times 10^{-27}}{4\pi m}$$

$$\geq \frac{6.624 \times 10^{-27}}{4 \times 3.14 \times 9.10 \times 10^{-28}} = 0.57 \text{ erg sec per gram approximately}$$

When $\Delta x = 0$, $\Delta v = \infty$ and vice-versa.

In the case of bigger particles (having considerable mass), the value of uncertainty product is negligible. If the position is known quite accurately, i.e., $\Delta x$ is very small, $\Delta v$ becomes large and vice-versa.

- In terms of uncertainty in energy $\Delta E$, and uncertainty in time $\Delta t$, this principle is written as,

$$\boxed{\Delta E.\Delta t \geq \frac{h}{4\pi}}$$

- Heisenberg replaced the concept of definite orbits by the concept of probability.

# Illustrations

***Illustration 34.*** Why electron cannot exist inside the nucleus according to Heisenberg's uncertainty principle ?

***Solution.*** Diameter of the atomic nucleus is of the order of $10^{-15}$ m

The maximum uncertainty in the position of electron is $10^{-15}$ m.

Mass of electron = $9.1 \times 10^{-31}$ kg.

$$\Delta x.\ \Delta p = \frac{h}{4\pi}$$

$$\Delta x \times (m.\Delta v) = h/4\pi$$

$$\Delta v = \frac{h}{4\pi} \times \frac{1}{\Delta x.m} = \frac{6.63 \times 10^{-34}}{4 \times \frac{22}{7}} \times \frac{1}{10^{-15} \times 9.1 \times 10^{-31}}$$

$\Delta v = 5.80 \times 10^{10}\ ms^{-1}$

This value is much higher than the velocity of light and hence not possible.

***Illustration 35.*** The mass of a particle is 1 mg and its velocity is $4.5 \times 10^5$ cm per second. What should be the wavelength of this particle if $h = 6.652 \times 10^{-27}$ erg second.

(1) $1.4722 \times 10^{-24}$ cm (2) $1.4722 \times 10^{-29}$ cm

(3) $1.4722 \times 10^{-32}$ cm (4) $1.4722 \times 10^{-34}$ cm

***Solution.*** Given that

$m = 1$ mg $= 1 \times 10^{-3}$ g

$c = 4.5 \times 10^5$ cm/sec.

$h = 6.652 \times 10^{-27}$ erg sec.

$$\therefore \lambda = \frac{h}{mc} = \frac{6.652 \times 10^{-27}}{1 \times 10^{-3} \times 4.5 \times 10^5} = \frac{6.652 \times 10^{-29}}{4.5} \text{ cm} = 1.4722 \times 10^{-29} \text{ cm}$$

***Illustration 36.*** Which of the following should be the wavelength of an electron if its mass is $9.1 \times 10^{-31}$ kg and its velocity is 1/10 of that of light and the value of h is $6.6252 \times 10^{-34}$ joule second?

(1) $2.446 \times 10^{-7}$ metre (2) $2.246 \times 10^{-9}$ metre

(3) $2.246 \times 10^{-11}$ metre (4) $2.246 \times 10^{-13}$ metre

***Solution.*** Given that

$m = 9.1 \times 10^{-31}$ kg

$c = \frac{1}{10}$ of velocity of light

or $c = \frac{1}{10} \times 3 \times 10^8$ metre/second i.e. $3 \times 10^7$ metre/second

$h = 6.6252 \times 10^{-34}$ joule second

$$\lambda = \frac{h}{mc} = \frac{6.6252 \times 10^{-34}}{9.1 \times 10^{-31} \times 3 \times 10^7} = \frac{6.6252 \times 10^{-34}}{27.3 \times 10^{-24}}$$

or $0.2426 \times 10^{-10}$ metre

or $2.426 \times 10^{-11}$ metre

***Illustration 37.*** What should be the momentum (in gram cm per second) of a particle if its De Broglie wavelength is 1 Å and the value of h is $6.6252 \times 10^{-27}$ erg second ?

(1) $6.6252 \times 10^{-19}$ (2) $6.6252 \times 10^{-21}$

(3) $6.6252 \times 10^{-24}$ (4) $6.6252 \times 10^{-27}$

***Solution.*** Given that

$\lambda = 1$ Å $= 1 \times 10^{-8}$ cm

$h = 6.6252 \times 10^{-27}$ erg second

$$\text{or } p = \frac{6.6252 \times 10^{-27}}{1 \times 10^{-8}} = 6.6252 \times 10^{-19} \text{ gram cm/sec.}$$

***Illustration 38.*** What should be the uncertainty in the velocity of an electron if the uncertainty in its position is 0.005 nm, the mass of electron is $9.109 \times 10^{-31}$ kg and the value of h is $6.6252 \times 10^{-34}$ joule/second?

(1) $2.316 \times 10^5$ (2) $1.158 \times 10^7$ (3) $2.316 \times 10^9$ (4) $2.316 \times 10^{11}$

***Solution.*** Uncertainty in position ($\Delta x$) = 0.005 nm = $0.005 \times 10^{-9}$ m = $5 \times 10^{-12}$ m

Mass of electron (m) = $9.109 \times 10^{-31}$ kg.

$$\therefore \quad \Delta v = \frac{h}{4\pi m \times \Delta x} = \frac{6.6252 \times 10^{-34}}{4 \times 3.14 \times 5 \times 10^{-12} \times 9.109 \times 10^{-31}} \text{ m/sec.}$$

$$\text{or} \quad \Delta v = \frac{6.6252 \times 10^{-34}}{4 \times 3.14 \times 5 \times 9.109 \times 10^{-43}}$$

$$\therefore \quad \Delta v = 1.15816 \times 10^7 \text{ m/sec.}$$

***Illustration 39.*** What should be the uncertainty in position if uncertainty in momentum is $1 \times 10^{-2}$ g cm/sec. and value of h is $6.6252 \times 10^{-34}$ Joule sec. ?

(1) $1.054 \times 10^{-22}$ m (2) $1.054 \times 10^{-25}$ m

(3) $0.525 \times 10^{-27}$ m (4 ) $1.054 \times 10^{-32}$ m

***Solution.*** Given that

$\Delta p = 1 \times 10^{-2}$ g cm/sec. = $1 \times 10^{-7}$ kg m/sec.

h = $6.6252 \times 10^{-34}$ Joule sec.

$$\Delta x \times \Delta p = \frac{h}{4\pi} \quad \therefore \quad \Delta x = \frac{h}{4\pi \times \Delta p}$$

$$\text{or} \quad \Delta x = \frac{6.6252 \times 10^{-34}}{4 \times 3.14 \times 10^{-7}} = 0.525 \times 10^{-27} \text{ m}$$

***Illustration 40.*** Which of the following has least De Broglie $\lambda$ if they have same velocity.

***1.*** $e^-$ ***2.*** p ***3.*** $CO_2$ ***4.*** $SO_2$

***Solution.*** $\lambda = \dfrac{h}{mv}$

$\therefore$ mass of $SO_2$ is greater than the mass of $e^-$, p, $CO_2$

= h constant

= v Same

$\therefore$ least $\lambda$ will be $SO_2$

$$\therefore \quad \lambda \propto \frac{1}{m}$$

***Illustration 41.*** If uncertainty in position of an $e^-$ is same as the $\Delta x$ of He atom. If $\Delta p$ of $e^-$ is $32 \times 10^5$ then find $\Delta p$ in He atom.

***Solution.*** $\Delta x \times \Delta p = \dfrac{h}{4\pi}$

Since $\Delta x$ is same for both.

therefore $\Delta p$ will be same by

$$\frac{\Delta x_e \times \Delta p_e \geq \frac{h}{4\pi}}{\Delta x_{(He)} \times \Delta P_{He} \geq \frac{h}{4\pi}} = \frac{\Delta Pe}{\Delta P_{He}} = 1$$

$\therefore \quad \Delta P_e = \Delta P_{He}$

$32 \times 10^5 = 32 \times 10^5$

$\Delta P_{He} = 32 \times 10^5$

***Illustration 42.*** Calculate the uncertainty in the position of a particle when the uncertainty in momentum is
***(a)*** $1 \times 10^{-3}$g cm sec$^{-1}$ ***(b)*** Zero.

***Solution.*** Given

$\Delta p = 1 \times 10^{-3}$ g cm sec$^{-1}$

$h = 6.62 \times 10^{-27}$ erg sec.

$\pi = 3.142$

According to uncertainty principle

$$\Delta x.\Delta p \geq \frac{h}{4\pi}$$

So, $$\Delta x \geq \frac{h}{4\pi}.\frac{1}{\Delta p}$$

$$\geq \frac{6.62\times10^{-27}}{4\times3.142}\times\frac{1}{10^{-3}} = 0.527 \times 10^{-24} \text{ cm}$$

(b) When the value of $\Delta p = 0$, the value of $\Delta x$ will be infinity.

## BEGINNER'S BOX–5

### *Heisenberg uncertainty principle*

**1.** Alveoli are the tiny sacs of air in the lungs whose average diameter is 50 pm. Consider an oxygen molecule trapped within a sac. Calculate uncertainty in the velocity of oxygen molecule?
(A) $1.98 \times 10^{-2}$ ms$^{-1}$ (B) 19.8 ms$^{-1}$ (C) $198 \times 10^{-4}$ ms$^{-1}$ (D) $19.8 \times 10^{-6}$ms$^{-1}$

**2.** Determine the de-Broglie wavelength associated with an electron in the 3rd Bohr's orbit of $He^+$ ion?
(A) 10 Å (B) 2 A (C) 5 Å (D) 1 Å

**3.** What is the potential drop through which an electron, with a de Broglie wavelength of 1.5Å, should be accelerated, if its de Broglie wavelength sholud be reduced to 1 Å?
(A) 110 volts (B) 70 volts (C) 83 volts (D) 55 volts

**4.** If $E_1$, $E_2$ and $E_3$ represent respectively the kinetic energies of an electron, an alpha particle and a proton each having same de Broglie wavelength then:
(A) $E_1 > E_3 > E_2$ (B) $E_2 > E_3 > E_1$ (C) $E_1 > E_2 > E_3$ (D) $E_1 = E_2 = E_3$

**5.** If the light of wavelength $5.77 \times 10^{-10}$ cm is used to detect an electron, then the uncertainly in velocity (approximately) will be– ($h = 6.6 \times 10^{-34}$ Js, $m_e = 9.1 \times 10^{-31}$ kg).
(A) $10^6$ m/s (B) $10^5$ m/s (C) $10^7$ m/s (D) None of these

**6*.** Which of the following statement is true referred to the above paragraph :
***I.*** Higher is the mass of the particle, error in measurement of velocity reduces.
***II.*** For an electron if uncertainly in position tends to zero then uncertainly in momentum is extremely small.
***III.*** If $\lambda_1 > \lambda_2$ are the two different wavelength used to detect the position of electron and uncertainty in velocity be $v_1$ and $v_2$ respectively then $v_2 > v_1$
(A) only I (B) I and II (C) I,II & III (D) I and III

**7.** The uncertainty in position and velocity of the particle are 0.1 nm and $5.27\times10^{-24}$ ms$^{-1}$ respectively, then the mass of the particle is : ($h = 6.625 \times 10^{-34}$Js)
(A) 200 g (B) 300 g (C) 100 g (D) 1000 g

**8.** In H-atom, if 'x' is the radius of the first Bohr orbit, de Broglie wavelength of an electron in 3rd orbit is :
(A) $3\pi x$ (B) $6\pi x$ (C) $\frac{9x}{2}$ (D) $\frac{x}{2}$

**9*.** Monochromatic radiation of wavelength $\lambda$ is incident on a hydrogen sample in ground state. Hydrogen atoms absorb a fraction of light and subsequently emit radiations of six different wavelengths. Find the wavelength $\lambda$
(A) 97.2 nm (B) 121.6 nm (C) 110.3 nm (D) none of these

# 13.0 WAVE MECHANICAL MODEL OF ATOM

## 13.1 Concept of Orbitals

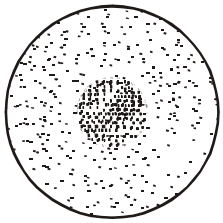
SL AL

According to Heisenberg's uncertainty principle it is not possible to determine precisely the position and momentum of an electron in the atom simultaneously. Therefore , Bohr's concept of well defined orbits is ruled out. In quantum mechanical model, we speak of probability or possibility of an electron with a particular energy being present in a certain region of space around the nucleus. The probability of finding the electron at a particular location is given by the square of wave function ($|\psi|^2$) corresponding to that location. There are certain regions around the nucleus where probability of finding the electron is high and there are certain regions where probability of finding the electron is low. The probability of finding the electron does not become zero even at large distances from the nucleus, although it may become negligible. Therefore, is not possible to draw a boundary that will enclose the region of 100 % probability.

However, for the sake of simplicity we draw arbitrary boundaries which enclose the regions where probability of finding the electron is maximum (about 90-95%). These regions of space around the nucleus where probability of finding the electron is maximum are called orbitals.

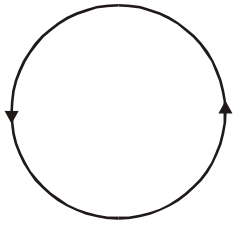
***An orbital may be defined as that region of space around the nucleus where the probility of finding an electron is maximum (90-95%).***

It is rather difficult to represent an orbital by a simple picture. Different methods are employed for this purpose. But the most common method is to represent an orbital as an electron cloud in terms of small dots, the intensity of dots being more in some region and less in other.



***Orbital***

***Electron-cloud representation of an orbital***



***Orbit***

***Bohr's orbit***

In terms of electron cloud representation, the probability of finding an electron in a particular region of space is directly proportional to the density of dots in that region.

The important differences between an ***orbit*** and an ***orbital*** are given in table.

***Differences between an Orbit and an Orbital :***

| | Orbit | | Orbital |
|---|---|---|---|
| 1. | It is a well-defined circular path followed by revolving electron around the nucleus. | 1. | It is a region of space around the nucleus of the atom where the electron is most likely to be found. |
| 2. | It represents planar motion of an electron. | 2. | It represents three-dimensional motion of an electron around the nucleus. |
| 3. | The maximum number of electrons in an orbit is $2n^2$ , where n stands for | 3. | An orbital cannot accommodate more than two electrons. |
| 4. | Orbits are circular in shape. | 4. | Orbitals have different shapes, e.g., s-orbitals are spherically symmetrical whereas p-orbitals are dumb-bell shaped. |
| 5. | Orbits are non-directional in character hence they cannot explain shapes of molecules. | 5. | Orbitals (expects s-orbitals) have directional character and hence they can account for shapes of molecules. |
| 6. | Concept of well-defined orbit is against Heisenberg's principle. | 6. | Concept of orbital is in accordance with Heisenberg's principle |

## 13.2 The wave function

SL AL

Each "Particle" is represented by a wave function Ψ(position, time) such that Ψ*Ψ = the probability of finding the particle at that position at that time.

The wavefunction is used in the Schrodinger equation. The Schrodinger equation plays the role of Newtons' laws and conservation of energy in classical mechanics - i.e., it predicts the future behaviour of a dynamic system. It does not predict analytically and precisely detailed outcome of an experiment, but given a large number of events, the Schrodinger equation will predict the distribution of results.

- Contains all the measurable information about the particle.
- Ψ*Ψ summed over all space = 1,
  (If particle exists, probability of finding it somewhere must be one)
- It is continuous.
- Allows energy calculations via the Schrodinger equation.
- Establishes the probability distribution in three dimensions.
- Permits calculation of most probable value (expectation value) of a given variable.

## 13.3 Schrodinger Equation in Cartesien Coordinates

SL AL

$$\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right)+\frac{8\pi^2 m}{h^2}(E-V)\Psi=0$$ ***Three dimension Schrodinger equation***

$$\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$$ ***One dimension Schrodinger equation***

Ψ = Wave function = f(x, y, z)
E = Total energy of particle
V = Potential energy of particle.

- The Schrodinger equation is a second order differential equation. It has infinite solutions.
- Out of infinite solutions only those solution are acceptable in which Ψ is continuous, finite and single valued.
- When solved with certain restriction , called boundary condition - only finite number of solutions are obtained.
- The acceptable solution corresponds to different states of electron in an atom.

***Significance of ψ***

***(i)*** ψ gives the complete description of state of system (like electron in an atom)
***(ii)*** ψ represents probability amplitude of particle wave.
***(iii)*** As such ψ has no physical significance.
***(iv)*** In an atom, each ψ represent an orbital like $\psi_{1s}$, $\psi_{2s}$, $\psi_{2p}$, etc.

***Significance of $\psi^2$***

The $\psi^2$ gives probability density of finding a particle at a point in space.
For electromagnetic waves intensity of light (I) is proportional to square of amplitude.

$$I \propto A^2 \propto \text{no. of photons}$$

Similarity $\psi^2 \propto$ probability of finding a particle in space.
This interpretation was given by Born hence known as ***Born interpretation***.
Probability of finding a particle in space in infinitesimally small volume element dv = dx dy dz, situated at coordinate (x, y, z) is :

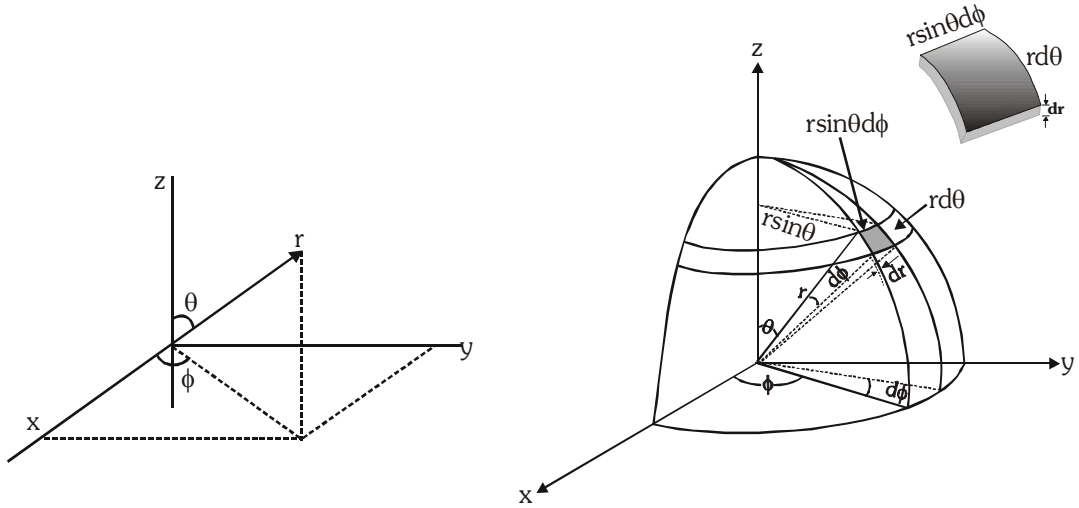
***Probability = $[\Psi(x, y, z)]^2$ (dx dy dz)***

***Probability density at a point (x,y,z) in space = $[\psi(x, y, z)]^2$***

## 13.4 Schrodinger Equation in Polar Coordinates

SL AL

It is difficult to solve the schrodinger equation for H-atom in cartesian coordinates. Hence the equation is transformed from cartesian to polar coordinates.




$$\psi\ (x\ ,\ y,\ z)\ =\ R(r).\Theta(\theta)\ \Phi(\phi)$$

The differential equation is transformed into polar coordinates by proper substitution, the resulting differential equation in polar coordinates is broken into three independent equations.

The three independent equations are :

***(a)*** Radial equation,

***(b)*** Zenith equations,

***(c)*** Azimuthal equation

The three equations are solved separately. The solution to radial equation which contain only 'r' terms gives radial function R. The solution to angular equation which contain only θ term give angular wave function Θ. The solution to azimuthal equation to give azimuthal function Φ. These three independent solution are combined to give complete wave function.

$$\psi\ =\ r.\theta.\phi$$

***Probability density at a point (r,θ,ϕ) in space*** $= \left[R(r)\Theta(\theta).\Phi(\phi)\right]^2$

Probability of finding an electron at coordinate (r,θ,ϕ) in infinitesimally small volume element $dv = r^2 \sin\theta\, d\theta\, d\phi\, dr$ is :

$$\textit{Probability} = \left[R(r)\,\Theta(\theta)\,\Phi(\phi)\right]^2 .r^2 .\sin\theta.d\theta\, d\phi\, dr$$

Radial probability density is probability density at distance r in a specified direction. Radial probability density at a constant angle is $= [R(r)]^2$.

Radial probability in a volume $4\pi r^2$.dr at distance 'r' from nucleus $= [R(r)]^2 . 4\pi r^2 .dr$

***Radial probability distribution*** $[P(r)] = [R(r)]^2\, 4\pi r^2$

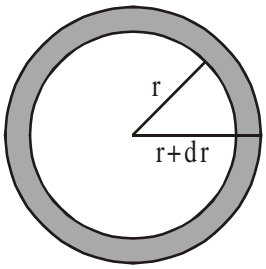
Radial probability distribution gives spherical sense of probability without any specified direction.

## 13.6 Radial probability distribution function (rpdf), $4\pi\, r^2 \psi^2(r)$

SL AL

It is often useful to know the likelihood of finding the electron in an orbital at any given distance away from the nucleus. This enables us to say at what distance from the nucleus the electron is most likely to be found, and also how tightly or loosely the electron is bound in a particular atom. This is expressed by the radial distribution function. For s-orbitals, the radial distribution function is given by multiplying the electron density by $4\pi r^2 \psi^2(r)$. Radial distribution function is the measure of the probability of finding the electron in a spherical shell between thickness r and (r + dr) from the nucleus, irrespective of the direction. For 1s orbital of H-atom : The wave function $\psi_1$,is independent of the angles θ and ϕ , and the desired probability is found by multiplying $|\psi^2|$ by volume of the thin shell.

❖ ***Volume of radial shell :***




$$= \begin{bmatrix}\text{Volume of sphere}\\ \text{with radius}\,(r+dr)\end{bmatrix} - \begin{bmatrix}\text{Volume of sphere}\\ \text{with radius}\,r\end{bmatrix}$$

$$= \frac{4}{3}\pi(r+dr)^3 - \frac{4}{3}\pi r^3$$

$$= \frac{4}{3}\pi(r^3 + 3r^2dr + 3rdr^2 + dr^3) - \frac{4}{3}\pi r^3 = \frac{4}{3}\pi[r^3 + 3r^2dr - r^3]$$

(As dr represents an extremely small thickness, the higher powers of dr such as $dr^2$ and $dr^3$ may be neglected.)

$\therefore$ Volume of shell $= \frac{4}{3}\pi \times 3r^2dr) = 4\pi r^2dr$

***Radial probability distribution = Radial probability density × Volume of radial shell***
***$= 4\pi r^2 \psi^2(r)dr$***

If we observe the radial probability distribution curve of 1s orbital, we find that it is quite different from radial probability density graph ($\psi^2$ vs. r). The radial probability density ($\psi^2$) is maximum close to the nucleus but the total probability is least corresponding to this volume. This is due to the reason that the volume of the shell near the nucleus is very small resulting in a small value of total probability. It is zero at the nucleus. As the distance from the nucleus increases the volume of the radial shell increases while $\psi^2$ decreases rapidly.

As a result of this, the probability keeps on increasing gradually and reaches a maximum value and then decreases gradually. The maximum in the curve indicates the most probable value and the corresponding distance from the nucleus is called distance of maximum probability ($r_0$). For hydrogen atom, this radius has a value of 53 pm.It is important to note that Bohr predicted that the electron will always be at r = 53 pm for hydrogen atom. However, according to wave mechanical model the electron is most likely to be found at this distance and there is probability of finding the electron at distances both shorter and larger than 53 pm.

❖ ***Chracteristics of radial distribution function :***

***(i)*** The number of maxima in radial distribution function plot are (n – 1).

***(ii)*** The maximum probability of finding the electron, for the ground state hydrogen atom (1s) is found to be at $a_0$ (first Bohr radius).

***(iii)*** For 2s, 3s, 3p orbitals, the number of maxima is more than one, indicating that there is maximum probability of finding the electron at the distance corresponding to the highest value of peak.
However, there is lesser probability of finding the electron at the other peaks. It shows that in a certain state, the electron spends some portion of its time very close to the nucleus.

***Ex.*** Find the distance at which probability of finding electron is maximum for 1s orbital in a He atom. The wave function orbital given as. $\psi_{1s} = \frac{4}{a_0^{3/2}}.e^{-\frac{2r}{a_0}}$

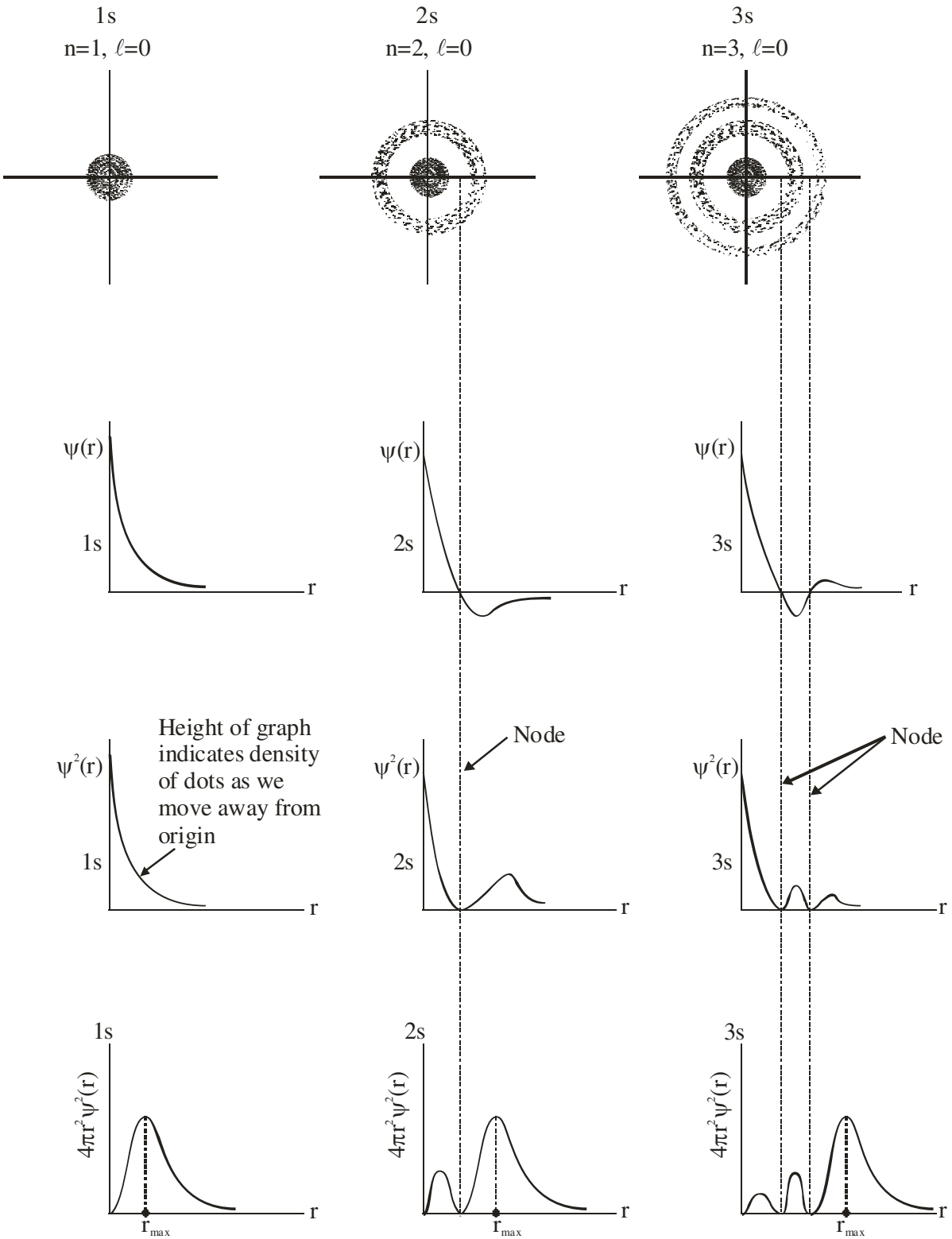
***Sol.*** Probability distribution function is $P(r) = \psi^2.4\pi r^2 = \left(\frac{16}{a_0^3}\right)e^{\left(-\frac{4r}{a_0}\right)}.4\pi r^2 \Rightarrow P(r) = k\,.\,r^2.\,e^{\frac{-4r}{a_0}}$

differentating $\frac{dP(r)}{dr} = 2r.e^{-\frac{4r}{a_0}} - \left(\frac{4}{a_0}\right)r^2.e^{-\frac{4r}{a_0}} = 0 \Rightarrow 1 = \frac{2r}{a_0} \Rightarrow r = \frac{a_0}{2}$

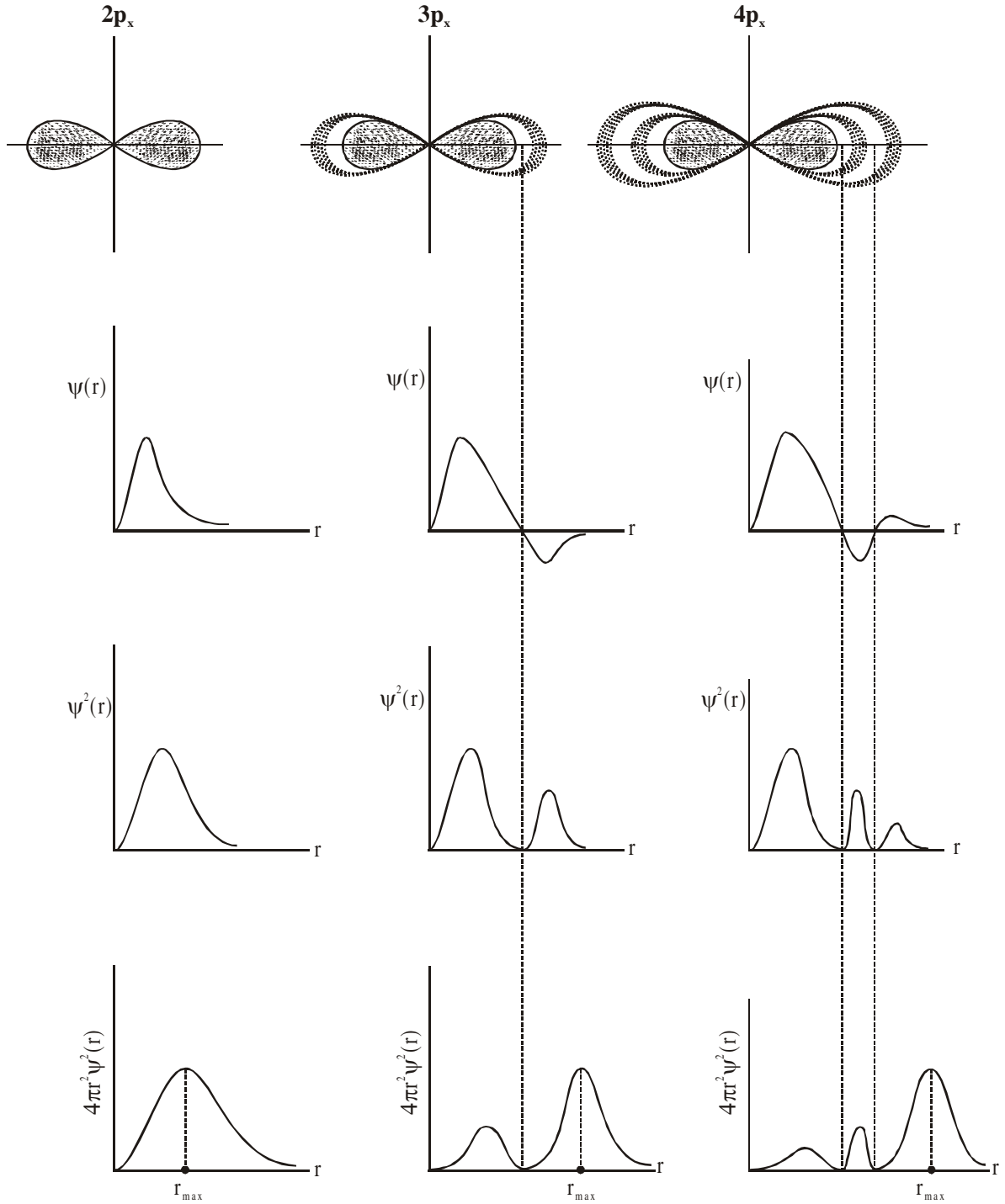
$\Rightarrow$ probability of finding electron is maximum at distance $\frac{a_0}{2}$ from nucleus.

❖ ***Electron-density distribution in 1s, 2s and 3s-orbitals***

The lower part of the fig. shows how the electron density, represented by $\psi^2$ varies as a function of distance from the nucleus. In the 2s and 3s - orbitals, the electron-density function drops to zero at certain distances from the nucleus. The spherical surfaces around the nucleus at which $\psi^2$ is zero are called nodes.


1s
n=1, ℓ=0
2s
n=2, ℓ=0
3s
n=3, ℓ=0
ψ(r)
1s
2s
3s
r
ψ²(r)
Height of graph indicates density of dots as we move away from origin
Node
Node
4πr²ψ²(r)
r_max

❖ ***Electron-density distribution in $2p_x$, $3p_x$ and $4p_x$-orbitals :***



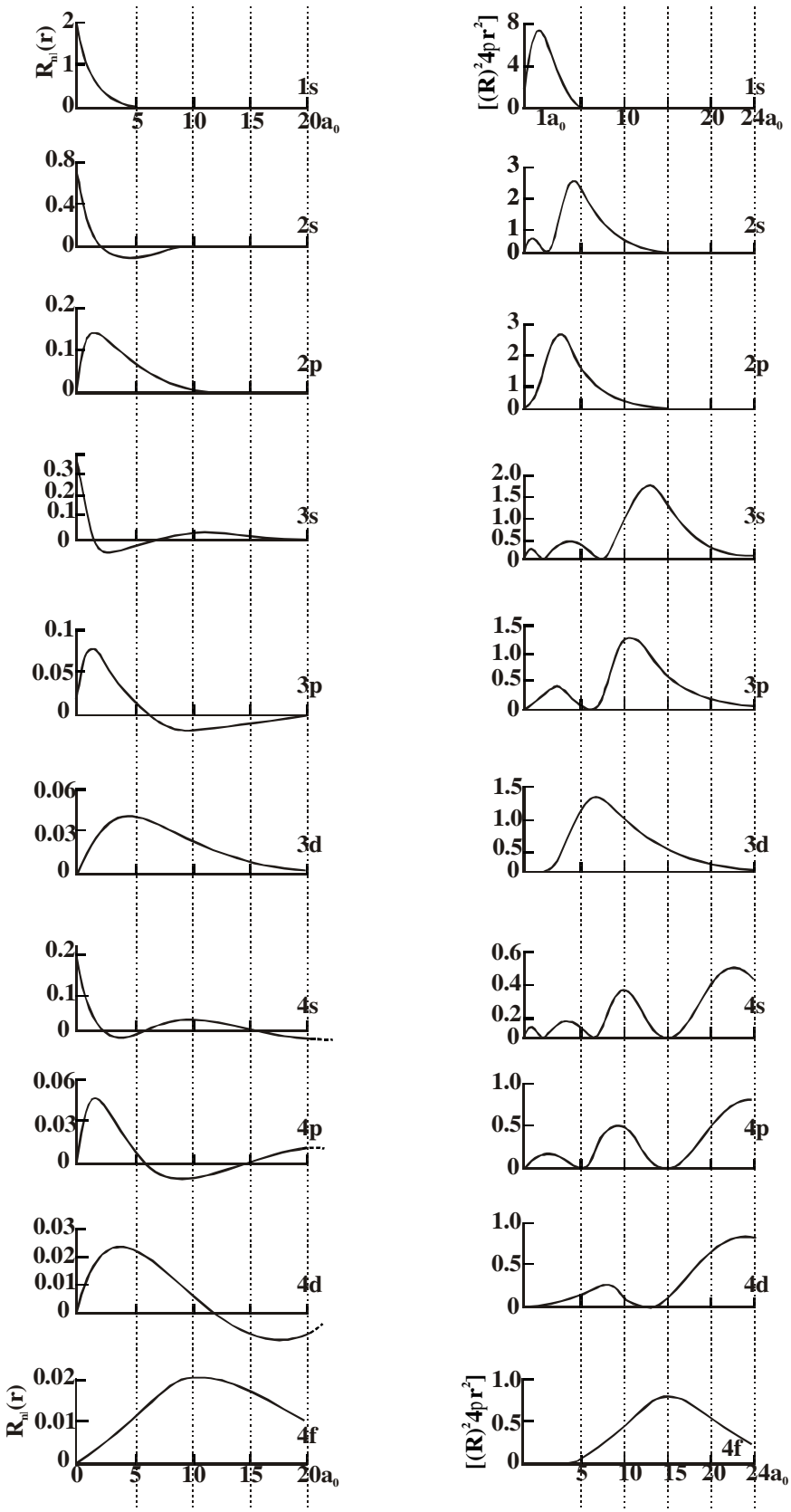


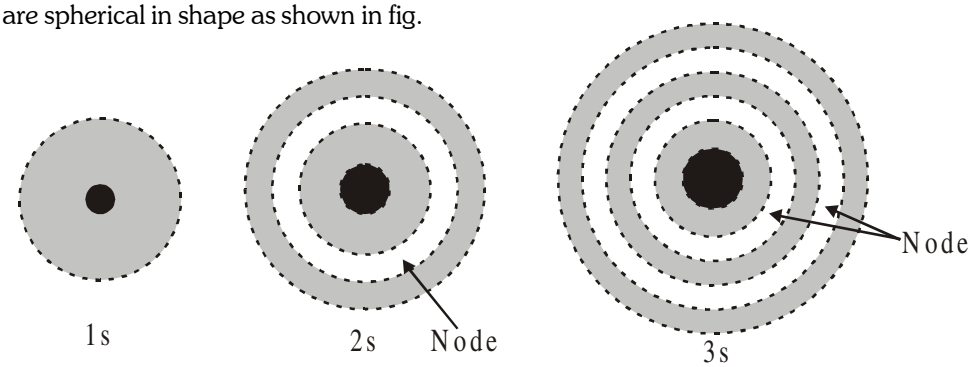

***Fig.*** *Radial function $R_{n\ell}(r)$ and radial probability distribution $[(R)^2 4\pi r^2]$ for the hydrogen like atom in the 1s state & thereby show that the most probable radial position, i.e., the radius with the highest radial probability density, is $a_0/Z$.*

## 13.7 Angular Probability distrubtion function

The angular probability gives an idea of shape and orientation of the orbitals.

❖ ***Shapes of s-orbitals***

The s-orbitals are spherically symmetrical about the nucleus, i.e., the probability of finding s electron is same in all directions from the nuclesus. The size of the orbital depends on the value of principal quantum number, there is one spherically symmetrical orbital. The 1s orbital is smaller than 2s-orbital and 2s-orbital is smaller than 3s, but all are spherical in shape as shown in fig.

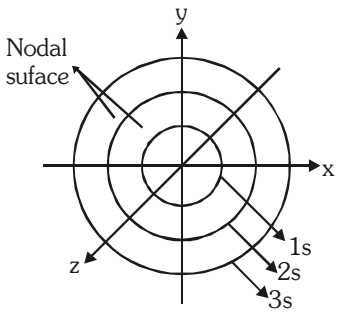



***Although the s-orbitals belonging to different shells are spherically symmetrical, yet they differ in certain respects as explained below :***

***(i)*** The probability of 1s electron is found to be maximum near the nucleus and decreases as the distance from the nucleus increases. In case of 2s electrons, the probability is again maximum near the nucleus and then decreases to zero and increases again and then decreases as the distance from the nucleus from the nucleus increases. The intermediate region (a spherical shell) where the probability is zero is called a nodal surface or simply node. Thus, 2s-orbital differs from 1s-orbital in having one node within it. Similarly, 3s has two nodes. in general, any ns orbital has (n -1) nodes.

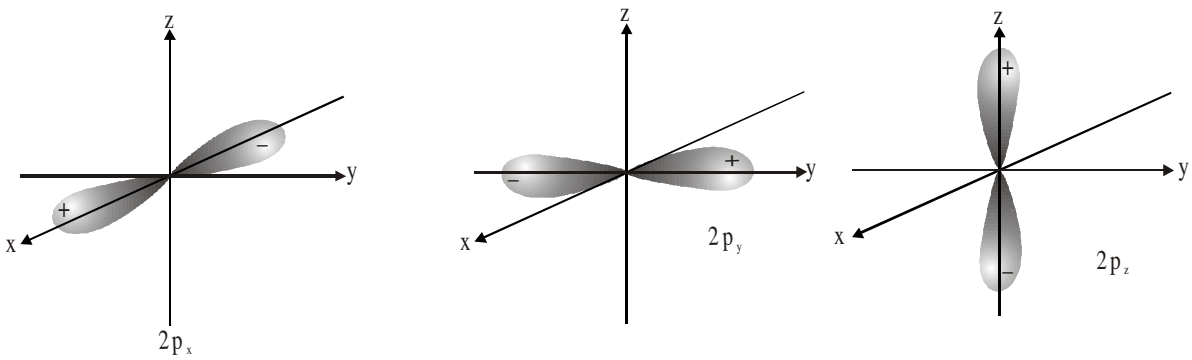
***(ii)*** The size and energy of the s-orbital increases as the principal quantum number inreases, i.e., the size and energy of s-orbital increases in the order 1s < 2s < 3s ....

***The s orbital of higher energy levels are also symmetrically spherical and can be represented as follows :***

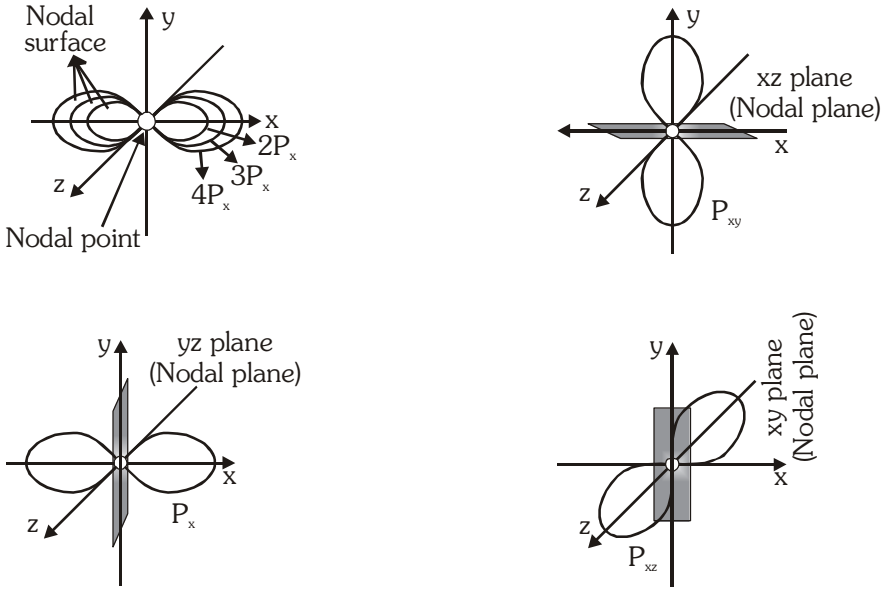



❖ ***Shape of p-orbitals***

There are three p-orbitals, commonly referred to as $p_x$, $p_y$ and $p_z$. These three p-orbitals, possess equivalent energy and therefore, have same relation with the nucleus. They, however, differ in their direction & distribution of the charge. These three p-orbitals are situated at right angle to another and are directed along x, y and z-axes (figure)



- Each p orbital has dumb bell shape (2 lobes which are separated from each other by a point of zero probability called nodal point or nucleus).
- The two lobes of each orbital are separated by a plane of zero electron density called nodal plane.
- Each p orbital of higher energy level are also dumb bell shape but they have nodal surface.

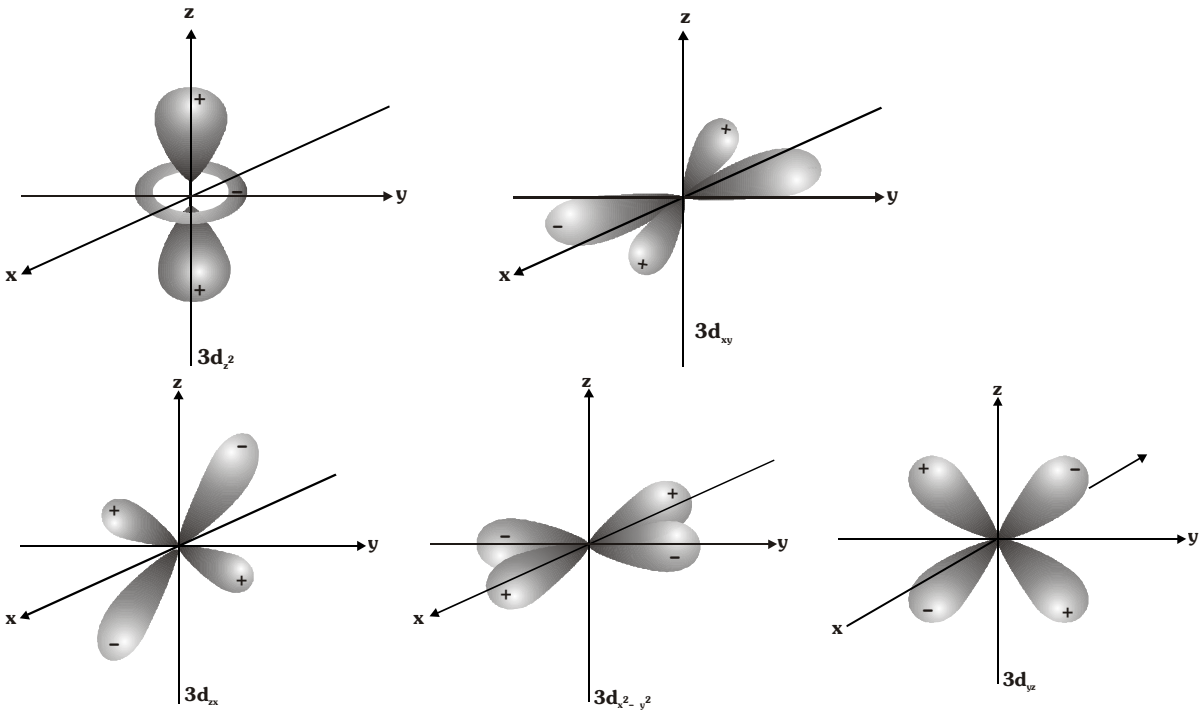



❖ ***Shape of d-orbitals***

When $\ell = 2$, 'm' has five values $-2, -1, 0, +1, +2$. It implies that d subshell of any energy shell has five orbitals. All the five orbitals are not identical in shape. Four of the d orbitals $d_{xy}$, $d_{yz}$, $d_{xz}$, $d_{x^2-y^2}$ contain four lobes while fifth orbital $d_{z^2}$ consists of only two lobes. The lobes $d_{xy}$ orbital lie between x and y axis. Similar is the case for $d_{yz}$ and $d_{xz}$. Four lobes of $d_{x^2-y^2}$ orbital are lying along x and y axis while the two lobes of $d_{z^2}$ orbital are lying along z axis and contain a ring of negative charge surrounding the nucleus in xy plane.

$m = -2, -1, 0, +1, +2$

Geometry of these $\left(d_{xy}, d_{yz}, d_{zx}, d_{z^2}, d_{x^2-y^2}\right)$ orbits $\rightarrow$ double dumb bell



❖ ***In d orbital***

***(i)*** Nodal Point → 1

***(ii)*** Nodal surfaces (Radial nodes) :

$3\,d_{xy}$ → 0 Nodal surface

$4\,d_{xy}$ → 1 Nodal surface

$5\,d_{xy}$ → 2 Nodal surfaces

$n\,d_{xy}$ → ( n – 3 ) Nodal surfaces

***(iii)*** Nodal plane (Angular nodes) :

$d_{xy}$ → xz & yz nodal plane

$d_{xz}$ → xy & zy nodal plane

$d_{zy}$ → zx & yx nodal plane

$d_{x^2-y^2}$ → 2, nodal planes at 45° angle to X-axis.

$d_{z^2}$ → 2 conical shape nodes

☞ ***Note :***

Orbitals of d subshell are equivalent in energy $d_{z^2}$ does not have any nodal plane.

❖ ***f-subshell***

When $\ell = 3$ (f subshell)

Then m = –3, –2, –1 , 0 , +1 , +2 , +3

- The structure of f-orbital is very complex
- f-subshell show that f subshell has 7 orbitals which are equivalent in Energy.

❖ ***Representation of the orbitals***

s subshell → | s | orbital

p subshell → | $p_x$ | $p_y$ | $p_z$ | orbital

d subshell → | $d_{xy}$ | $d_{yz}$ | $d_{z^2}$ | $d_{xz}$ | $d_{x^2-y^2}$ | orbital

f subshell → | $f_{x^3}$ | $f_{y^3}$ | $f_{z^3}$ | $f_{xyz}$ | $f_{x(y^2-z^2)}$ | $f_{y(z^2-x^2)}$ | $f_{z(x^2-y^2)}$ | orbital

## BEGINNER'S BOX–7

***Wave mechanical model***

***1*.*** Consider ψ (wave function) of 2s atomic orbital of H-atom is -

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}\,a_0^{3/2}}\left[2 - \frac{r}{a_0}\right]e^{-\frac{r}{2a_0}}$$

Find distance of radial node from nucleus in terms of $a_0$.

(A) $r = a_0$ (B) $r = 2\,a_0$ (C) $r = a_0$ (D) data insufficient

***2*.*** For an orbital in $B^{+4}$ radial function is :

$$R(r) = \frac{1}{9\sqrt{6}}\left(\frac{z}{a_0}\right)^{\frac{3}{4}}(4-\sigma)\sigma\, e^{-\sigma/2}$$

where $\sigma = \frac{Zr}{a_0}$ and $a_0 = 0.529$ Å ; Z = atomic number, r = radial distance from nucleus.

The radial node of orbital is at distance from nucleus.

(A) 0.529 Å (B) 2.12 Å (C) 1.06 Å (D) 0.423 Å

**3*.** The wave function for an orbital is H-atom is given as

$$\left(\frac{\sqrt{2}}{81\sqrt{\pi}}\right)\left(\frac{1}{a_0}\right)^{\frac{3}{2}}\left(6-\frac{r}{a_0}\right)\left(\frac{r}{a_0}\right)e^{-\frac{r}{3a_0}}.\sin\theta\sin\phi$$

The orbital is :

(A) 2s (B) 3p (C) 2p (D) 3d

**4*.** $\psi_{1s}=\frac{1}{\sqrt{\pi}a_0^{3/2}}e^{-\frac{r}{a_0}}$

Find the distance 'r' from nucleus at which $e^-$ finding probability is max. [For H-atom] $a_0 \rightarrow$ I Bohr radius.

***Comprehension for Q. 5 to Q.7***

According to quantum mechanical model of H-like species, an electron can be represented by a wave function ($\psi$) which contains all dynamic information about the electron. The nature of wave function depends on the type of the orbital to which the electron belongs.

For an orbital

$$\psi=\left[\frac{\sqrt{2}}{81\sqrt{3\pi}}\right]\left(\frac{1}{a_0}\right)^{3/2}(27-18\sigma+2\sigma^2)e^{-\frac{\sigma}{3}}$$

Where, $\sigma=\left(\frac{Zr}{a_0}\right)$, r = radial distance from nucleus, $a_0$ = 52.9 pm

**5*.** The number of radial and angular nodes possible for the orbital given above are respectively :

(A) zero, zero (B) 0, 2 (C) 2, 0 (D) 2, 1

**6*.** The orbital could possibly be :

(A) 4s (B) 4p (C) 3s (D) 3p

**7*.** Which of the following represents the position of one of the radial nodes for Z = 1 ?

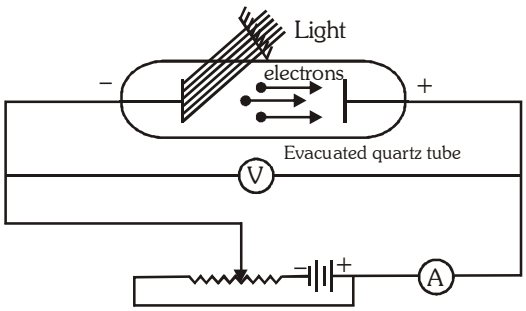
(A) $r=\frac{1}{2}(3+\sqrt{3})a_0$ (B) $r=\frac{1}{2}(3-\sqrt{3})a_0$ (C) $r=\frac{3}{2}(3-\sqrt{6})a_0$ (D) $r=\frac{3}{2}(3+\sqrt{3})a_0$

## 17.0 PHOTOELECTRIC EFFECT

SL AL

***(i)*** Sir J.J. Thomson observed that when a light of certain frequency strikes the surface of a metal, electrons are ejected from the metal. This phenomenon is known as photoelectric effect and the ejected electrons are called photoelectrons.

***(ii)*** A few metals, which are having low ionisation energy like Cesium, show this effect under the action of visible light but many more show it under the action of more energetic ultraviolet light.



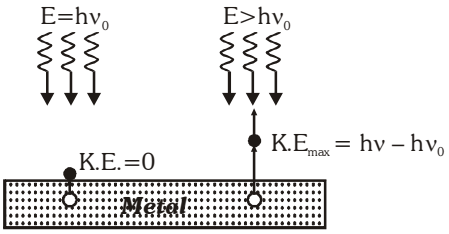
***The experimental findings are summarized as below :***

- Electrons come out as soon as the light (of sufficient energy) strikes the metal surface.

- The light of any frequency will not be able to cause ejection of electrons from a metal surface. There is a minimum frequency, called the threshold (or critical) frequency, which can just cause the ejection. This frequency varies with the nature of the metal. The higher the frequency of the light, the more energy the photoelectrons have. Blue light results in faster electrons than red light.

- Photoelectric current is increased with increase intensity of light of same frequency, if emission is permitted, i.e. a bright light yields more photoelectrons than a dim one of the same frequency, but the electron energies remain the same.

- Light must have stream of energy particles or quanta of energy ($h\nu$). Suppose, the threshold frequency of light required ejecting electrons from a metal is $\nu_0$, when a photon of light of this frequency strikes a metal it imparts its entire energy ($h\nu_0$) to the electron.




"This energy enables the electron to break away from the atom by overcoming the attractive influence of the nucleus". Thus each photon can eject one electron. If the frequency of light is less than $\nu_0$ there is no ejection of electron. If the frequency of light is higher than $\nu_0$ (let it be $\nu$), the photon of this light having higher energy ($h\nu$), will impart some energy to the electron that is needed to remove it away from the atom. The excess energy would give a certain velocity (i.e. kinetic energy) to the electron.

$$h\nu = h\nu_0 + K.E.$$

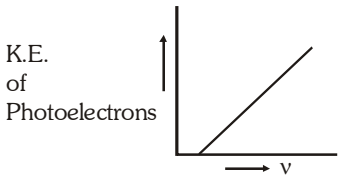
$$h\nu = h\nu_0 + \tfrac{1}{2}\ m\nu^2$$

$$\tfrac{1}{2}\ m\nu^2 = h\nu - h\nu_0$$

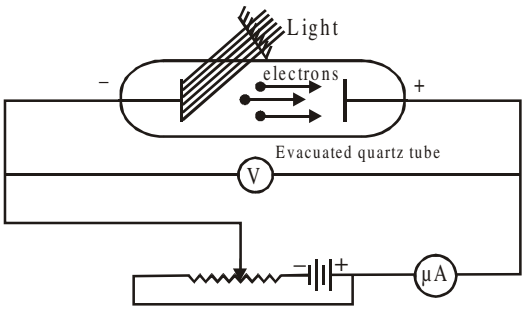
where $\nu$ = frequency of the incident light

$\nu_0$ = threshould frequency

$h\nu_0$ is the threshold energy (or) the work function denoted by $\phi = h\nu_0$ (minimum energy of the photon to liberate electron). It is constant for particular metal and is also equal to the ionization potential of gaseous atoms. The kinetic energy of the photoelectrons increases linearly with the frequency of incident light. This, if the energy of the ejected electrons is plotted as a function of frequency, it result in a straight line whose slope is equal to Planck's constant 'h' and whose intercept is $h\nu_0$.



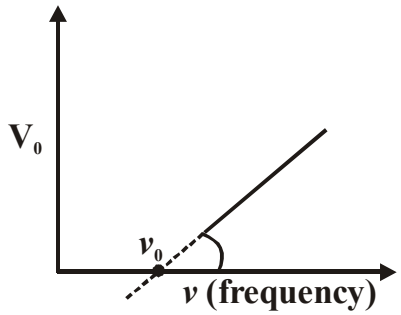

❖ ***Stopping Potential ($V_0$)***




When a suitable radiation is incident on the surface of metal plate, electrons are ejected from its surface. If the collector is at a positive terminal w.r.t. emitter E, the electrons are attracted by it. It leads to flow of current, called ***Photocurrent*** in the circuit, which is measured by a micro ammeter ($\mu$A). It will depend on no. of electrons ejected and K.E. of ejected electrons.

If the collector is maintained at a negative potential w.r.t. the emitter, the electrons are repelled by it. The electrons, which have sufficient kinetic energy, reach the collector despite its negative polarity.
Now , if we increase the reverse potential , the photo current gradually decreases and becomes zero at a particular rever se potential. This minimum applied reverse potential to stop photocurre nt is called ***Stopping Potential ($V_0$)***. Hence the maximum kinetic ene rgy of photo electrons can be written as -

$$K.E._{max} = eV_0 = h\upsilon - \phi$$



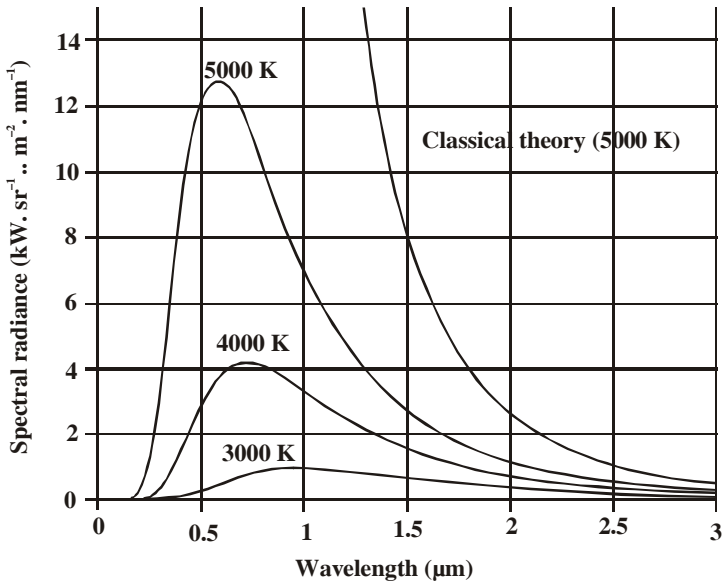

## 18.0 BLACK BODY RADIATION & EXPLANATION BY PLANCK'S QUANTUM THEORY

SL AL

An ideal black body may be defined as :

***A perfect absorber and a perfect emitter of radiations which means that it absorbs and emits respectively radiations of all frequencies which fall on its surface.***

This means that a black body absorbs all the radiations that are incident or falling on it. However, when such a body is heated, it emits the energy in the form of radiations. When a black body such as an iron rod is heated in a furnance, it undergoes a series of changes in colour. With rise in temperature, it intially becomes dull red in colour and then becomes more and more red as temperature increases.




The red colour changes to yellow and then to white and finally it becomes blue at very high temperature. These observations are not in agreement with the wave theory of radiations since according to this theory , the heat energy supplied must increase the intensity of the same colour i.e. red and black body is not expected to undergo change in colour only greater number of photons should be emitted.

## Illustrations

***Illustration 43.*** A photon of wavelength 3000 Å strikes a metal surface, the work function of the metal being 2.20 eV. Calculate
***(i)*** the energy of the photon in eV
***(ii)*** the kinetic energy of the emitted photo electron and
***(iii)*** the velocity of the photo electron.

***Solution.*** ***(i)*** Energy of the photon

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.6\times10^{-34}\,Js)(3\times10^{8}\,ms^{-1})}{3\times10^{-7}\,m} = 6.6 \times 10^{-19}\ J$$

$$1eV = 1.6 \times 10^{-19}\ J$$

$$\text{Therefore } E = \frac{6.6\times10^{-19}\,J}{1.6\times10^{-19}\,J/ev} = 4.125\ eV$$

***(ii)*** Kinetic energy of the emitted photo electron
Work function = 2.20 eV
Therefore, KE = 2.475 – 2.20 = 1.925 eV = $3.08 \times 10^{-19}$ J

***(iii)*** Velocity of the photo electron

$$KE = \frac{1}{2}mv^2 = 3.08 \times 10^{-19} \text{ J}$$

$$\text{Therefore, velocity (v)} = \sqrt{\frac{2 \times 3.08 \times 10^{-19}}{9.1 \times 10^{-31}}} = 8.22 \times 10^5 \text{ ms}^{-1}$$

***Illustration 44*.*** Photoelectrons are liberated by ultra violet light of wavelength 2000 Å from a metallic surface for which the photoelectric threshold is 4000 Å. Calculate the de Broglie wavelength of electrons emitted with maximum kinetic energy.

***Solution.*** K.E. = Quantum Energy – Threshold energy

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{2000 \times 10^{-10}} - \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4000 \times 10^{-10}}$$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{10^{-10}} \left(\frac{1}{2000} - \frac{1}{4000}\right) = 4.969 \times 10^{-19} \text{ Joule.}$$

$$\frac{1}{2}mv^2 = 4.969 \times 10^{-19} \Rightarrow m^2v^2 = 2 \times 4.969 \times 10^{-19} \times 9.1 \times 10^{-31}$$

$$mv = 9.51 \times 10^{-25} \Rightarrow \lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{9.51 \times 10^{-25}} = 0.696 \times 10^{-9} \text{ m}$$

## BEGINNER'S BOX–9

### *Photoelectric Effect*

**1.** ***(a)*** Calculate the kinetic energy of a photoelectron emitted by a sodium surface when light of wavelength 400 nm is incident on it. The work function of sodium is 2.28 eV.

***(b)*** Calculate the value of the longest wavelength which can result in the emission of a photoelectron from a sodium surface.

**2.** Ultraviolet light of wavelength 280 nm is used in an experiment of photoelectric effect with lithium (w = 2.5 eV) cathode. Find

***(a)*** Maximum K.E. ***(b)*** Stopping potential

**3.** The therehold frequency $\nu_0$ for a metal is $6 \times 10^{14}$ s$^{-1}$. Calculate the kinetic energy of an electron emitted when radiation of frequency $\nu = 1.1 \times 10^{15}$ s$^{-1}$ hits the metal.

**4.** When electromagnetic radiation of wavelength 310 nm fall on the surface of Sodium, electrons are emitted with K.E. = 1.5 eV. Determine the work function ($W_0$) of Sodium.

**5*.** The energy required to remove an electron from metal X is $E = 3.31 \times 10^{-20}$ J. Calculate the maximum wavelength of light that can photoeject an electron from metal X.

(A) 4 μm (B) 6 μm (C) 7 μm (D) 5 μm

**6.** The thereshold frequency $\nu_0$ for a metal for a metal is $7.0 \times 10^{14}$ s$^{-1}$. Calculate the kinetic energy of an electron emitted when radiation of frequency $\nu = 1.0 \times 10^{15}$ s$^{-1}$ hits the metal.

## GOLDEN KEY POINTS

- Revolutions per sec = $v / 2\pi$

$$r = \frac{0.657 \times Z^2 \times 10^{16}}{n^3}$$

- Time for one revolution = $2\pi r / v = \dfrac{1.52 \times 10^{-16} \times n^3}{Z^2}$
- No two elements will have identical line spectrum since no two elements have identical energy level therefore the line spectrum of the elements are described as finger prints differing from each other like the finger prints of the human beings.
- Since line spectrum is obtained by the emission of energy through the atoms of the element therefore line spectrum is also called as atomic spectrum.
- Frequency, $\nu = \dfrac{c}{\lambda}$
- Energy/photon, $E = h\nu = \dfrac{hc}{\lambda}$

  Also, $E = \dfrac{12375}{\lambda} eV$, if $\lambda$ is in Å
- Electronic energy change during transition, $\Delta E = E_{n_2} - E_{n_1}$ $n_2 > n_1$, emission spectra if electron jumps from $n_2$ to $n_1$ shell and absorption spectra if electron excites from $n_1$ to $n_2$ shell.
- Radius of $n^{th}$ Bohr orbit of H atom, $r_n = \dfrac{n^2h^2}{4\pi^2me^2K}$ (where $K = 9 \times 10^9$)

  $r_1$ for H = 0.529 Å ; $r_n$ for H like atom $r_n = 0.529 \times \dfrac{n^2}{Z}$ Å
- Velocity of electron in $n^{th}$ Bohr orbit of H atom, $v = \dfrac{2\pi KZe^2}{nh}$

  $v = 2.18 \times 10^8 \dfrac{Z}{n}$ cm/sec
- Energy of electron in $n^{th}$ Bohr orbit of H atom, $E = \dfrac{2\pi^2mZ^2e^4K^2}{n^2h^2}$

  where n = 1, 2, 3.....

  [$E = -13.6 \times \dfrac{Z^2}{n^2}$ kcal/mole (1 cal = 4.18 J)]

  $E_1$ for H = $-21.72 \times 10^{-12}$ erg = $-13.6$ eV, $E_1$ for H like atom = $E_1$ for H $\times Z^2$
- Wavelength emitted during transition in H atom,

$$\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = \frac{2\pi^2me^4}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ (in C.G.S.)}$$

- Photoelectric effect $h\nu = w + \dfrac{1}{2}mu^2$ or $h\nu$ = I.E. + K.E.

- Possible transitions for a jump from $n_2$ to $n_1$ = $\sum(n_2 - n_1)$

- de Broglie equation : $\lambda = \frac{h}{mu} = \sqrt{\frac{h^2}{2 \times K.E. \times m}}$

  where $\lambda$ is wavelength, m is mass and u is velocity of particle.

- Heisenberg uncertainty principle :

  $\Delta p.\Delta x \geq \frac{h}{4\pi}$

  $\Delta u.\Delta x \geq \frac{h}{4\pi m}$

  where $\Delta p$, $\Delta u$ and $\Delta x$ are uncertainties in momentum, velocity and position respectively. Planck's constant is h and m is mass of subatomic particle.

- Total no. of $e^-$ in main energy shell = $2n^2$
  Total no. of $e^-$ in a subshell = $2(2\ell + 1)$
  Maximum no. of $e^-$ in an orbital = 2
  Total no. of orbitals in a subshell = $(2\ell + 1)$
  No. of subshells in main energy shell = n
  No. of orbitals in a main energy shell = $n^2$

- Orbital angular momentum $L = \frac{h}{2\pi}\sqrt{\ell(\ell+1)}$

- Spin angular momentum $S = \frac{h}{2\pi}\sqrt{s(s+1)}$ ; $S = \frac{1}{2}$

- Spin only magnetic moment $\mu_s = \frac{eh}{2\pi mc}\sqrt{s(s+1)}$ or $\mu = \sqrt{n(n+2)}$ B.M. (n = no. of unpaired electrons)

- Orbital magnetic moment $\mu_s = \frac{eh}{4\pi mc}\sqrt{s(s+1)}$

- Nodal planes : Radial nodes = $n - \ell - 1$, Angular nodes = $\ell$, Total nodes = $(n - 1)$

- A term multiplicity is also defined as $M = 2|s| + 1$ where $|s|$ represents total spin = $\frac{1}{2} \times n_{\text{unpaired electrons}}$.

  Hence Hund's rule says that configuration should be such that multiplicity is maximum.

# SOME WORKED OUT EXAMPLES

***Illustration 1.***

Find the wavelengths of the first line of $He^+$ ion spectral series whose interval with extreme lines is

$$\frac{1}{\lambda_1}-\frac{1}{\lambda_2} = 2.7451 \times 10^4 \text{ cm}^{-1}$$

***Solution***

Extreme lines means first and last

$$\frac{1}{\lambda_1}-\frac{1}{\lambda_2} = RZ^2\left[\frac{1}{n_1^2}-\frac{1}{\infty^2}\right] - RZ^2\left[\frac{1}{n_1^2}-\frac{1}{(n_1+1)^2}\right]$$

$$\text{or } \frac{1}{\lambda_1}-\frac{1}{\lambda_2} = \frac{RZ^2}{(n_1+1)^2}$$

$$2.7451 \times 10^4 = \frac{109677.76\times 2^2}{(n_1+1)^2}$$

$(n_1 + 1) = 4$

$n_1 = 3$

Wavelength of first line,

$$\frac{1}{\lambda} = 109677.76 \times 2^2 \times \left[\frac{1}{3^2}-\frac{1}{4^2}\right]$$

$\lambda = 4689 \times 10^{-8}$ cm $= 4689$ Å

***Illustration 2.***

Find the wavelength emitted during the transition of electron in between two levels of $Li^{2+}$ ion whose sum is 5 and difference is 3.

***Solution.***

Let the transition occurs between the level $n_1$ and $n_2$ and $n_2 > n_1$

Given that $n_1 + n_2 = 5$

$n_2 - n_1 = 3$

$\therefore \quad n_1 = 1$ and $n_2 = 4$

$$\text{Therefore, } \frac{1}{\lambda} = R_h \times Z^2\left[\frac{1}{(1)^2}-\frac{1}{(4)^2}\right] = 109678 \times (3)^2\left[\frac{15}{16}\right]$$

$\therefore \quad \lambda = 1.08 \times 10^{-6}$ cm

***Illustration 3.***

The Lyman series of the hydrogen spectrum can be represented by the equation.

$$v = 3.2881 \times 10^{15} \text{ s}^{-1}\left[\frac{1}{(1)^2}-\frac{1}{(n)^2}\right]$$

(where n = 2, 3,.....)

Calculate the maximum and minimum wavelength of lines in this series.

***Solution.***

$$\bar{v} = \frac{1}{\lambda} = \frac{v}{c} = \frac{3.2881\times 10^{15}}{3\times 10^8} \text{ m}^{-1}\left[\frac{1}{(1)^2}-\frac{1}{n^2}\right]$$

Wavelength is maximum $(\bar{\nu}_{min})$ when n is minimum so that $\frac{1}{n^2}$ is maximum

$$\therefore \quad \bar{\nu}_{min} = \frac{1}{\lambda_{max}} = \frac{3.2881\times10^{15}}{3\times10^{8}}\left[\frac{1}{(1)^2}-\frac{1}{(2)^2}\right]$$

$$\therefore \quad \lambda_{max} = \frac{3\times10^{8}}{3.2881\times10^{15}}\times\frac{4}{3}$$

$= 1.2165 \times 10^{-7}$ m $= 121.67$ nm

Wavelength is minimum $(\bar{\nu}_{max})$ when n is $\infty$

i.e. series converge

$$\therefore \quad \nu_{max} = \frac{1}{\lambda_{min}} = \frac{3.2881\times10^{15}}{3\times10^{8}}$$

$\therefore \quad \lambda_{min} = 0.9124 \times 10^{-7}$m 91.24 nm

***Illustration 4*.***

When certain metal was irradiated with light frequency $0.4 \times 10^{13}$ Hz the photo electrons emitted had twice the kinetic energy as did photo electrons emitted when the same metal was irradiated with light frequency $1.0 \times 10^{13}$ Hz. Calculate threshold frequency $(\nu_0)$ for the metal.

***Solution.***

$h\nu = h\nu_0 + KE$

$KE_1 = h(\nu_1 - \nu_0)$

$$KE_2 = h(\nu_2 - \nu_0) = \frac{KE_1}{2}$$

$$\therefore \frac{\nu_2-\nu_0}{\nu_1-\nu_0} = \frac{1}{2} \Rightarrow \frac{1.0\times10^{13}-\nu_0}{0.4\times10^{13}-\nu_0} = \frac{1}{2} \Rightarrow \nu_0 = 1.6 \times 10^{13} \text{ Hz}$$

***Illustration 5.***

Iodine molecule dissociates into atoms after absorbing light of 3000 Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms. (Bond energy of $I_2$ = 240 kJ (mol).

***Solution.***

Energy given to iodine molecule

$$\frac{hc}{\lambda} = \frac{6.62\times10^{-34}\times3\times10^{8}}{3000\times10^{-10}} = 6.62 \times 10^{-19} \text{ J}$$

Also energy used for breaking up

$$I_2 \text{ molecule} = \frac{240\times10^{3}}{6.023\times10^{23}} = 3.984\times10^{-19}\text{J}$$

$\therefore$ Energy used in imparting kinetic to two atoms $= (6.62 - 3.984) \times 10^{-19}$ J

$$\therefore \text{ KE of iodine atom} = \frac{(6.62-3.984)}{2}\times10^{-19} = 1.318 \times 10^{-19} \text{ J}$$

***Illustration 6*.***

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 ?

***Solution.***

Wavelength is emitted in UV region and thus $n_1 = 1$

For H atom $= \frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{n^2}\right]$

$\therefore \frac{1}{121.6 \times 10^{-9}} = 1.097 \times 10^7\left[\frac{1}{1^2} - \frac{1}{n^2}\right]$

$\therefore$ n = 2

Also the energy released is due to collision and all the kinetic energy is released in form of photon.

$\therefore \frac{1}{2}mv^2 = \frac{hc}{\lambda}$

$\therefore \frac{1}{2} \times 1.67 \times 10^{-27} \times v^2 = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{121.6 \times 10^{-9}}$

$\therefore$ v = $4.43 \times 10^4$ m/sec

***Illustration 7.***

Find the energy in kJ per mole of electronic charge accelerated by a potential of 2 volt.

***Solution.***

Energy in joules = charge in coulombs × potential difference in volt

$= 1.6 \times 10^{-19} \times 6.02 \times 10^{23} \times 2 = 19.264 \times 10^4$ J or 192.264 kJ

***Illustration 8.***

Which hydrogen like ionic species has wavelength difference between the first line of Balmer and first line of Lyman series equal to $59.3 \times 10^{-9}$ m ? Neglect the reduced mass effect.

***Solution.***

Wave number of first Balmer line of an species with atomic number Z is given by

$\bar{v}' = RZ^2\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = \frac{5RZ^2}{36}$

Similarly wave number of $\bar{v}$ of first Lyman line is given by

$\bar{v} = RZ^2\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \frac{3}{4}RZ^2$ ; $\bar{v} = \frac{1}{\lambda}$ and $\bar{v}' = \frac{1}{\lambda'}$

$\therefore \quad \lambda' - \lambda = \frac{36}{5RZ^2} - \frac{4}{3RZ^2} = \frac{1}{RZ^2}\left[\frac{36}{5} - \frac{4}{3}\right] = \frac{88}{15RZ^2}$

$\therefore \quad Z^2 = \frac{88}{59.3 \times 10^{-9} \times 15 \times 1.097 \times 10^7} = 9$ or Z = 3

$\therefore$ Ionic species is $Li^{2+}$

***Illustration 9.***

***(i)*** What is highest frequency photon that can be emitted from hydrogen atom ? What is wavelength of this photon ?

***(ii)*** Find the longest wavelength transition in the Paschen series of $Be^{3+}$.

***(iii)*** Find the ratio of the wavelength of first and the ultimate line of Balmer series of $He^+$ ?

***Solution.***

***(i)*** Highest frequency photon is emitted when electron comes from infinity to $1^{st}$ energy level.

$$E = -\frac{13.6Z^2}{1^2} = -13.6\ eV$$

or, $13.6 \times 1.6 \times 10^{-19}$ Joule $= 2.176 \times 10^{-18}$ Joule

$E = h\nu$

$$\therefore \quad \nu = \frac{E}{h} = \frac{2.176 \times 10^{-18} J}{6.626 \times 10^{-34} Js} = 0.328 \times 10^{16}\ Hz$$

$$\nu = \frac{c}{\lambda} \qquad \therefore \lambda = \frac{3 \times 10^8}{0.328 \times 10^{16}} = 9.146 \times 10^{-8}\ m$$

***(ii)*** $\bar{\nu} = R_H \times Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

For He ; Z = 4 ; For Paschen series $n_1 = 3$

For longest wavelength $n_2 = 4$

$$\frac{1}{\lambda} = 109678 \times (4)^2 \times \left[\frac{1}{3^2} - \frac{1}{4^2}\right] = 109678 \times 16 \times \left[\frac{1}{9} - \frac{1}{16}\right] = 109678 \times 16 \times \frac{7}{144}$$

$\lambda = 1172.20$ Å

***(iii)*** Wave number of first line of Balmer,

$$\bar{\nu}_1 = RZ^2\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = \frac{5 \times 4R}{36} = \frac{5R}{9}$$

$\therefore$ Wavelength of first line of Balmer $= \frac{9}{5R}$

Wave number of ultimate line of Balmer, $\bar{\nu}_2 = RZ^2\left[\frac{1}{2^2} - \frac{1}{\infty}\right] = \frac{4R}{4} = R$

$\therefore$ Wavelength of ultimate line of Balmer $= \frac{1}{R}$

$\therefore$ Ratio $= \frac{9}{5}$

***Illustration 10.***

An electron beam can undergo difraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.0 Å.

***Solution.***

For an electron

$\frac{1}{2}mv^2 = eV$ where V is accelerating potential

$$\lambda = \frac{h}{mv}$$

$$\therefore \quad \frac{1}{2}m\left(\frac{h}{m\lambda}\right)^2 = eV$$

$$\therefore \quad V = \frac{1}{2} \times \frac{h^2}{m\lambda^2 e} = \frac{1 \times (6.625 \times 10^{-34})^2}{2 \times 9.108 \times 10^{-31} \times (1.0 \times 10^{-10})^2 \times 1.602 \times 10^{-19}} = 150.40\ volt$$

***Illustration 11.***

The angular momentum of an electron in a Bohr's orbit of H-atom is $4.2178 \times 10^{-34}$ kgm$^2$/sec. Calculate the wavelength of the spectral line emitted when electrons falls from this level to next lower level.

***Solution.***

$$mvr = \frac{nh}{2\pi}$$

$$\frac{nh}{2\pi} = 4.2178 \times 10^{-34}$$

$$n = \frac{4.2178 \times 10^{-34} \times 2 \times 3.14}{6.625 \times 10^{-34}} = 4$$

$$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

The wavelength for transition from n = 4 to n = 3

$$\frac{1}{\lambda} = 109678\left[\frac{1}{3^2} - \frac{1}{4^2}\right]$$

$\lambda = 1.8 \times 10^{-4}$ cm.

***Illustration 12*.***

The kinetic energy of an electron in H like atom is 6.04 eV. Find the area of the third Bohr orbit to which this electron belongs. Also report the atom.

***Solution.***

K.E. = 6.04 in 3$^{rd}$ orbit

$E_{total}$ = K.E. + P.E. = K.E. – 2 × K.E.

$\Rightarrow$ –K.E. = – 6.04 eV

$E_1$ for H = –13.6 eV and not for any orbit E = – 6.04 eV for H atom. Thus, atom for which K.E. is given is other than H.

$E_n$ H like atom = $E_{nH} \times Z^2$

$$\frac{E_1}{n^2} \times Z^2 \Rightarrow 6.04 = \frac{13.6}{3^2} \times Z^2$$

$Z^2 = 3.99 \approx 4 \Rightarrow Z = 2$

$\therefore$ The atom is $He^+ \Rightarrow r_n = 0.529 \times \frac{n^2}{Z} = 0.529 \times \frac{3^2}{2} = 2.3805$ Å

$$\text{Area, } \pi r^2 = \frac{22}{7} \times \left(2.3805 \times 10^{-8}\right)^2 = 17.8 \times 10^{-16} \text{ cm}^2$$

***Illustration 13*.***

$O_2$ 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 atom of oxygen requires 498 kJmol$^{-1}$. What is the maximum wavelength effective for photo chemical dissociation of $O_2$ ?

***Solution.***

We know

$$P_2 \xrightarrow{h\nu} O_{Normal} + O_{Excited}$$

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

Energy required for simple dissociation of $O_2$ into two normal atoms = $498 \times 10^3$Jmol$^{-1}$

$$= \frac{498 \times 10^8}{6.023 \times 10^{23}} \text{Jmol}^{-1}$$

If one atom in excited state has more energy, i.e.. 1.967 eV
$= 1.967 \times 1.602 \times 10^{-19}$ J
The energy required for photochemical dissociation of $O_2$

$$= \frac{498 \times 10^3}{6.023 \times 10^{23}} + 1.967 \times 1.602 \times 10^{-19}$$

$= 82.68 \times 10^{-20} + 31.51 \times 10^{-20} = 114.19 \times 10^{-20}$ Joule

$$E = \frac{hc}{\lambda}$$

$$114.19 \times 10^{-20} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{\lambda}$$

$\lambda = 1740.2 \times 10^{-10}$ m = 1740.2 Å.

***Illustration 14.***

The wave-mechanical model of atom is based upon :-
(A) de Broglie concept of dual character of matter
(B) Heisenberg's uncertainty principle
(C) Schrodinger wave equation
(D) All the above three

***Ans. (D)***

***Illustration 15.***

An orbital is correctly described by :-
(A) $\Psi^2$ (B) $\Psi$ (C) $|\Psi^2|\Psi$ (D) none

***Ans. (A)***

***Illustration 18.***

In the first bohr orbit of H atom the energy of an electron is –13.6 eV. The possible energy value (s) of excited state (s) for electron in Bohr orbit of hydrogen is/are :-
(A) –3.4 eV (B) –4.2 eV (C) 6.8 eV (D) +6.8 eV

***Solution.***

$$E_n = \frac{-13.6}{n^2} eV$$

$$\text{For } n = 2,\ E_2 = \frac{-13.6}{4} = -3.4 eV$$

So, ***(A)*** is the correct answer.

***Illustration 22.***

If an electron in H atom has an energy of –78.4 kcal/mol. The orbit in which the electron is present is :-
(A) $1^{st}$ (B) $2^{nd}$ (C) $3^{rd}$ (D) $4^{th}$

***Solution.***

$$E^n = \frac{-313.6}{n^2} kcal/mol \Rightarrow -78.4 = \frac{-313.6}{n^2} \quad \therefore n = 2$$

***Illustration 23.***

What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition, n = 4 to n = 2 in the $He^+$ spectrum ?
(A) n = 4 to n = 2 (B) n = 3 to n = 2 (C) n = 3 to n = 1 (D) n = 2 to n = 1

***Solution.***

$$\bar{v} = \frac{1}{\lambda} = \left(\frac{1}{2^2} - \frac{1}{4^2}\right) RZ^2 = \frac{3}{4} R$$

In H–spectrum for the same $\bar{\nu}$ or $\lambda$ as $Z = 1$, $n = 1$, $n_2 = 2$

So, ***(D)*** is the correct answer.

So, ***(B)*** is the correct answer.

***Illustration 25.***

If the radius of 2nd Bohr orbit of hydrogen atom is $r_2$. The radius of third Bohr orbit will be :-

(A) $\frac{4}{9}r_2$ (B) $4r_2$ (C) $\frac{9}{4}r_2$ (D) $9r_2$

***Solution.***

$$r = \frac{n^2h^2}{4\pi^2mZe^2}$$

$$\therefore \frac{r_2}{r_3} = \frac{2^2}{3^2} \quad \therefore r_3 = \frac{9}{4}r_2$$

So, ***(C)*** is the correct answer.

***Illustration 26.***

Difference between $n^{th}$ and $(n + 1)^{th}$ Bohr's radius of H–atom is equal to its $(n - 1)^{th}$ Bohr's radius. The value of n is :-

(A) 1 (B) 2 (C) 3 (D) 4

***Solution.***

$r_n \propto n^2$

But $r_{n+1} - r_n = r_n - 1$

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

$n = 4$

So ***(D)*** is the correct answer

***Illustration 27.***

The dissociation energy of $H_2$ is 430.53 kJ $mol^{-1}$. If $H_2$ is dissociated by illumination with radiation of wavelength 253.7 nm. The fraction of the radiant energy which will be converted into kinetic energy is given by :-

(A) 8.86% (B) 2.33% (C) 1.3% (D) 90%

***Solution.***

$$\frac{hc}{\lambda} = \frac{430.53 \times 10^3}{6.023 \times 10^{23}} + \text{K.E.}$$

$$\text{K.E.} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{253.7 \times 10^{-9}} - \frac{430.53 \times 10^3}{6.023 \times 10^{23}} = 6.9 \times 10^{-20}$$

$$\therefore \text{Fraction} = \frac{6.9 \times 10^{-20}}{7.83 \times 10^{-19}} = 0.088 = 8.86\%$$

***Illustration 28.***

No. of wave in third Bohr's orbit of hydrogen is :-

(A) 3 (B) 6 (C) 9 (D) 12

***Solution.***

$$\text{Number of waves} = \frac{\text{Circumference}}{\text{Wavelength}}$$

$$\frac{2\pi r}{\lambda} = \frac{2\pi r}{h/mv} = \frac{2\pi}{h}(mvr) = \frac{2\pi}{h} \times \frac{nh}{2\pi}$$

$\therefore n = 3$

So, ***(A)*** is the correct answer.

***Illustration 29.***

In the hydrogen atoms, the electrons are excited to the $5^{th}$ energy level. The number of the lines that may appear in the spectrum will be :-

(A) 4 (B) 8 (C) 10 (D) 12

***Solution.***

No. of lines produced for a jump from fifth orbit to $1^{st}$ orbit is given by

$$= \frac{n(n-1)}{2} = \frac{5(5-1)}{2} = 10$$

So, ***(C)*** is the correct answer.

***Illustration 30.***

Light of wavelength $\lambda$ shines on a metal surface with intensity x and the metal emits Y electrons per second of average energy, Z. What will happen to Y and Z if x is doubled ?

(A) Y will be double and Z will become half
(B) Y will remain same and Z will be doubled
(C) Both Y and Z will be doubled
(D) Y will be doubled but Z will remain same

***Solution.***

When intensity is doubled, number of electrons emitted per second is also doubled but average energy of photoelectrons emitted remains the same.

So, ***(D)*** is the correct answer.

*****

# ANSWERS

## BEGINNER'S BOX-1

**1.** $3.155 \times 10^{-26}$ kg **2.** $10^{-15}$ **3.** $6.3 \times 10^{6}$ m/s

## BEGINNER'S BOX-2

**1.** 37.35 % **2.** n = 25 **3.** $2.65 \times 10^{-19}$ **4.** $1.125 \times 10^{22}$
**5.** 1000m

## BEGINNER'S BOX-3

**1.** (C) **2.** (A) **3.** (B) **4.** (D) **5.** (C)
**6.** (A) **7.** (C) **8.** (D) **9.** (B) **10.** (D)
**11.** (D)

## BEGINNER'S BOX-4

**1.** (B) **2.** (B) **3.** $2.65 \times 10^{-11}$ m **4.** 937.3 Å

## BEGINNER'S BOX-5

**1.** (B) **2.** (C) **3.** (C) **4.** (A) **5.** (C)
**6.** (D) **7.** (C) **8.** (B) **9.** (A)

## BEGINNER'S BOX-6

**1.** (D) **2.** (D) **3.** (B) **4.** (C) **5.** (D)
**6.** (C) **7.** (B)

## BEGINNER'S BOX-7

**1.** (B) **2.** (D) **3.** (B) **4.** $r = a_0 = 0.529$ Å
**5.** (C) **6.** (C) **7.** (D)

## BEGINNER'S BOX-8

**1.** (D) **2.** (D) **3.** (D) **4.** (C) **5.** (A)
**6.** (A) **7.** (C)
**8.** (a) $0 \times (\pm 1/2) = 0$
(b) $0 \times (\pm 1/2) = 0$
(c) $1 \times (\pm 1/2) = \pm 1/2$
(d) $3 \times (\pm 1/2) = \pm 3/2$
(e) $5 \times (\pm 1/2) = \pm 5/2$
**9.** (C)

## BEGINNER'S BOX-9

**1.** (a) 0.82 eV, (b) 544 nm **2.** (a) 1.93 eV, (b) 1.93 volts
**3.** $3.313 \times 10^{-19}$ J **4.** 2.5 eV
**5.** (B) **6.** $1.988 \times 10^{-19}$ J

## EXERCISE – 1 MCQ (SINGLE CHOICE CORRECT)

**1.** When Lithium $\left({}^{7}_{3}Li\right)$ vapours were filled in discharge tube for anode ray experiment, the anode rays were found to contain only $Li^{+}$ ions. Thus the anode ray particle contains :

(A) 1 proton only
(B) 3 proton and 4 neutron only
(C) 3 proton, 4 neutron and 2 electrons
(D) 3 proton, 3 neutrons and 3 electrons

**2.** E/m ratio of a particle of charge 2 unit and mass 4 amu is

(A) $4.8 \times 10^{7}$ C/kg
(B) 0.5 C/kg
(C) $4.8 \times 10^{4}$ C/kg
(D) $8 \times 10^{-20}$ C/kg

**3.** In the different experiements, α-particles, proton, deuteron and neutron are projected towards gold nucleus with the same kinetic energy. The distance of closest approach will be minimum for

(A) α-particle
(B) proton
(C) dueteron
(D) neutron

**4.** The ratio of the energy of a photon of 2000 Å wavelength radiation to that of 4000 Å radiation is

(A) 1 / 4
(B) 4
(C) 1 / 2
(D) 2

**5.** Which of the following electromagnetic radiation have greater frequency?

(A) X - rays
(B) Ultraviolet rays
(C) Radio waves
(D) Visible rays

**6.** Two electromagnetic radiations have wave numbers in the ratio 2 : 3. Their energies per quanta will be in the ratio

(A) 3 : 2
(B) 9 : 4
(C) 4 : 9
(D) 2 : 3

**7.** A photon of 400 nm is absorbed by a gas molecule and then the molecule re-emits two photons. One re-emitted photon has wavelength 500 nm. Assuming that there is no change in the energy of molecule, the wavelength of second re-emitted photon is

(A) 100 nm
(B) 2000 nm
(C) -100 nm
(D) 900 nm

**8.** A green bulb and a red bulb are emitting the radiations with equal power. The correct relation between numbers of photons emitted by the bulbs per second is

(A) $n_g = n_r$
(B) $n_g < n_r$
(C) $n_g > n_r$
(D) unpredictable

**9.** In the emission of photoelectrons, the number of photoelectrons emitted per unit time depends upon

(A) energy of the incident radiation
(B) intensity of the incident radiation
(C) frequency of the incident radiation
(D) wavelength of the incident radiation

**10.** Radiation of $\lambda$ = 155 nm was irradiated on Li (work function = 5 eV) plate. The stopping potential (in V) is _____.

(A)3 V
(B) 8 V
(C) 9 V
(D) 5 V

**11.** The speed of electron revolving in the 4th orbit of a hydrogen like atom or ion is 1094 km/s. The atom or ion is

(A) H
(B) $He^{+}$
(C) $Li^{2+}$
(D) $Be^{3+}$

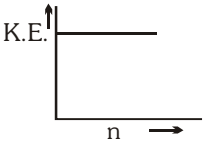
**12.** The first Lyman transition in the hydrogen spectrum has $\Delta E$ = 10.2 eV. The same energy change is observed in the second Balmer transition of :-

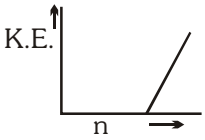
(A) $Li^{2+}$
(B) $Li^{+}$
(C) $He^{+}$
(D) $Be^{3+}$

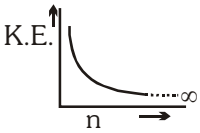
**13.** A single electron is revolving in orbits around a stationary nucleus (z = 5). The energy required to excite the electron from third to fourth Bohr orbit will be :-

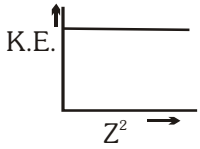
(A) 4.5 eV (B) 8.53 eV (C) 25 eV (D) 16.53 eV

**14.** Which is correct graph :-

(A) 


(B) 


(C) 


(D) 


**15.** The energy required to remove an electron from the surface of sodium metal is 3.3 eV. What is the longest wavelength of radiation with which it can show photoelectric effect?

***Use h = 6.6 × 10$^{-34}$ J.s***

(A) $1.75 \times 10^{-7}$ m (B) $3.75 \times 10^{-5}$ m (C) $1.75 \times 10^{-5}$ m (D) $3.75 \times 10^{-7}$ m

**16.** In a sample of H–atoms, electron transits from 6$^{th}$ orbit to 2$^{nd}$ orbit in multi step. Then total spectral lines (without Balmer series) will be :–

(A) 6 (B) 10 (C) 4 (D) 0

**17.** The maximum energy is present in any electron at :-

(A) Nucleus (B) Ground state

(C) First excited state (D) Infinite distance from the nucleus

**18.** The third line in Balmer series corresponds to an electronic transition between which Bohr's orbits in hydrogen :-

(A) $5 \rightarrow 3$ (B) $5 \rightarrow 2$ (C) $4 \rightarrow 3$ (D) $4 \rightarrow 2$

**19.** The total number of neutrons in dipositive zinc ion with mass number 70 is :-

(A) 34 (B) 40 (C) 36 (D) 38

**20*.** If $\lambda_0$ is the threshold wavelength for photoelectric emission, $\lambda$ wavelength of light falling on the surface of metal, and m mass of electron, then de Broglie wavelength of emitted electron is :-

(A) $\left[\frac{h(\lambda\lambda_0)}{2mc(\lambda_0-\lambda)}\right]^{\frac{1}{2}}$ (B) $\left[\frac{h(\lambda_0-\lambda)}{2mc\lambda\lambda_0)}\right]^{\frac{1}{2}}$ (C) $\left[\frac{h(\lambda-\lambda_0)}{2mc\lambda\lambda_0)}\right]^{\frac{1}{2}}$ (D) $\left[\frac{h\lambda\lambda_0}{2mc}\right]^{\frac{1}{2}}$

**21.** The shortest wavelength of $He^+$ in Balmer series is x, then longest wavelength in the Paschene series of $Li^{+2}$ is

(A) $\frac{36x}{5}$ (B) $\frac{16x}{7}$ (C) $\frac{9x}{5}$ (D) $\frac{5x}{9}$

**22.** How fast is an electron moving if it has a wavelength equal to distance travelled in one second -

(A) $\sqrt{\frac{m}{h}}$ (B) $\sqrt{\frac{h}{m}}$ (C) $\sqrt{\frac{h}{p}}$ (D) $\sqrt{\frac{h}{2\times K.E.}}$

**23.** An electron in a hydrogen atom in its ground state absorbs energy equal to ionisation energy of $Li^{+2}$. The wavelength of the emitted electron is :-

(A) $3.32 \times 10^{-10}$ m (B) 1.17 Å (C) $2.32 \times 10^{-9}$ nm (D) 3.33 pm

**24.** An electron, a proton and an alpha particle have kinetic energy of 16 E, 4E and E respectively. What is the qualitative order of their de Broglie wavelengths :-

(A) $\lambda_e > \lambda_p = \lambda_\alpha$ (B) $\lambda_p = \lambda_\alpha > \lambda_e$ (C) $\lambda_p > \lambda_e > \lambda_\alpha$ (D) $\lambda_\alpha < \lambda_e >> \lambda_p$

**25.** The ratio of difference in wavelengths of 1st and 2nd lines of Lyman series in H-like atom to difference in wavelength for 2nd and 3rd lines of same series is :-

(A) 2.5 : 1 (B) 3.5 : 1 (C) 4.5 : 1 (D) 5.5 : 1

**26.** If radius of second stationary orbit (in Bohr's atom) is R. Then radius of third orbit will be :-

(A) R/3 (B) 9R (C) R/9 (D) 2.25 R

**27.** The wavelength associated with a gold weighing 200 g and moving at a speed of 5 m/h is of the order :-

(A) $10^{-10}$ m (B) $10^{-20}$ m (C) $10^{-30}$ m (D) $10^{-40}$ m

**28.** Electromagnetic radiations having $\lambda$ = 310 Å are subjected to a metal sheet having work function = 12.8 eV. What will be the velocity of photoelectrons with maximum Kinetic Energy....

(A) 0, no emission will occur (B) $2.18 \times 10^6$ m/s

(C) $2.18\sqrt{2} \times 10^6$ m/s (D) $8.72 \times 10^6$ m/s

**29.** If in Bohr's model, for unielectronic atom, time period of revolution is represented as $\boldsymbol{T_{n,z}}$ where ***n*** represents shell no. and ***z*** represents atomic number then the value of $T_{1,2} : T_{2,1}$ will be :-

(A) 8 : 1 (B) 1 : 8 (C) 1 : 1 (D) None of these

**30*.** Which orbital is non-directional :-

(A) s (B) p (C) d (D) All

**31.** The number of waves made by a Bohr electron in an orbit of maximum magnetic quantum number + 2 :

(A) 3 (B) 4 (C) 2 (D) 1

**32.** Uncertainty in position is twice the uncertainty in momentum Uncertainty in velocity is :-

(A) $\sqrt{\frac{h}{\pi}}$ (B) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$ (C) $\frac{1}{2m}\sqrt{\hbar}$ (D) $\frac{h}{4\pi}$

**33.** Angular momentum for P–shell electron :–

(A) $\frac{3h}{\pi}$ (B) Zero (C) $\frac{\sqrt{2}h}{2\pi}$ (D) None

**34.** In compound $FeCl_2$ the orbital angular momentum of last electron in its cation & magnetic moment (in Bohr Magneton) of this compound are :-

(A) $(\sqrt{6})\hbar, \sqrt{35}$ (B) $(\sqrt{6})\hbar, \sqrt{24}$ (C) $0, \sqrt{35}$ (D) none of these

**35.** Which is true about $\psi$ :-

(A) $\psi$ represents the probability of finding an electron around the nucleus

(B) $\psi$ represent the amplitude of the electron wave

(C) Both A and B

(D) None of these

## EXERCISE – 2 MCQ (ONE OR MORE CHOICE CORRECT)

**1.** 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 speed

**2.** The change in orbital angular momentum corresponding to an electron transition inside a hydrogen atom can be
(A) $\frac{h}{4\pi}$ (B) $\frac{h}{\pi}$ (C) $\frac{h}{2\pi}$ (D) $\frac{h}{8\pi}$

**3.** In which of these options do both constituents of the pair have the same magnetic moment -
(A) $Zn^{2+}$ and $Cu^{+}$ (B) $Co^{2+}$ and $Ni^{2+}$ (C) $Mn^{4+}$ and $Co^{2+}$ (D) $Mg^{2+}$ and $Sc^{+}$

**4.** If the wave number of 1st line of Balmer series of H-atom is '$x$' then:
(A) wave number of 1st line of lyman series of the $He^{+}$ ion will be $\frac{108x}{5}$
(B) wave number of 1st line of lyman series of the $He^{+}$ ion will be $\frac{36x}{5}$
(C) the wave length of 2nd line of lyman series of H-atom is $\frac{5}{32x}$
(D) the wave length of 2nd line of lyman series of H-atom is $\frac{32x}{5}$

**5*.** 1st excitation potential for the H-like (hypothetical) sample is 24 V. Then :
(A) Ionisation energy of the sample is 36 eV (B) Ionisation energy of the sample is 32 eV
(C) Binding energy of 3rd excited state is 2 eV (D) 2nd excitation potential of the sample is $\frac{32\times 8}{9}$ V

**6.** The species has same number of electrons in outer most and penultimate shell -
(A) Ca (B) Ar (C) $V^{+3}$ (D) $Fe^{3+}$

**7.** Mn (Z = 25) = $1s^3\ 1p^9\ 2s^3\ 2p^9\ 2d^1$
Which of the following change is required so that Mn have above ground state electronic configuration :
(A) Change in the value of $\ell$ (azimuthal quantum number) for any subshell
(B) Change in the possible values of $\ell$ (azimuthal quantum number)
(C) Change in the pauli rule
(D) Change in the $(n + \ell)$ rule

**8.** Select the correct statement(s):
(A) All electromagnetic radiation travel with speed of light in vaccum.
(B) Energy of photon of UV light is lower than that of yellow light.
(C) $He^{+}$ and H have similar spectrum.
(D) The total energy of an electron in unielectronic specie is greater than zero

**9.** Choose the incorrect statement(s):

(A) Increasing order of wavelength is

Micro waves > Radio waves > IR waves > visible waves > UV waves

(B) The order of Bohr radius is ($r_n$ : where n is orbit number for a given atom) $r_1 < r_2 < r_3 < r_4$

(C) The order of total energy is ($E_n$ : where n is orbit number for a given atom) $E_1 > E_2 > E_3 > E_4$

(D) The order of velocity of electron in H, $He^+$, $Li^+$, $Be^{3+}$ species in second Bohr orbit is

$Be^{3+} > Li^{+2} > He^+ > H$

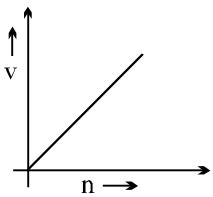
**10.** Select the correct curve(s) :

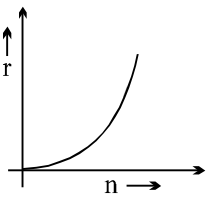
If v = velocity of electron in Bohr's orbit

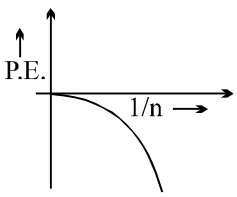
r = Radius of electron in Bohr's orbit

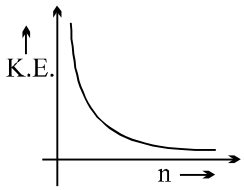
P.E. = Potential energy of electron in Bohr's orbit

K.E. = Kinetic energy of electron in Bohr's orbit.

(A) 


(B) 


(C) 

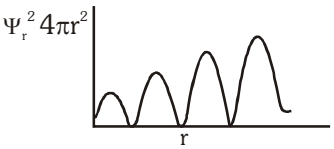

(D) 


**11.** The orbital angular momentum of an electron is $\sqrt{3}\frac{h}{\pi}$. Which of the following may not be the permissible value of angular momentum of this electron revolving in unknown Bohr orbit ?

(A) $\frac{h}{2\pi}$ (B) $\frac{h}{\pi}$ (C) $3.\frac{h}{\pi}$ (D) $2.\frac{h}{\pi}$

## *Match the Column*

**12*.** Column I & Column II contain data on Schrondinger Wave-Mechanical model, where symbols have their usual meanings. Match the columns :-

| ***Column I*** | ***Column II (Type of orbital)*** |
|---|---|
| (A) | (p) 4s |
| (B)   | (q) $5p_x$ |
| (C) $\Psi(\theta, \phi) = K$ (independent of $\theta$ & $\phi$) | (r) 3s |
| (D) atleast one angular node is present | (s) $6d_{xy}$ |

**13.** ***Column-I*** | ***Column-I***

(A) Electron moving in 2nd orbit in $He^+$ ion electron is — (P) Radius of orbit in which moving is 0.529 Å

(B) Electron moving in 3rd orbit in H-atom — (Q) Total energy of electron is (–) 13.6 × 9eV

(C) Electron moving in 1st orbit in $Li^{+2}$ ion — (R) Velocity of electron is $\frac{2.188 \times 10^6}{3}$ m/sec

(D) Electron moving in 2nd orbit is $Be^{+3}$ ion — (S) De-broglie wavelength of electron is $\sqrt{\frac{150}{13.6}}$ Å

***Comprehension Based Questions***

***Comprehension-1***

The general electronic configuration of outer most and penultimate shell is given as $(n-1)s^2\ (n-1)p^6\ (n-1)d^x ns^2$. Then for an element with n = 4 and x = 7.

**14.** The number of protons present in the divalent cation of the element of above configuration is :-

(A) 25 (B) 26 (C) 27 (D) 28

**15.** The element is isoelectronic with which of the following species :-

(A) $Fe^-$ (B) $Ni^+$ (C) $Cu^{2+}$ (D) All of these

**16.** The number of unpaired electron in the trivalent cation of the given element in isolated gaseous state is :-

(A) 0 (B) 3 (C) 4 (D) 1

***Comprehension-2***

The French physicist Louis de Broglie in 1924 postulated that matter, like radiation, should exhibit a dual behaviour. He proposed the following relationship between the wavelength λ of a material particle, its linear momentum p and planck constant h.

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

The de Broglie relation implies that the wavelength of a particle should decreases as its velocity increases. It also implies that for a given velocity heavier particles should have shorter wavelength than lighter particles. The waves associated with particles in motion are called matter waves or de Broglie waves. These waves differ from the electromagnetic waves as they

(i) have lower velocities

(ii) have no electrical and magnetic fields and

(iii) are not emitted by the particle under consideration.

The experimental confirmation of the de Broglie relation was obtained when Davisson and Germer, in 1927, observed that a beam of electrons is diffracted by a nickel crystal. As diffraction is a characteristic property of waves, hence the beam of electron behaves as a wave, as proposed by de Broglie.

Werner Heisenberg considered the limits of how precisely we can measure properties of an electron or other microscopic particle like electron. He determined that there is a fundamental limit of how closely we can measure both position and momentum. The more accurately we measure the momentum of a particle, the less accurately we can determine its position. The converse is also true. This is summed up in what we now call the "Heisenberg uncertainty principle: It is impossible to determine simultaneously and precisely both the momentum and position of a particle. The product of uncertainty in the position, Δx and the uncertainty in the momentum Δ(mv) must be greater than or equal to $\frac{h}{4\pi}$. i.e.

$$\Delta x\ \Delta(mv) \geq \frac{h}{4\pi}$$

**17.** The correct order of wavelength of Hydrogen ($_1H^1$), Deuterium ($_1H^2$) and Tritium ($_1H^3$) moving with same kinetic energy is

(A) $\lambda_H > \lambda_D > \lambda_T$ (B) $\lambda_H = \lambda_D = \lambda_T$ (C) $\lambda_H < \lambda_D < \lambda_T$ (D) $\lambda_H < \lambda_D > \lambda_T$

**18.** The transition, so that the de-Broglie wavelength of electron becomes 3 times of its initial value in $He^+$ ion will be

(A) $2 \rightarrow 5$ (B) $3 \rightarrow 2$ (C) $2 \rightarrow 6$ (D) $1 \rightarrow 2$

**19.** If the uncertainty in velocity & position is same, then the uncertainty in momentum will be

(A) $\sqrt{\frac{hm}{4\pi}}$ (B) $m\sqrt{\frac{h}{4\pi}}$ (C) $\sqrt{\frac{h}{4\pi m}}$ (D) $\frac{1}{m}\sqrt{\frac{h}{4\pi}}$

## EXERCISE – 3 SUBJECTIVE

**1.** The wavelength of a certain line in the Paschen series is 1093.6 nm. What is the value of $n_{high}$ for this line [$R_H = 1.0973 \times 10^{+7}\ m^{-1}$].

**2.** Wavelength of the Balmer $H_\alpha$ line (first line) is 6565 Å. Calculate the wavelength of $H_\beta$ (second line).

**3.** Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral line of lowest energy in the visible region of its atomic spectrum.

**4.** A photon having $\lambda$ = 854 Å causes the ionization of a nitrogen atom. Give the I.E. per mole of nitrogen in KJ.

**5.** Calculate energy of electron which is moving in the orbit that has its radius, Sixteen times the radius of first Bohr orbit for H-atom.

**6.** The electron energy in hydrogen atom is given by $E_n = \dfrac{-21.7 \times 10^{-12}}{n^2}$ ergs. Calculate the energy required to remove an $e^-$ completely from n = 2 orbit. What is the largest wavelength in cm of light that can be used to cause this transition.

**7*.** The velocity of $e^-$ in a certain Bohr orbit of the hydrogen atom bears the ratio 1 : 275 to the velocity of light. What is the quantum no. "n" of the orbit and the wave no. of the radiation emitted for the transition form the quantum state (n + 1) to the ground state.

**8.** A doubly ionised lithium atom is hydrogen like with atomic number Z = 3. Find the wavelength of the radiation required to excite the electron in $Li^{2+}$ from the first to the third Bohr orbit.

**9.** Estimate the difference in energy between I and II Bohr Orbit for a hydrogen 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 like species does this At. no. correspond to:

**10*.** 1.8 g atoms of hydrogen are excited to radiations. The study of spectra indicates that 27% of the atoms are in $3^{rd}$ energy level and 15% of atoms in $2^{nd}$ energy level and the rest in ground state. If I.P. of H is $21.7 \times 10^{-12}$ erg. Calculate.

(i) No. of atoms present in III & II energy level.

(ii) Total energy evolved when all the atoms return to ground state.

**11.** The energy of an excited H-atom is –3.4 eV. Calculate angular momentum of $e^-$.

**12.** The vapours of Hg absorb some electrons accelerated by a potential difference of 4.5 volt as a result of it light is emitted. If the full energy of single incident $e^-$ is supposed to be converted into light emitted by single Hg atom, find the wave no. of the light.

**13.** The hydrogen atom in the ground state is excited by means of monochromatic radiation of wavelength x $A^0$. The resulting spectrum consists of 15 different lines. Calculate the value of x.

**14.** If the average life time of an excited state of H atom is of order $10^{-8}$ sec, estimate how many orbits an $e^-$ makes when it is in the state n = 2 and before it suffers a transition to n = 1 state.

**15*.** A single electron orbits around a stationary nucleus of charge +Ze where Z is a constant from the nucleus and e is the magnitude of the electric charge. The hydrogen like species required 47.2 eV to excite the electron from the second Bohr orbit to the third Bohr orbit. Find -

(i) the value of Z give the hydrogen like species formed.

(ii) the kinetic energy and potential energy of the electron in the first Bohr orbit.

**16*.** A stationary $He^+$ ion emitted a photon corresponding to a first line of the Lyman series. The photon liberated a photoelectron from a stationary H atom in ground state. What is the velocity of photoelectron ?

## EXERCISE – 4 RECAP OF AIEEE/JEE (MAIN)

**1.** An atom has a mass of 0.02 kg and uncertainty in its velocity is $9.218 \times 10^{-6}$ m/s then uncertainty in position is ($h = 6.626 \times 10^{-34}$ Js) **[AIEEE 2002]**

(A) $2.86 \times 10^{-28}$ m (B) $2.86 \times 10^{-32}$ cm (C) $1.5 \times 10^{-27}$ m (D) $3.9 \times 10^{-10}$ m

**2.** Energy of H- atom in the ground state is –13.6 eV, Hence energy in the second excited state is- **[AIEEE 2002]**

(A) –6.8 eV (B) –3.4 eV (C) –1.51 eV (D) –4.3 eV

**3.** Uncertainty in position of a particle of 25 g in space is $10^{-5}$ m. Hence uncertainty in velocity ($ms^{-1}$) is (Planck's constant $h = 6.6 \times 10^{-34}$ Js) **[AIEEE-2002]**

(A) $2.1 \times 10^{-28}$ (B) $2.1 \times 10^{-34}$ (C) $0.5 \times 10^{-34}$ (D) $5.0 \times 20^{-24}$

**4.** The orbital angular momentum for an electron revolving in an orbit is given by $\sqrt{\ell(\ell+1)} \cdot \frac{h}{2\pi}$. This momentum for an s-electron will be given by **[AIEEE-2003]**

(A) $\sqrt{2}.\frac{h}{2\pi}$ (B) $+\frac{1}{2}.\frac{h}{2\pi}$ (C) zero (D) $\frac{h}{2\pi}$

**5.** The de Broglie wavelength of a tennis ball of mass 60 g moving with a velocity of 10 metres per second is approximately : **[AIEEE 2003]**

(A) $10^{-25}$ metres (B) $10^{-33}$ metres (C) $10^{-31}$ metres (D) $10^{-16}$ metres

**6.** In Balmer series of lines of hydrogen spectrum, the third line from the red end corresponds to which one of the following inter-orbit jumps of the electron for Bohr orbits in an atom of hydrogen ? **[AIEEE-2003]**

(A) $2 \rightarrow 5$ (B) $3 \rightarrow 2$ (C) $5 \rightarrow 2$ (D) $4 \rightarrow 1$

**7.** The orbital angular momentum for an electron revolving in an orbit is given by $\sqrt{\ell(\ell+1)} \cdot \frac{h}{2\pi}$. This momentum for an s-electron will be given by **[AIEEE-2003]**

(A) $\sqrt{2}.\frac{h}{2\pi}$ (B) $+\frac{1}{2}.\frac{h}{2\pi}$ (C) zero (D) $\frac{h}{2\pi}$

**8.** The wavelength of the radiation emitted, when in a hydrogen atom electron falls from infinity to stationary state 1, would be **[AIEEE-2004]**

(Rydberg constant = $1.097 \times 10^{7}$ $m^{-1}$) :

(A) $9.1 \times 10^{-8}$ nm (B) 192 nm (C) 406 nm (D) 91 nm

**9.** According to Bohr's theory angular momentum of electron in 5th shell is :- **[AIEEE-2006]**

(A) 1.0 h/π (B) 10 h/π (C) 2.5 h/π (D) 25 h/π

**10.** Uncertainty in the position of an electron (mass = $9.1 \times 10^{-31}$ Kg) moving with a velocity 300 $ms^{-1}$, accurate upto 0.001%, will be :- ($h = 6.63 \times 10^{-34}$ Js) **[AIEEE-2006]**

(A) $5.76 \times 10^{-2}$ m (B) $1.92 \times 10^{-2}$ m (C) $3.84 \times 10^{-2}$ m (D) $19.2 \times 10^{-2}$ m

**11.** The ionziation enthalpy of hydrogen atom is $1.312 \times 10^6$ J mol$^{-1}$. The energy required to excite the electron in the atom from n =1 to n =2 is **[AIEEE-2008]**

(A) $8.51 \times 10^5$ J mol$^{-1}$ (B) $6.56 \times 10^5$ J mol$^{-1}$ (C) $7.56 \times 10^5$ J mol$^{-1}$ (D) $9.84 \times 10^5$ J mol$^{-1}$

**12.** In an atom, an electron is moving with a speed of 600 m/s with an accuracy of 0.005%. Certainity with which the position of the electron can be located is ($h = 6.6 \times 10^{-34}$ kg m$^2$ s$^{-1}$, mass of electron, $e_m = 9.1 \times 10^{-31}$ kg):- **[AIEEE-2009]**

(A) $1.92 \times 10^{-3}$ m (B) $3.84 \times 10^{-3}$ m (C) $1.52 \times 10^{-4}$ m (D) $5.10 \times 10^{-3}$ m

**13*.** Calculate the wavelength (in nanometer) associated with a proton moving at $1.0 \times 10^3$ ms$^{-1}$ (Mass of proton = $1.67 \times 10^{-27}$ kg and $h = 6.63 \times 10^{-34}$ Js) :- **[AIEEE-2009]**

(A) 2.5 nm (B) 14.0 nm (C) 0.032 nm (D) 0.40 nm

**14*.** The energy required to break one mole of Cl–Cl bonds in $Cl_2$ is 242 kJ mol$^{-1}$. The longest wavelength of light capable of breaking a single Cl–Cl bond is ($C = 3 \times 10^8$ ms$^{-1}$ and $N_A = 6.02 \times 10^{23}$ mol$^{-1}$) **[AIEEE-2010]**

(A) 494 nm (B) 594 nm (C) 640 nm (D) 700 nm

**15.** Ionisation energy of $He^+$ is $19.6 \times 10^{-18}$ J atom$^{-1}$. The energy of the first stationary state (n = 1) of $Li^{2+}$ is:- **[AIEEE-2010]**

(A) $8.82 \times 10^{-17}$ J atom$^{-1}$ (B) $4.41 \times 10^{-16}$ J atom$^{-1}$

(C) $-4.41 \times 10^{-17}$ J atom$^{-1}$ (D) $-2.2 \times 10^{-15}$ J atom$^{-1}$

**16.** A gas absorbs a photon of 355 nm and emits at two wavelengths. If one of the emissions is at 680 nm, the other is at :- **[AIEEE-2011]**

(A) 743 nm (B) 518 nm (C) 1035 nm (D) 325 nm

**17*.** The frequency of light emitted for the transition n = 4 to n = 2 of $He^+$ is equal to the transition in H atom corresponding to which of the following :- **[AIEEE-2011]**

(A) n = 3 to n = 1 (B) n = 2 to n = 1 (C) n = 3 to n = 2 (D) n = 4 to n = 3

**18.** The wave number of the first emission line in the Balmer series of H-Spectrum is : (R = Rydberg constant) : **[JEE-Main 2013]**

(A) $\frac{3}{4}R$ (B) $\frac{9}{400}R$ (C) $\frac{5}{36}R$ (D) $\frac{7}{6}R$

**19.** The de Broglie wavelength of a car of mass 1000 kg and velocity 36 km/hr is : ($h = 6.63 \times 10^{-34}$ Js) **[JEE-Main 2013]**

(A) $6.626 \times 10^{-31}$ m (B) $6.626 \times 10^{-34}$ m (C) $6.626 \times 10^{-38}$ m (D) $6.626 \times 10^{-30}$ m

**20.** For which of the following particles will it be most difficult to experimentally verify the de-Broglie relationship? **[JEE-Main 2014]**

(A) a dust particle (B) an electron (C) a proton (D) an $\alpha$-particle.

**21.** If the binding energy of the electron in a hydrogen atom is 13.6 eV, the energy required to remove the electron from the first excited state of $Li^{++}$ is : **[JEE-Main 2014]**

(A) 13.6 eV (B) 30.6 eV (C) 122.4 eV (D) 3.4 eV

**22.** Based on the equation $\Delta E = -2.0 \times 10^{-18} J\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$ the wavelength of the light that must be absorbed to excite hydrogen electron from level n = 1 to level n = 2 will be ($h = 6.625 \times 10^{-34}$ Js, $C = 3 \times 10^8$ $ms^{-1}$) **[JEE-Main 2014]**

(A) $2.650 \times 10^{-7}$ m (B) $1.325 \times 10^{-7}$ m (C) $1.325 \times 10^{-10}$ m (D) $5.300 \times 10^{-10}$ m

**23.** If $\lambda_0$ and $\lambda$ be the threshold wavelength and wavelength of incident light, the velocity of photoelectron ejected from the metal surface is **[JEE-Main 2014]**

(A) $\sqrt{\frac{2hc}{m}\left(\frac{\lambda_0 - \lambda}{\lambda\lambda_0}\right)}$ (B) $\sqrt{\frac{2h}{m}\left(\frac{1}{\lambda_0} - \frac{1}{\lambda}\right)}$ (C) $\sqrt{\frac{2h}{m}(\lambda_0 - \lambda)}$ (D) $\sqrt{\frac{2hc}{m}(\lambda_0 - \lambda)}$

**24.** Ionization energy of gaseous Na atoms is 495.5 $kjmol^{-1}$. The lowest possible frequency of light that ionizes a sodium atom is **($h = 6.626 \times 10^{-34}$ Js, $N_A = 6.022 \times 10^{23}$ $mol^{-1}$)** **[JEE-Main 2014]**

(A) $3.15 \times 10^{15}$ $s^{-1}$ (B) $4.76 \times 10^{14}$ $s^{-1}$ (C) $1.24 \times 10^{15}$ $s^{-1}$ (D) $7.50 \times 10^4$ $s^{-1}$

**25*.** Which of the following is the energy of a possible excited state of hydrogen ? **[JEE-Main-2015]**

(A) +13.6 eV (B) – 6.8 eV (C) – 3.4 eV (D) + 6.8 eV

**26.** At temperature T, the average kinetic energy of any particle is $\frac{3}{2}$ kT- The de Broglie wavelength follows the order : **[JEE-Main 2015]**

(A) Visible photon > Thermal electron > Thermal neutron

(B) Thermal proton > Thermal electron > Visible photon

(C) Visible photon > Thermal neutron > Thermal electron

(D) Thermal proton > Visible photon > Thermal electron

**27*.** A stream of electrons from a heated filament was passed between two charged plates kept at a potential difference V esu. If e and m are charge and mass of an electron, respectively, then the value of $h/\lambda$ (where $\lambda$ is wavelength associated with electron wave) is given by: **[JEE-Main 2016]**

(A) me V (B) 2me V (C) $\sqrt{meV}$ (D) $\sqrt{2meV}$

**28.** The radius of the second Bohr orbit for hydrogen atom is : **[JEE-Main 2017]**

(Planck's Const. $h = 6.6262 \times 10^{-34}$ Js; mass of electron $= 9.1091 \times 10^{-31}$ kg; charge of electron $e = 1.60210 \times 10^{-19}$ C; permittivity of vacuum $\epsilon_0 = 8.854185 \times 10^{-12}$ $kg^{-1}$ $m^{-3}A^2$)

(A) 2.12 Å (B) 1.65Å (C) 4.76 Å (D) 0.529 Å

**29.** If the shortest wavelength in Lyman series of hydrogen atom is A, then the longest wavelength in Paschen series of $He^+$ is : **[JEE-Main 2017]**

(A) $\frac{36A}{5}$ (B) $\frac{9A}{5}$ (C) $\frac{36A}{7}$ (D) $\frac{5A}{9}$

**30.** The electron in the hydrogen atom undergoes transition from higher orbitals to orbital of radius 211.6 pm. This transition is associated with:- **[JEE-Main 2017]**

(A) Brackett series (B) Balmer series (C) Lyman series (D) Paschen series

**31.** The de-Broglie's wavelength of electron present in first Bohr orbit of 'H' atom is : ***[JEE-Main 2018]***

(A) $\frac{0.529}{2\pi}$ Å (B) 2p × 0.529Å (C) 0.529Å (D) 4 × 0.529Å

**32.** Ejection of the photoelectron from metal in the photoelectric effect experiment can be stopped by applying 0.5 V when the radiation of 250 nm is used. The work function of the metal is : ***[JEE-Main 2018]***

(A) 5 eV (B) 4 eV (C) 5.5 eV (D) 4.5 eV

**33.** Which of the following statements is false ? ***[JEE-Main 2018]***

(A) Photon has momentum as well as wavelength.

(B) Splitting of spectral lines in electrical field is called Stark effect.

(C) Frequency of emitted radiation from a black body goes from a lower wavelength to higher wavelength as the temperature increases.

(D) Rydberg constant has unit of energy.

**34.** Which of the following combination of statements is true regarding the interpretation of the atomic orbitals ? ***[JEE-Main 2019]***

(a) An electron in an orbital of high angular momentum stays away from the nucleus than an electron in the orbital of lower angular momentum.

(b) For a given value of the principal quantum number, the size of the orbit is inversely proportional to the azimuthal quantum number.

(c) According to wave mechanics, the ground state angular momentum is equal to $\frac{h}{2\pi}$

(d) The plot of $\psi$ Vs r for various azimuthal quantum numbers, shows peak shifting towards higher r value.

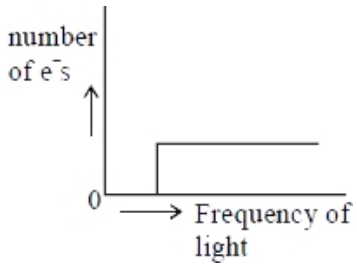
(A) (b), (c) (B) (a), (d) (C) (a), (b) (D) (a), (c)

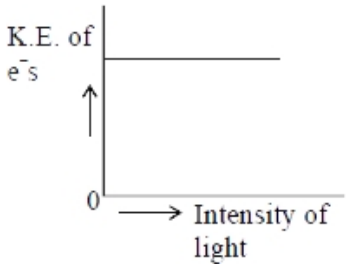
**35.** For emission line of atomic hydrogen from $n_i = 8$ to $n_f =$ the plot of wave number $(\bar{v})$ against $\left(\frac{1}{n^2}\right)$ (The Rydberg constant, $R_H$ is in wave number unit). ***[JEE-Main 2019]***

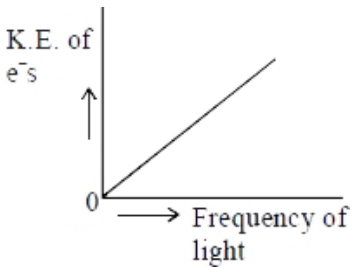
(A) Linear with slope - $R_H$ (B) Linear with intercept - $R_H$

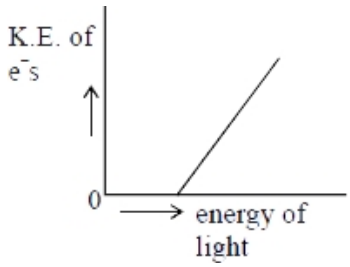
(C) Non linear (D) Linear with slope $R_H$

**36.** Which of the graphs shown below does not represent the relationship between incident light and the electron ejected form metal surface ? ***[JEE-MAIN2019]***

(A)



(B)



(C)



(D)


**37.** The ground state energy of hydrogen atom is –13.6 eV. The energy of second excited state $He^+$ ion in eV is : **[JEE-Main 2019]**

(A) –6.04 (B) –27.2 (C) –54.4 (D) –3.4

**38.** The de Broglie wavelength ( $\lambda$ ) associated with a photoelectron varies with the frequency (v) of the incident radiation as, [$v_0$ is threshold frequency] **[JEE-Main 2019]**

(A) $\lambda \propto \frac{1}{(v - v_0)^{\frac{3}{2}}}$ (B) $\lambda \propto \frac{1}{(v - v_0)^{\frac{1}{2}}}$ (C) $\lambda \propto \frac{1}{(v - v_0)^{\frac{1}{4}}}$ (D) $\lambda \propto \frac{1}{(v - v_0)}$

**39.** Heat treatment of muscular pain involves radiation of wavelength of about 900 nm. Which spectral line of H–atom is suitable for this purpose ?

[$R_H = 1 \times 10^5$ cm$^{-1}$, h = $6.6 \times 10^{-34}$ Js, c = $3 \times 10^8$ ms$^{-1}$] **[JEE-Main 2019]**

(A) Paschen, $5 \rightarrow 3$ (B) Paschen, $\infty \rightarrow 3$ (C) Lyman, $\infty \rightarrow 1$ (D) Balmer, $\infty \rightarrow 2$

**40.** If the de Broglie wavelength of the electron in $n^{th}$ Bohr orbit in a hydrogenic atom is equal to $1.5\ \pi a_0$($a_0$ is Bohr radius), then the value of n/z is : **[JEE-Main 2019]**

(A) 1.0 (B) 0.75 (C) 0.40 (D) 1.50

**41.** What is the work function of the metal if the light of wavelength 4000 Å generates photoelectrons of velocity $6 \times 10^5$ ms$^{-1}$ form it

(Mass of electron = $9 \times 10^{-31}$ kg Velocity of light = $3 \times 10^8$ ms$^{-1}$ Planck's constant = $6.626 \times 10^{-34}$ Js Charge of electron = $1.6 \times 10^{-19}$ JeV$^{-1}$) **[JEE-Main 2019]**

(A) 0.9 eV (B) 4.0 eV (B) 2.1 eV (D) 3.1 eV

**42.** If p is the momentum of the fastest electron ejected from a metal surface after the irradiation of light having wavelength $\lambda$, then for 1.5 p momentum of the photoelectron, the wavelength of the light should be : **[JEE-Main 2019]**

(Assume kinetic energy of ejected photoelectron to be very high in comparison to work function)

(A) $\frac{1}{2}\lambda$ (B) $\frac{3}{4}\lambda$ (C) $\frac{2}{3}\lambda$ (D) $\frac{4}{9}\lambda$

**43.** For any given series of spectral lines of atomic hydrogen, let $\Delta\bar{v} = \bar{v}_{max} - \bar{v}_{min}$ be the difference in maximum and minimum frequencies in cm$^{-1}$. The ratio $\Delta\bar{v}_{Lyman} / \Delta\bar{v}_{Balmer}$ is : **[JEE-Main 2019]**

(A) 27 : 5 (B) 4 : 1 (C) 5 : 4 (D) 9 : 4

**44.** Which one of the following about an electron occupying the 1s orbital in a hydrogen atom is incorrect ? (The Bohr radius is represented by $a_0$) **[JEE-Main 2019]**

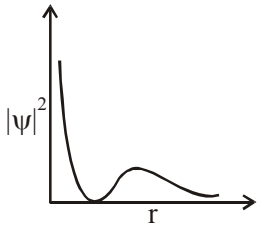
(A) The electron can be found at a distance $2a_0$ from the nucleus

(B) The probability density of finding the electron is maximum at the nucleus.

(C) The magnitude of potential energy is double that of its kinetic energy on an average.

(D) The total energy of the electron is maximum when it is at a distance $a_0$ from the nucleus.

**45.** The graph betweeen $|\psi|^2$ and r(radial distance) is shown below. This represents :- ***[JEE-Main 2019]***

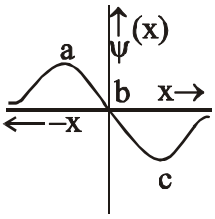



(A) 3s orbital (B) 1s orbital (C) 2p orbital (D) 2s orbital

**46.** The ratio of the shortest wavelength of two spectral series of hydrogen spectrum is found to be about 9. The spectral series are: ***[JEE-Main 2019]***

(A) Paschen and P fund (B) Lyman and Paschen (C) Brackett and Piund (D) Balmer and Brackett

**47.** The electrons are more likely to be found : ***[JEE-Main 2019]***




(A) in the region a and b (B) in the region a and c (C) only in the region c (D) only in the region a

**48.** Among the following, the energy of 2s orbital is lowest in : ***[JEE-Main 2019]***

(A) K (B) Na (C) Li (D) H

## EXERCISE – 5 RECAP OF IIT-JEE/JEE (ADVANCED)

**1.** Given in hydrogenic atom $r_n$, $V_n$, E, $K_n$ stand for radius, potential energy, total energy and kinetic energy in $n^{th}$ orbit. Find the value of U,v,x,y. ***[JEE 2006]***

| | |
|---|---|
| (A) $U = \frac{V_n}{K_n}$ | (p) 1 |
| (B) $\frac{1}{r_n} \propto E^x$ | (q) –2 |
| (C) $r_n \propto Z^y$ (Z = Atomic number) | (r) –1 |
| (D) v = (Orbital angular momentum of electron in its lowest energy) | (s) 0 |

**2.** Match the entries in ***Column I*** with the correctly related quantum number(s) in ***Column II***. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS. ***[JEE 2008]***

| ***Column I*** | ***Column II*** |
|---|---|
| (A) Orbital angular momentum of the electron in a hydrogen-like atomic orbital | (p) Principal quantum number |
| (B) A hydrogen-like one-electron wave function obeying Pauli principle | (q) Azimuthal quantum number |
| (C) Shape, size and orientation of hydrogen like atomic orbitals | (r) Magnetic quantum number |
| (D) Probability density of electron at the nucleus in hydrogen-like atom | (s) Electron spin quantum number |

***Paragraph for questions 8 to 10*** ***[JEE 2010]***

The hydrogen-like species $Li^{2+}$ is in a spherically symmetric state $S_1$ with one radial node. Upon absorbing light the ion undergoes transition to a state $S_2$. The state $S_2$ has one radial node and its energy is equal to the ground state energy of the hydrogen atom.

**3*.** The state $S_1$ is :-

(A) 1s (B) 2s (C) 2p (D) 3s

**4*.** Energy of the state $S_1$ in units of the hydrogen atom ground state energy is :-

(A) 0.75 (B) 1.50 (C) 2.25 (D) 4.50

**5*.** The orbital angular momentum quantum number of the state $S_2$ is :-

(A) 0 (B) 1 (C) 2 (D) 3

**6*.** The work function ($\phi$) 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 :- ***[JEE 2011]***

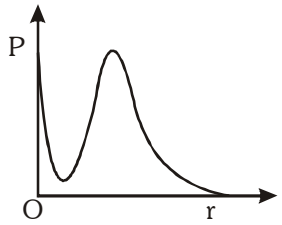
| Metal | Li | Na | K | Mg | Cu | Ag | Fe | Pt | W |
|---|---|---|---|---|---|---|---|---|---|
| $\phi$(eV) | 2.4 | 2.3 | 2.2 | 3.7 | 4.8 | 4.3 | 4.7 | 6.3 | 4.75 |

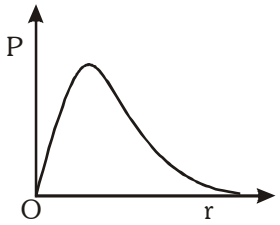
**7*.** The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is [$a_0$ is Bohr radius] ***[JEE 2012]***

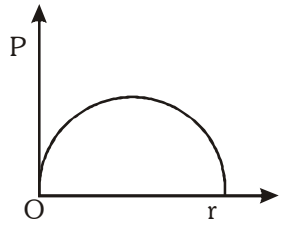
(A) $\frac{h^2}{4\pi^2 m a_0^2}$ (B) $\frac{h^2}{16\pi^2 m a_0^2}$ (C) $\frac{h^2}{32\pi^2 m a_0^2}$ (D) $\frac{h^2}{32\pi^2 m a_0^2}$

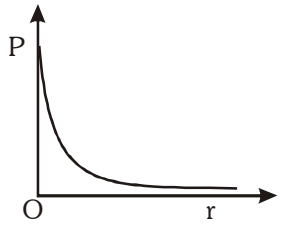
**8.** Not considering the electronic spin the degeneracy of the second excited state (n = 3) of H atom is 9, while the degeneracy of the second excited state of H is ***[JEE 2015]***

**9*.** P is the probability of find the 1s electron of hydrogen atom in a spherical shell of infinitesimal thickness, dr, at a distance r from the nucleus. The volume of this shell is $4\pi r^2 dr$. The qualitative sketch of the dependence of P on r is ***[JEE 2016]***

(A)


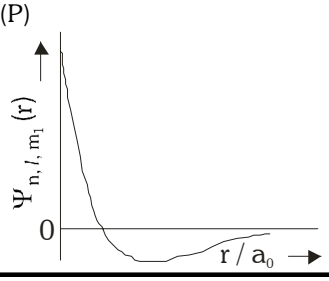

(B)



(C)



(D)



***Answer Q.12, Q.13 and Q.14 by appropriately matching the information given in the three columns of the following table.***

The wave function, $\Psi_{n,l,m_1}$ is a mathematical function whose value depends upon spherical polar coordinates (r, θ, ϕ) of the electron and characterized by the quantum numbers n, $l$ and $m_1$. Here r is distance from nucleus, θ is colatitude and ϕ is azimuth. In the mathematical functions given in the Table, Z is atomic number and $a_0$ is Bohr radius.

| ***Column I*** | ***Column 2*** | ***Column 3*** |
|---|---|---|
| (I) 1s orbital | (i) $\Psi_{n,l,m_1} \propto \left(\frac{Z}{a_0}\right)^{3/2} e^{-\left(\frac{Zr}{a_0}\right)}$ | (P)   |
| (II) 2s orbital | (ii) One radial node | (Q) Probability density at nucleus $\propto \frac{1}{a_0^3}$ |
| (III) $2p_z$ orbital | (iii) $\Psi_{n,l,m_1} \propto \left(\frac{Z}{a_0}\right)^{5/2} re^{-\left(\frac{Zr}{2a_0}\right)} \cos\theta$ | (R) Probability density is maximum at nucleus |
| (IV) $3d_z^2$ orbital | (iv) xy-plane is a nodal plane | (S) Energy needed to excite electron from n = 2 state to n = 4 state is $\frac{27}{32}$ times the energy needed to excite electron from n = 2 state to n = 6 state |

**12.** For the given oribtal in Coumn 1, the only CORRECT combination for any hydrogen-like species is **[JEE 2017]**

(A) (IV) (iv) (R) (B) (II) (ii) (P) (C) (III) (iii) (P) (D) (I) (ii) (S)

**13.** For $He^+$ ion, the only INCORRECT combination is **[JEE 2017]**

(A) (II) (ii) (Q) (B) (I) (i) (S) (C) (I) (i) (R) (D) (I) (iii) (R)

**14.** For hydrogen atom, the only CORRECT combination is **[JEE 2017]**

(A) (I) (iv) (R) (B) (I) (i) (P) (C) (II) (i) (Q) (D) (I) (i) (S)

**15.** The ground state energy of hydrogen atom is –13.6 eV. Consider an electronic state $\Psi$ of $He^+$ whose energy, azimuthal quantum number and magnetic quantum number are –3.4 eV, 2 and 0 respectively. Which of the following statement(s) is(are) true for the state $\Psi$?

(1) It has 2 angular nodes

(2) It has 3 radial nodes

(3) It is a 4d state

(4) The nuclear charge experienced by the electron in this state is less than 2e, where e is the magnitude of the electronic charge. **[JEE 2019]**

# ANSWERS

## EXERCISE-1

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | C | A | D | D | A | D | B | B | B | A |
| Que. | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Ans. | B | C | D | C | D | A | D | B | B | A |
| Que. | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Ans. | B | B | B | A | B | D | C | C | D | A |
| Que. | 31 | 32 | 33 | 34 | 35 | | | | | |
| Ans. | A | C | A | B | B | | | | | |

## EXERCISE-2

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | AC | BC | AC | AC | BCD | BC | BCD | AC | AC | BCD |
| Que. | 11 | | | | | | | | | |
| Ans. | AB | | | | | | | | | |

- ***Match the Column***

**12*.** (A) → (p), (B) → (p,q,s), (C) → (p,r), (D) → (q,s) **13.** (A) → (s), (B) → r, (C) → (q), (D) → (p)

- ***Comprehension Based Questions***

***Comprehension-1 :*** **14.** (C) **15.** (D) **16.** (C)

***Comprehension-2 :*** **17.** (A) **18.** (C) **19.** (A)

## EXERCISE-3

**1.** (6) **2.** 4863 Å **3.** $1.827 \times 10^5$ J/mol **4.** 1403 kJ/mol

**5.** $-1.36 \times 10^{-19}$ Joules **6.** $5.425 \times 10^{-12}$ ergs, $3.7 \times 10^{-5}$ cm

**7*.** 2 ; $9.75 \times 10^4$ $cm^{-1}$ **8.** 113.74 A°

**9.** 10.2 eV, Z=2 **10*.** $292.68 \times 10^{21}$ atoms, $162.60 \times 10^{21}$ atoms, 832.50 kJ

**11.** $h/\pi$ **12.** $3.63 \times 10^6 m^{-1}$

**13.** 938 A° **14.** $8 \times 10^6$

**15*.** (i) Z = 5, (ii) 340 eV, –680 eV **16*.** $3.09 \times 10^8$ cm/sec

## EXERCISE-4

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | A | C | A | C | B | C | C | D | C | B |
| Que. | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Ans. | D | A | D | A | C | A | B | C | C | A |
| Que. | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Ans. | B | B | A | C | C | A | D | A | C | B |
| Que. | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 |
| Ans. | B | D | C | D | D | C | A | B | B | B |
| Que. | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | | |
| Ans. | C | D | D | D | D | B | B | A | | |

## EXERCISE-5

**1.** (A)- q, (B)- p, (C)- r, (D)- s

**2.** (A)- q,r (B)- p, q, r, s (C)- p, q, r (D)- p, q

**3*.** (B)

**4*.** (C)

**5*.** (B)

**7*.** (4)

**8*.** (C)

**10.** (3)

**11*.** (B)

**12.** (B)

**13.** (D)

**14.** (D)

**15.** (1,3)

# GASEOUS STATE

## Recap of Early Classes

In our earlier classes we have studied about classification of matter on the basis of physical state as well as on the basis of chemical state. We have learnt that primarily matter can be classified into three states - solids, liquids and gases (apart from plasma and other non classical states). We have also learnt that state of matter and phase are two different entities which are often confused as similar terms. This chapter will aim at analysing the gaseous state which is characterised by high kinetic energy of particles and weak inter particle attractions. We shall first study the ideal gas behaviour and will then try to understand the deviation of certain gases from ideal behaviour through analysis of real gas behaviour.

## Index


**1.0 INTRODUCTION**

1.1 Difference between states of matter

**2.0 MEASURABLE PROPERTIES OF GASES**

2.1 Mass

2.2 Volume

2.3 Temperature

2.4 Pressure

2.5 Density

**3.0 GAS LAWS**

3.1 Boyle's law

3.2 Charles' law

3.3 Gay-Lussac's law : Dependence of Pressure on Temperature

3.4 Avogadro's Law

3.5 The combined gas Law

**4.0 THE IDEAL GAS EQUATION**

**5.0 DALTON'S LAW OF PARTIAL PRESSURES**

5.1 Amagat's law of partial Volume

**6.0 GRAHAM'S LAW OF DIFFUSION AND EFFUSION**

6.1 Limitations of this law

**7.0 KINETIC THEORY OF GASES**

7.1 Different types of molecular velocities

7.2 Distribution of molecular speeds

7.3 Collision frequency & mean free path

**8.0 BAROMETRIC FORMULA**

**9.0 REAL GAS**

9.1 Volume correction

9.2 Pressure correction

9.3 Characteristics of 'a' and 'b'

**10.0 LIQUEFACTION OF GASES AND CRITICAL POINTS**

10.1 Andrews Isotherms

**EXERCISE-1**

**EXERCISE-2**

**EXERCISE-3**

**EXERCISE-4**

**EXERCISE-5**

# GASEOUS STATE

## 1.0 INTRODUCTION

Matter is made up of atoms or molecules. The arrangement of these molecules determines the state of matter. There are three recognised state of matter : Solid, Liquid and Gas. Matter can change between states when the temperature or pressure is changed. State changes of matter are physical rather than chemical.

### 1.1 Difference between states of matter

SL

| | Gas | Liquid | Solid |
|---|---|---|---|
| *(i)* | Assumes the shape and volume of its container. it occupies | Assumes the shape of the part of the container which | Retains a fixed volume and shape. |
| *(ii)* | Particles can move past one another. | Particles can move/slide past one another. | Rigid-particles locked into place. |
| *(iii)* | Compressible, lots of free space between particles space. | Not easily compressible, little between particles. | Not easily compressible, little free space between particles. |
| *(iv)* | Flows easily, particles can move past one another. | Flows easily, particles can move/slide past one another. | Does not flow easily, rigid-particles cannot move/slide one past another |
| *(v)* | Low density. | Intermediate density. | High density. |
| *(vi)* | Very small intermolecular attraction but high kinetic energy. | Considerable intermolecular kinetic energy. | Intermolecular forces are high, vibrational motion only. |

## 2.0 MEASURABLE PROPERTIES OF GASES

### 2.1 Mass

SL

The gases do possess mass. The mass of gas is generally used in the form of number of moles which is related as

*(i)* ***no. of moles*** $= \dfrac{\text{wt. in gm}}{\text{molecular mass of gases}} \left(n = \dfrac{w}{M}\right)$

Two other useful formulae to calculate number of moles of gas are –

*(ii)* ***number of moles*** $= \dfrac{\text{no. of molecules of given gas}}{\text{Avogadro's number of molecules}} \left(n = \dfrac{N}{N_A}\right)$

*(iii)* ***no. of moles*** $= \dfrac{\text{volume of given gas in litres at NTP *}}{22.4\,L}$

***Note : *Strictly speaking NTP and STP are different ( NTP means normal temperature and pressure – 1 atm and 273 K and STP means standard temperature and pressure – 1 bar and 273 K) however for most numerical solving they can be assumed to be same.***

When container contains more than one gas then molecular mass of mixture is termed as effective molecular mass (EMM) which is intermediate between molecular masses of all the gases present in the container.

$$\textit{Effective molecular mass} = \frac{\text{Total mass of all the gases present in the container}}{\text{Total no. of moles of all gases present in the container}}$$

## 2.2 Volume

SL

Volume of gas is nothing but volume of the container in which it is present.

Relation between different units of volume

***$1\ m^3 = 10^3\ dm^3 = 10^3$ litre $= 10^6\ cm^3 = 10^6$ ml $= 10^9\ mm^3$.***

## 2.3 Temperature

SL

***Degree of hotness or coldness of a body is measured by temperature***

$$\frac{C}{100} = \frac{K-273}{100} = \frac{F-32}{180}$$

***C – Celcius scale,*** ***K – Kelvin scale,*** ***F – Fahrenheit scale***

***Note :*** *In all the problems of gaseous state (i.e. in all gas law equations), temperature must be expressed in kelvin scale. i.e. ,* ***t °C + 273 = TK***

## 2.4 Pressure

SL

Force acting per unit area

$$P = \frac{F}{A}$$

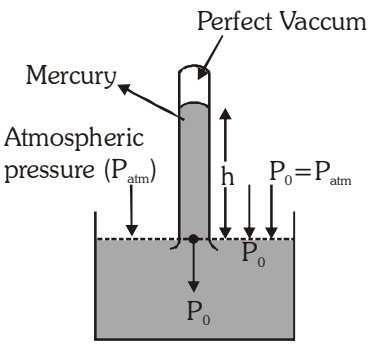
- **Pressure Measuring Devices**

Generally, the instruments used for the calculation of pressure of a gas are ***barometer*** and ***manometer.***

***(i)*** ***Barometer :*** A barometer is an instrument that is used for the measurement of atmospheric pressure.

The construction of the barometer is as follows -

A thin narrow calibrated capillary tube is filled up to the brim, with a liquid such as mercury, and is inverted into a trough filled with the same fluid. Now depending on the external atmospheric pressure, the level of the mercury inside the tube will adjust itself, the reading of which can be monitored. When the mercury column inside the capillary comes to rest, then the net forces on the column should be balanced.




$\Rightarrow$ $P_0 \times A = \rho A \times gh$

$\Rightarrow$ $\boxed{P_0 = \rho gh}$ ; where $\rho$ is the density of the fluid.

***(ii)*** ***Manometer :***

***(a)*** ***Open end manometer :*** It consists of a U-shaped tube partially filled with mercury. One limb of the tube is shorter than the other. The shorter limb is connected to the vessel containing the gas whereas the longer limb is open as shown in fig. The mercury in the longer tube is subjected to the atmospheric pressure while mercury in the shorter tube is subjected to the pressure of the gas.

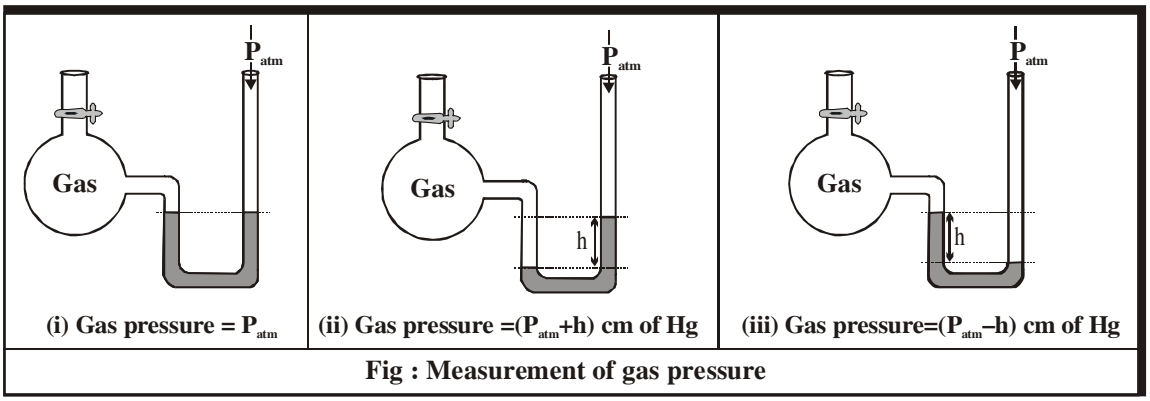



**Fig : Measurement of gas pressure**

Where $P_{atm}$ = 76 cm of Hg and h = Height in cm of Hg

There are three possibilities as described below :

***(i)*** If the level of Hg in the two limbs is same, then gas pressure = atmospheric pressure ($P_{atm}$).

***(ii)*** If the level of Hg in the longer limbs is higher, gas pressure

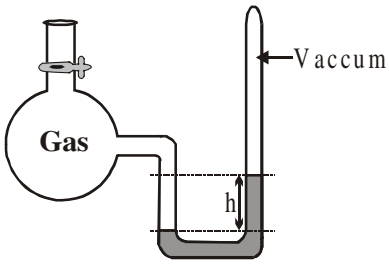
$= P_{atm}$ + (difference between the two levels)

$= P_{atm} + h$.

***(iii)*** If the level of Hg in the shorter limb is higher, then gas pressure

$= P_{atm}$ – (difference between the two levels)

$= P_{atm} - h$.




**Closed end manometer**

***(b) Closed end manometer :*** This is generally used to measure low gas pressure. It also consists of U-tube with one limb shorter than the other and partially filled with mercury as shown in fig.

The space above mercury on the closed end is completely evacuated. The shorter limb is connected to the vessel containing gas. The gas exerts pressure on the mercury in the shorter limb and forces its level down.

***Gas pressure = [Difference in the Hg level in two limbs]***

***Units of pressure:***

| | | |
|---|---|---|
| 1 atm | = | 76 cm of Hg |
| | = | 760 mm of Hg |
| | = | 760 torr |
| | = | $1.01325 \times 10^5$ N/m$^2$ |
| | = | 101.325 kPa |
| | = | 1.01325 bar |
| | = | 14.7 lb/In$^2$ (Psi) |
| | = | 10.33 meters of $H_2O$ |

## 2.5 Density

SL

Mass per unit volume

$$d = \frac{m}{V}$$

***Units***

CGS : g/cm$^3$

MKS : kg/m$^3$

Relation : 1 kg/m$^3$ = $10^{-3}$ g/cm$^3$

# Illustrations

***Illustration 1.*** Calculate the mass of mercury in a uniform column 760 mm high and 1.00 $cm^2$ in cross sectional area. Is there any change in.

***(a)*** mass and

***(b)*** pressure of column of same height but with 2.00$cm^2$ cross sectional area is taken ?

(density of Hg = 13.6 g/$cm^3$)

***Solution.*** 760 mm = 76 cm

$\therefore$ $V = 76 \times 1 = 76\ cm^3$

$\therefore$ Mass = V × d = 76 × 13.6 = 1033.6 g

***(a)*** If area of cross-section is 2$cm^2$ (doubled) then volume is also doubled hence,

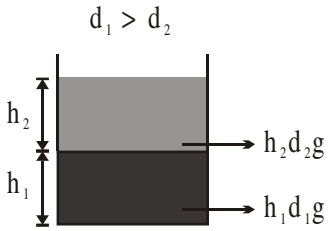
$\therefore$ Mass = 76 × 2 × 13.6 = 2067.2 g

***(b)*** This mass would rest on twice the area and so exert the same pressure.

***Illustration 2*.*** What will be the pressure if two immiscible fluid is filled according to given diagram.

(a) Find the pressure at the bottom of tank.

(b) Find the pressure at the middle point of bottom layer.




***Solution.*** (a) $P_{atm} + h_2d_2g + h_1d_1g$ ;

(b) $P_{atm} + h_2d_2g + \frac{h_1}{2}d_1g$

## BEGINNER'S BOX–1

### *Measurable Properties of Gases*

**1.** 413K temperature on Celsius scale Fahrenheit scale will manifest at, respectively

(A) 140°C, 252°F (B) 140°C, 284°F (C) 40°C, 381°F (D) 486°C, 140°F

**2.** 1 bar pressure in is equal to

(A) 0.987 Atm (B) 101.325 Atm (C) 101.325 mmHg (D) 76 mmHg

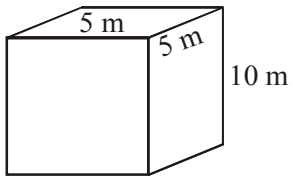
**3.** No. of mole of $CH_4$ gas present in 2.4 g of gas are:

(A) .15 (B) 1.5 (C) 15 (D) .015

**4.** How high a column of air would be necessary to cause the barometer to read 76 cm of Hg, if the atmosphere were of uniform density 1.2 kg/$m^3$ ? The density of Hg = 13.6 × $10^3$ Kg/$m^3$.

(A) 8613 meters (B) 8613 centimeter (C) 8.613 meter (D) 8613 mm

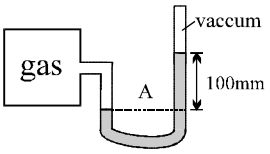
**5.** How much water can be occupied in the following cube .

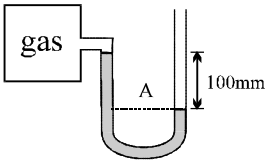


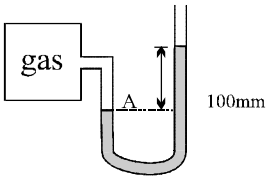

(A) 250 L (B) $2.5\times10^5$L (C) $2.5\times10^5$ mL (D) 2.5L

**6.** How much pressure will be felt by a gas balloon which at 100 m depth in a sea form sea level.
***[Pressure at ground level = $10^5$ Pa, g = 9.8 m/s$^2$]***
(A) 100 Pa (B) 98 Pa (C) $9.8 \times 10^5$ Pa (D) $1.08 \times 10^6$ Pa

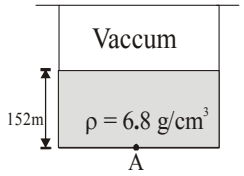
**7*.** Calculate the pressure of the gas in cm of Hg in each case (liquid used is Hg). (Assume $P_{atm}$ = 1 atm)

***(i)***



***(ii)***



***(iii)***



**8.** Calculate the pressure at the point A in :
(i) N/m$^2$ (ii) mm of Hg
(iii) m of $H_2O$ (iv) torr (v) atm




**9.** A closed beaker of circular cross section radius 4 cm is filled with Hg upto height 10 cm. Find the force exerted by the mercury on the bottom of the beaker.

## 3.0 GAS LAWS

SL AL

The gas laws are a set of laws that describe the relationship between thermodynamic temperature (T), pressure (P) and volume (V) of gases.

### 3.1 Boyle's law

SL AL

It states "at a constant temperature (T), the pressure (P) of a given mass (or moles, n) of any gas varies inversely with the volume (V)". Pressure (P) and volume (V) of gases.

i.e. $P \propto \frac{1}{V}$ (for given n and T)

or, $PV = K$ = constant

For two or more gases at constant temperature

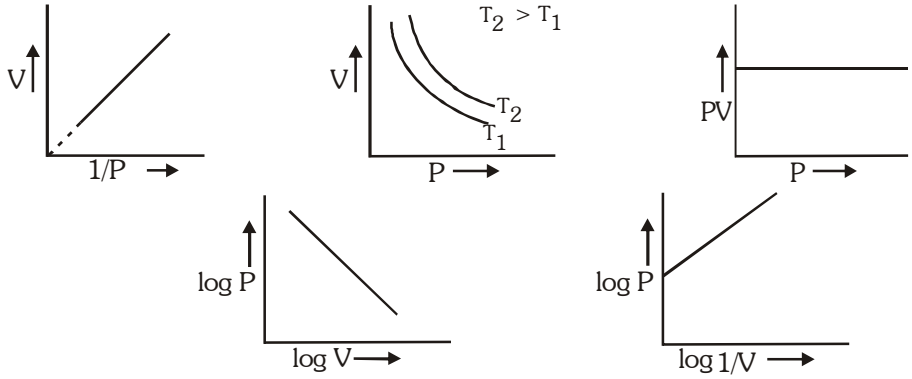
$P_1V_1 = P_2V_2 = ..... = K$

Also, density $d \propto \frac{1}{V}$

Hence $P \propto d$

or $\frac{P_1}{d_1} = \frac{P_2}{d_2} = ..... = K$

***Graphical representation:***




These plots drawn at constant temperature for a gas are called Isotherms.

## Illustrations

***Illustration 3.*** The diameters of a bubble at the surface of a lake is 4 mm and at the bottom of the lake is 1 mm. If atmospheric pressure is 1 atm and the temperature of the lake-water and the atmosphere are equal, what is the depth of the lake ? (The density of lake-water and Hg are 1 gm/ml and 13.6 gm/ml respectively. Also neglect the contribution of pressure due to surface tension).

***Solution.*** The pressure on the bubble = 1 atm (when it is at the surface)

The pressure on the bubble = P atm (say) (when it is at the bottom)

The volume of the bubble = $\frac{1}{6}\pi(0.1)^3$

$P \times \frac{1}{6}\pi \times (0.1)^3 = 1 \times \frac{1}{6}\pi(0.4)^3$

or $P = 64$ atm.

Thus the pressure due to water is 63 atm ($\therefore$ atmospheric pressure = 1 atm)

Now, consider the depth of lake is h cm

$\therefore \quad 63 \times 76 \times 13.6 \times g = h \times 1 \times g$

or $\quad h = 63 \times 76 \times 13.6$ cm $= 65116.8$ cm.

***Illustration 4*.*** A 10 cm volume of air is trapped by a column of Hg, 8 cm long in capillary tube horizontally fixed as shown below at 1 atm pressure. Calculate the length of air column when the tube is fixed at same temperature.

***(a)*** Vertically with open end up

***(b)*** Vertically with open end down

***(c)*** At 45°C from with open end up

(fig. 1)

***Solution.*** ***(a)*** When the capillary tube is held as vertically open end up (fig.2), The pressure on the air column = atmospheric pressure + pressure of 8 cm Hg column

= 76 + 8 = 84 cm of Hg.

Let, at this condition the length of the air column = $\ell_2$

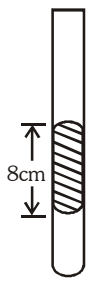
and the length of air column when capillary is horizontally fixed

= $\ell_1$ = 10 cm and pressure on air column = 1atm.

Let the cross section of the capillary = a $cm^2$

$\therefore \; 76 \times 10 \times a = 84 \times \ell_2 \times a$

or $\ell_2 = \frac{76 \times 10}{84} = 9.04$ cm



(fig. 2)

***(b)*** When the capillary tube is held as vertically open end down (fig.3), the pressure on the air column

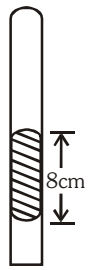
= atmospheric pressure – pressure of 8 cm Hg column

= 76 – 8 = 68 cm of Hg.

Let at this condition the length of air column = $\ell_3$.

$\therefore 68 \times \ell_3 \times a = 76 \times 10 \times a$

or $\ell_3 = \dfrac{76 \times 10}{68} = 11.17$ cm



(fig. 3)

***(c)*** When the capillary is held at 45° with open end up, the weight of Hg is partially borne by, the gas and partially by the Hg. The pressure on the gas due to Hg column

= 8 × cos 45°

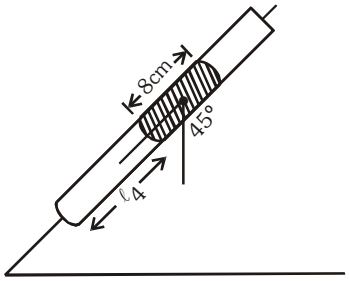
$= 8 \times \dfrac{1}{\sqrt{2}} = \dfrac{8}{\sqrt{2}}$ = cm of Hg

$\therefore$ total pressure on the gas = $\left(76 + \dfrac{8}{\sqrt{2}}\right)$ cm of Hg.

Let length of air column at this pressure = $\ell_4$.

$\therefore \quad \ell_4 \times a \times \left(76 + \dfrac{8}{\sqrt{2}}\right) = 10 \times a \times 76$

$\therefore \quad \ell_4 = \left(\dfrac{10 \times 76}{76 + 8/\sqrt{2}}\right) = 9.3$ cm



(fig. 4)

## 3.2. Charles' law

SL AL

It states "at constant pressure, the volume of a given mass of a gas, increases or decreases by $\dfrac{1}{273.15}$ th of its volume at 0°C for every rise or fall of one degree in temperature".

$$\frac{V_t}{V_0} = 1 + \frac{1}{273.15}t \quad \text{(at constant n and P)}$$

or $\quad V_t = V_0\left(1 + \dfrac{t}{273.15}\right)$

or $\quad V_t = \dfrac{V_0(273.15 + t)}{273.15}$

0°C on the Celsius scale is equal to 273.15 K at the Kelvin or absolute scale. i.e. $T_t$ (Temperature in Kelvin scale) = 273.15 + t

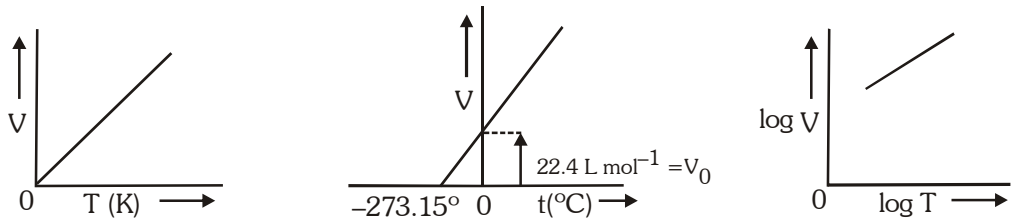
$\therefore$ From the above equation we get $\dfrac{V_t}{V_0} = \dfrac{T_t}{T_0}$

or $\quad \dfrac{V_t}{T_t} = \dfrac{V_0}{T_0}$

i.e. The volume of a given gas is proportional to the absolute temperature.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{(at constant P)}$$

***Graphical representation:***




Graphs between V and T at constant pressure are called Isobars.

## 3.3 Gay-Lussac's law : Dependence of Pressure on Temperature

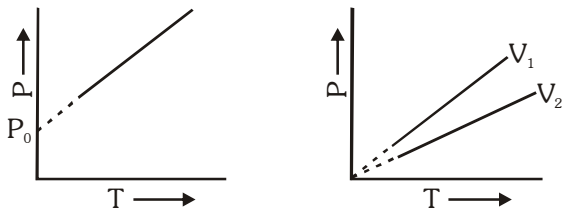
SL AL

It states "at constant volume, the pressure of a given mass of a gas is directly proportional to the absolute temperature of the gas".

$P \propto T$ or $P = KT$

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

***Graphical representation:***




The plots drawn at constant volume for a gas is called as Isochore.

## Illustrations

***Illustration 5.*** An iron tank contains helium at a pressure of 3.0 atm at 27°C. The tank can withstand a maximum pressure of 10 atm. The building in which tank has been placed catches fire predict whether the tank will blow up first or melt. (melting point of iron is 1535°C)

***Solution.*** $P_1 = 3.0$, $T_1 = 300$ K

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow \frac{3.0}{300} = \frac{P_2}{1808}$$

$$P_2 = \frac{3.0 \times 1808}{300} = 18.08 \text{ atm}$$

Since at melting point it is greater than the maximum pressure, therefore it will blow up.

## 3.4 Avogadro's Law

SL AL

It states "equal volumes of any two gases at the same temperature and pressure contain the same number of molecules".

$V \propto n$ (At constant P and T)

or, $\frac{V_1}{n_1} = \frac{V_2}{n_2}$

### 3.5 The combined gas Law

SL AL

It states "for a fixed mass of gas, the volume is directly proportional to absolute temperature and inversely proportional to the pressure".

Boyle's Law, $V \propto \frac{1}{P}$ (at constant n, T)

Charle's Law, $V \propto T$ (at constant n, P)

Therefore, $V \propto \frac{T}{P}$ or $V = K\frac{T}{P}$ or $\frac{PV}{T} = K$ or $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

## 4.0 THE IDEAL GAS EQUATION

SL AL

An ideal gas is defined to be a system in which there are no inter molecular/interatomic forces. Such a system can only exist as a gas. Any real system will approach ideal gas behaviour in the limit that the pressure is extremely low and the temperature is high enough to overcome attractive intermolecular forces.

An ideal gas is a gas to go which the laws of Boyle and Charles are strictly applicable under all conditions of temperatures and pressures.

From Boyle's law we get,

$V \propto 1/P$ (at constant n and T)

From charles law we get,

$V \propto T$ (at constant n and P)

From Avogadro's law we get,

$V \propto n$ (at constant T and P)

Combining the above three equations we get

$V \propto \frac{nT}{P}$ or $V = R\frac{nT}{P}$ [Where R = ideal gas constant]

***or PV = nRT***

Ideal gas equation is a relation between four variables and it describes the state of any gas. For this reason, it is also called Equation of State.

- **Dimension of R**

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

$$= \frac{(\text{Force}/\text{Area}) \times (\text{Area} \times \text{Length})}{\text{Mole} \times \text{Degree(K)}}$$

$$= \frac{\text{Force} \times \text{Length}}{\text{Mole} \times \text{Degree(K)}} = \frac{\text{Work or energy}}{\text{Mole} \times \text{Degree (K)}}$$

- **Physical significance of R**

The dimensions of R are energy per mole per kelvin and hence it represents the amount of work (or energy) that can be obtained from one mole of a gas when its temperature is raised by 1K.

- **Units of R**

***(i)*** In lit-atm $R = \dfrac{1\text{ atm} \times 22.4\text{ lit}}{273\text{ K}} = 0.0821\text{ lit-atm mol}^{-1}\text{K}^{-1}$

***(ii)*** In C.G.S system $R = \dfrac{1 \times 76 \times 13.6 \times 980\text{ dyne cm}^{-2} \times 22400\text{ cm}^3}{273\text{ K}} = 8.314 \times 10^7\text{ erg mole}^{-1}\text{K}^{-1}$.

***(iii)*** In M.K.S. system $R = 8.314\text{ Joule mole}^{-1}\text{K}^{-1}$. [$10^7$ erg = 1 joule]

***(iv)*** In calories $R = \dfrac{8.314 \times 10^7\text{ erg mole}^{-1}\text{K}^{?1}}{4.184 \times 10^7\text{ erg}} = 1.987 \approx 2\text{ calorie mol}^{-1}\text{K}^{-1}$.

## Illustrations

***Illustration 6*.*** 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 large flask exerts a pressure of 1.053 atm and the smaller on 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).

***Solution.*** For NO gas :-

$$n_{NO} = \frac{PV}{RT} = \frac{1.053 \times 250}{0.0821 \times 300 \times 1000} = 1.069 \times 10^{-2}$$

For $O_2$ gas :- $n_{O_2} = \dfrac{0.789 \times 100}{0.0821 \times 300 \times 1000} = 0.32 \times 10^{-2}$

| Now, | $2NO$ | $+ \; O_2$ | $\longrightarrow N_2O_4$ |
|---|---|---|---|
| Mole before reaction | $(1.069 \times 10^{-2})$ | $(0.32 \times 10^{-2})$ | 0 |
| Mole after reaction | $0.429 \times 10^{-2}$ | 0 | $0.32 \times 10^{-2}$ |

Moles of NO left = $4.29 \times 10^{-3}$

$P_{NO} \times V = nRT$ Given T = 220 K

$$V = \frac{250 + 100}{1000} = \frac{350}{1000}\text{ litre}$$

$$P_{NO} \times \frac{350}{1000} = 4.29 \times 10^{-3} \times 0.821 \times 220$$

$P_{NO}$ (left) = 0.221 atm.

## BEGINNER'S BOX–2

***Gas Law's***

***1.*** Calculate the weight of $CH_4$ in a 9 litre cylinder at 16 atm and 27° C. (R = 0.08 L atm K–1)

***2.*** A gas occupies 300 mL at 27°C and 730 mm pressure. What would be its volume at STP ?

***3.*** 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?

**4.** 3.7 gm of a gas at 25°C occupied the same volume as 0.184 gm of hydrogen at 17°C and at the same pressure. What is the molecular mass of the gas ?

**5.** 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 ?

**6.** Calculate the density of $CO_2$ at 100°C and 800 mm Hg pressure.

**7.** A gas occupies 0.418 litre at 740 mm of Hg and 27 °C . Calculate :

(a) its volume at STP

(b) molecular weight if gas weighs 3.0 g

(c) new pressure of gas if the weight of gas is increased to 7.5 g and temperature becomes 280 K

(d) the volume of vessel at 300 K

**8.** A balloon filled with helium raises to a certain height at which it gets fully inflated to a volume of $1 \times 10^5$ litre. If at this altitude temperature and atmospheric pressure is 268 K and $2 \times 10^{-3}$ atm respectively, what weight of helium is required to fully inflated the balloon ?

**9.** A 0.5 $dm^3$ flask contains gas A and 1 $dm^3$ flask contains gas B at the same temperature. If density of A = 3 $g/dm^3$ and that of B = 1.5 $g/dm^3$ and the molar mass of A = 1/2 of B, the ratio of pressure exerted by gases is :

(A) $\frac{P_A}{P_B} = 2$ (B) $\frac{P_A}{P_B} = 1$ (C) $\frac{P_A}{P_B} = 4$ (D) $\frac{P_A}{P_B} = 3$

**10.** According to Charle's law :

(A) $\left(\frac{dV}{dT}\right)_P$ = k (constant) (B) $\left(\frac{dV}{dT}\right)_P = P$ (C) $\left(\frac{dV}{dT}\right)_P = V$ (D) $\left(\frac{dV}{dT}\right) = T$

## 5.0 DALTON'S LAW OF PARTIAL PRESSURES

SL AL

Dalton's law of partial pressure states "at a given temperature, the total pressure exerted by two or more non-acting gases occupying a definite volume in equal to the sum of the partial pressures of the component gases."

$P_{Total} = p_1 + p_2 + p_3 + .....$ (At constant V and T)

$$= \left(\frac{n_1}{V} + \frac{n_2}{V} + \frac{n_3}{V} + .....\right)RT = (n_1 + n_2 + n_3 + .....)\frac{RT}{V} = \frac{nRT}{V}$$

Where $n = n_1 + n_2 + n_3 + .....$ = Total moles, V = Total volume

$$P_{Total} = \sum p_i = \frac{RT}{V}\sum n_i$$

Dalton's law of partial pressure is applicable only to non-reacting gases.

If the two non-reacting gases A and B having $n_A$ and $n_B$ number of moles respectively are filled in a vessels of volume V at temperature T, Then

$PV = (n_A + n_B)\,RT$ ....(i)

Partial pressure may be calculated as

$p_AV = n_ART,\ p_BV = n_BRT$

Total pressure $(p_A + p_B)\,V = (n_A + n_B)RT$ .....(ii)

from (i) and (ii)

$P = p_A + p_B$

$$\frac{p_A}{P} = \frac{n_A RT/V}{(n_A + n_B)RT/V} = \frac{n_A}{n_A + n_B} = x_A \text{ (mole fraction of A)}$$

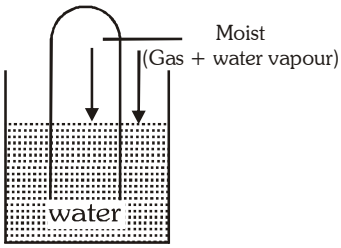
$p_A = x_A \times P$, similarly $p_B = x_B \times P$

Partial pressure of a component = Mole fraction × total pressure.

It has been observed that gases are generally collected over water and therefore are moist.

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

The pressure exerted by water vapour is constant with water at a particular temperature is called as aqueous tension, which varies directly with the temperature and becomes 760 mm at 100°C.




$$\text{Relative Humidity (RH)} = \frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water}}$$

Pressure of dry gas = Pressure of moist gas – aqueous tension.

## 5.1 AMAGAT'S LAW OF PARTIAL VOLUME

AL

According to this law at constant temperature and pressure, the total volume of mixture of gases which don't react is equal to the sum of partial volumes of each component present in mixture.

$V_T = V_1 + V_2 + V_3 + \ldots\ldots$

***Partial Volume***

Partial volume of any component is defined as the volume occupied by that particular component measured under the given condition of pressure and temperature.

$PV = nRT$

$V \propto n$

***Partial volume***

Let us consider a three non-reacting gases A, B and C are present in a container which have no. of moles $n_A$, $n_B$ and $n_C$ respectively. For each gas partial volume is

$$V_A = n_A\left(\frac{RT}{P}\right), \quad V_B = n_B\left(\frac{RT}{P}\right) \quad \text{and} \quad V_C = n_C\left(\frac{RT}{P}\right)$$

***Total volume***

$$V_T = V_A + V_B + V_C = (n_A + n_A + n_A)\left(\frac{RT}{P}\right) = n_T\left(\frac{RT}{P}\right)$$

## Illustrations

***Illustration 7.*** A vessel of 2 lit capacity contains hydrogen at 380 mm pressure at 27°C. 16gm of $O_2$ is added to the container then find the total pressure and partial pressure where R = 0.0821Latm $mol^{-1}k^{-1}$.

***Solution.*** For $H_2$ gas :

Given V= 2L and $p_{H_2} = \frac{380}{760} = \frac{1}{2}$atm

$p_{H_2}V = n_{H_2}RT$

$1 = n_{H_2} \times 0.0821 \times 300$

$$n_{H_2} = \frac{10000}{821 \times 300} = \frac{1}{24.6}$$

Moles of $O_2$ $= \frac{16}{32} = \frac{1}{2}$ Partial pressure of $H_2$ gas $(p_{H_2}) = \frac{1}{2} = \frac{n_{H_2}}{n_{H_2} + n_{o_2}} \times P$

$$\frac{1}{2} = \frac{\frac{1}{24.6}}{\frac{1}{24.6} + \frac{1}{2}} \times P \quad \text{or} \quad P = 6.65 \text{ atm}$$

***Illustration 8.*** 1 mole of $N_2$ and 3 moles of $H_2$ are mixed in 8.21 lit container at 300 K to form $NH_3$. If equilibrium average molecular mass was found to be 34/3 gram then find partial pressure of each component.

***Solution.***

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

Initially 1 3 0

at equilibrium $(1 - x)$ $3(1 - x)$ $2x$

Total moles $= 1 - x + 3 - 3x + 2x = (4 - 2x)$ moles

Given Average molecular mass $= \frac{34}{3}$

$$\frac{34}{3} = \frac{28(1-x) + 2(3-3x) + 17(2x)}{(4-2x)}$$

$$\frac{34}{3}(4 - 2x) = 34 \Rightarrow 4 - 2x = 3 \Rightarrow x = 1/2$$

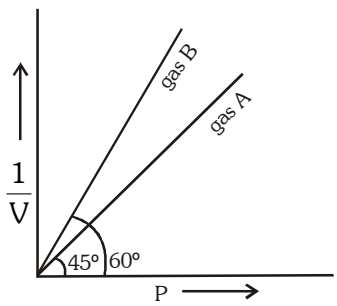
So total no. of moles = 3

$$PV = nRT \Rightarrow P = \frac{nRT}{V} = \frac{3 \times 0.821 \times 300}{8.21} = 9 \text{ atm}$$

$$p_{N_2} = \frac{1-x}{3} \times P = \frac{0.5}{3} \times 9 = 1.5 \text{ atm}$$

$$p_{H_2} = \frac{3-3x}{3} \times P = \frac{1.5}{3} \times 9 = 4.5 \text{ atm}$$

***Illustration 9*.*** At constant temperature of 273K, $\frac{1}{V}$ Vs P are plotted for 2 ideal gases A and B as shown. Find out the number of moles of gas A and B.




***Solution.*** $PV = nRT$, $P = \frac{1}{V} nRT$

$$\frac{1}{V} = \frac{1}{nRT} P$$

***Comparing by equation :***

$y = mx + C$

$C = 0$

$m = \frac{1}{nRT}$ $(m = \tan\theta)$

$\tan\theta = \frac{1}{nRT}$ $n_A = \frac{1}{RT\tan\theta}$

$$n_A = \frac{1}{0.0821 \times 273 \times \tan 45^\circ} \Rightarrow n_A = \frac{1}{22.4}$$

$$n_B = \frac{1}{RT\tan 60^\circ} = \frac{1}{22.4\sqrt{3}}$$

***Illustration 10.*** A 500 ml bulb is filled with $CH_4$ at a pressure of 1 atm and oxygen at a pressure of 4 atm at 27°C.

The mixture is then exploded, when the reaction $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O\ (\ell)$ occurs. Calculate the pressure if the final temperature is 27°C. Aqueous tension at 27°C is 26.7 mm.

***Solution.*** Partial pressure of $CH_4$, $(p_{CH_4}) = 1$ atm

Partial pressure of $O_2$, $(p_{O_2}) = 4$ atm

$\therefore$ moles of $CH_4$ present, $(n_{CH_4}) = \dfrac{1 \times 0.5}{RT} = \dfrac{0.5}{RT}$

$\therefore$ moles of $O_2$ present $(n_{O_2}) = \dfrac{4 \times 0.5}{RT} = \dfrac{2}{RT}$

$CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(\ell)$

Initially $\dfrac{0.5}{RT}$ $\dfrac{2}{RT}$

Finally $\dfrac{1}{RT}$ $\dfrac{0.5}{RT}$

After the reaction, moles of residual $O_2 = \dfrac{2}{RT} - \dfrac{1}{RT} = \dfrac{1}{RT}$

After the reaction, moles of $CO_2$ produced $= \dfrac{0.5}{RT}$

Hence total no. of moles of $O_2$ and $CO_2 = \dfrac{1.5}{RT}$

$\therefore$ total pressure due to $O_2$ and $CO_2 = \dfrac{1.5}{RT} \times \dfrac{RT}{0.5} = 3$ atm

$\therefore$ pressure exerted by the entire gaseous components

$$= 3 + \frac{26.7}{760} = 3 + 0.03513 = 3.0513 \text{ atm}$$

***Illustration 11.*** A sample of butane gas $C_4H_{10}$ of unknown mass is contained in a vessel of unknown volume V at 25°C and a pressure of 760 mmHg. To this vessel 8.6787 g of neon gas is added in such a way that no butane is lost from the vessel. The final pressure in the vessel is 1920 mm Hg at the same temperature. Calculate the volume of the vessel and the mass of butane.

***Solution.*** Partial pressure of $C_4H_{10}$ $(p_1) = 760$ mm Hg

By Dalton's law of partial pressure, $P_{total} = p_1 + p_2$

$1920 = 760 + p_2$ or $p_2 = 1160$ mm Hg

$p_2 = x_2 \times p_{total}$

where $x_2 =$ mole fraction of Ne

$$x_2 = \frac{p_2}{P_{total}} = \frac{1160}{1920} = 0.60 \text{ ; Moles of Ne} = \frac{8.6787}{20.2} = 0.43$$

$$x_2 = \frac{n_2}{n_1 + n_2} \text{ ; } 0.60 = \frac{0.43}{0.43 + n_1} \Rightarrow n_1 = 0.28$$

Molecular weight of $C_4H_{10} = 48 + 10 = 58$

so, amount of $C_4H_{10} = n_1 \times 58 = 16.24$ g

again for $C_4H_{10}$

$$PV = n_1RT \; ; T = 273 + 25 = 298 \text{ K}, P = \frac{760}{760}\text{atm} = 1 \text{ atm}$$

$$V = \frac{n_1RT}{P} = \frac{0.28 \times 0.0821 \times 298}{1} = 6.85 \text{ L}$$

***Illustration 12.*** A mixture of CO and $CO_2$ is found to have a density of 1.50 g/litre at 30°C and 730 mm. Calculate the composition of mixture.

***Solution.*** For mixture, P = (730/760) atm,

T = 303 K, d = 150 g litre$^{-1}$

$$\therefore \; PV = nRT = (w/M)\,RT \Rightarrow P(w/VM)\,RT \Rightarrow P = \frac{d}{M}RT$$

$$\therefore \; \frac{730}{760} = \frac{1.50}{M} \times 0.0821 \times 303$$

$\therefore$ M = 38.85

Let $n_1$ moles of CO and $(100 - n_1)$ moles of $CO_2$ are present in 100 moles.

$$\therefore \quad \text{Average molecular weight (M)} = \frac{n_1 \times 28 + (100 - n_1) \times 44}{100} = 38.85 \Rightarrow n_1 = 32.19$$

$\therefore$ mole % of CO = 32.19, and mole % of $CO_2$ = 67.81.

***Illustration 13*.*** An open vessel at 27°C is heated until 3/5$^{th}$ of the air in it has been expelled. Assuming that the volume of the vessel remains constant. Find

***(a)*** the temperature at which vessel was heated ?

***(b)*** the air escaped out if vessel is heated to 900 K ?

***(c)*** temperature at which half of the air escapes out ?

***Solution.*** One should clearly note the fact that on heating a gas in a vessel there are the number of moles of gas which go out, the volume of vessel remains constant.

Let initial moles of air at 300 K be 'n'. On heating 3/5 moles of air are escaped out at temperature T.

$$\therefore \text{ Moles of air left at temperature T} = \left(n - \frac{3}{5}n\right) = \frac{2n}{5}$$

***(a)*** Under simillar conditions of P and V

$$n_1T_1 = n_2T_2$$

$$n \times 300 = \frac{2n}{5} \times T \quad \Rightarrow T = 750 \text{ K}$$

***(b)*** On heating vessel to 900 K, let $n_1$ moles be left again $n_1T_1 = n_2T_2$

$$n_1 \times 900 = 300 \times n \quad \Rightarrow n_1 = \frac{1}{3}n$$

$$\therefore \text{ moles escaped out} = n - \frac{n}{3} = \frac{2}{3}n \text{ moles}$$

***(c)*** Let n/2 moles are escaped out at temperature T then

$$n_1T_1 = n_2T_2$$

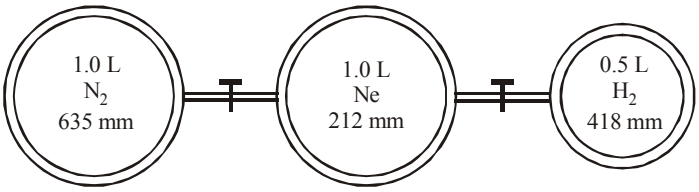
$$n/2 \times T = n \times 300$$

$$T = 600 \text{ K}$$

## BEGINNER'S BOX–3

### *Dalton's Law*

**1.** Consider the arrangement of bulbs shown below:




What is the pressure of the system when all the stopcocks are opened?

**2*.** Equal weights of $CH_4$ and $O_2$ are mixed in an empty container of one litre at 27°C. Calculate

***(a)*** the fraction of total pressure exerted by $O_2$

***(b)*** the total pressure if the weights of gases are 32 g each

**3.** Two gases A and B having molecular weights 60 and 45 respectively are enclosed in a vessel. The wt. 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.

**4.** 5 litre of $N_2$ under a pressure of 2 atm, 2 litre of $O_2$ at 5.5 atm and 3 litre of $CO_2$ at 5 atm are mixed. The resultant volume of the mixture is 15 litre. Calculate the total pressure of the mixture and partial pressure of each constituent.

**5.** A 10 litre flask at 298 K contains a gaseous mixture of CO and $CO_2$ at a total pressure of 2 atm. If 0.20 mole of CO is present , find its partial pressure and also that of $CO_2$.

**6.** Equal weights of methane and hydrogen are mixed in an empty container at 25°C. The fraction of total pressure exerted by hydrogen is :

(A) 1/2 (B) 8/9 (C) 16/19 (D) 1/9

## 6.0 GRAHAM'S LAW OF DIFFUSION AND EFFUSION

SL AL

### *Diffusion*

The process of mixing of gases by random motion of the molecules is called diffusion.

### *Effusion*

When gas is confined to a container at high pressure than in the surrounding atmosphere it will escape from a small hole which is opened in the container until the pressure outside and inside have been equalised. This process is called effusion.

The difference between diffusion and effusion is that in the former case, the gas spontaneously passes through a porous partition while in the case of effusion, the gas is passed out through a small orifice or hole by applying some external pressure.

***Graham's law of diffusion states "under the same conditions of temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their molecular masses or their densities."***

Mathematically , $r \propto \sqrt{\frac{1}{M}}$ or $\sqrt{\frac{1}{d}}$ or, $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$

Where $r_1$ and $r_2$ are the rates of diffusion of gases 1 and 2.
$M_1$ and $M_2$ are their molecular masses.
$d_1$ and $d_2$ are their densities.

***Rate of diffusion interms of volume diffused :***

$$\text{Rate of diffusion} = \frac{\text{Volume of gas diffused}}{\text{Time taken for diffusion}}$$

or $$r = \frac{V}{t}$$

Let $V_1$ be the volume of gas 1 and $V_2$ be the volume of gas 2, then

$$r_1 = \frac{V_1}{t_1} \qquad r_2 = \frac{V_2}{t_2}$$

$$\therefore \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \frac{V_1 t_2}{V_2 t_1}$$

***(i) Comparison of times taken for the same volume of two gases*** :

Let the times of diffusion for the same volume of two gases be $t_1$ and $t_2$ respectively. Then

$$\frac{r_1}{r_2} = \frac{V/t_1}{V/t_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \quad \text{or} \quad \frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

***(ii) Comparision of the volumes of the gases that diffuse in same time :***

Let $V_1$ and $V_2$ be the volume of two gases that diffuse in same time t. Then,

$$\frac{r_1}{r_2} = \frac{V_1/t}{V_2/t} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \quad \text{or} \quad \frac{r_1}{r_2} = \frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

***Note :*** *When a gas at pressure P and temperature T is separated from vacuum by a small hole of cross sectional area $A_0$, the rate of effusion of the gas is given by*

$$\textit{Rate of effusion} = \frac{kPA_0N_A}{(2\pi MRT)^{1/2}}$$

## 6.1 Limitations of this law

SL AL

***(i)*** The laws of diffusion and effusion are applicable only when the pressure difference is very small.

***(ii)*** Correctly speaking the rate of diffusion and effusion are not constant throughout the time interval, but these rates may be assumed constant for a small time interval.

## Illustrations

***Illustration 14*.*** The pressure in a bulb dropped from 2000 to 1500 mm of mercury in 47 minutes when the contained oxygen leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas of molecular weight 79 in the molar ratio of 1 : 1 at a total pressure of 4000 mm of mercury was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 minutes.

**Solution.** $r \propto \frac{P}{\sqrt{M}}$ $\quad r = \frac{kp}{\sqrt{M}}$

$$-\frac{dp}{dt} = \frac{kp}{\sqrt{M}}$$

$$-\int_{p_i}^{p_f} \frac{dp}{p} = \frac{k}{\sqrt{M}} \int_0^t dt$$

$$\ell n \frac{p_1}{p_2} = \frac{kt}{\sqrt{M}}$$

$$\ell n \frac{2000}{1500} = \frac{k}{\sqrt{M}} \times 47$$

$$\frac{k}{\sqrt{M}} = 6.12 \times 10^{-3} \qquad k = 3.462 \times 10^{-2}$$

$$\frac{\ell n \frac{2000}{p_2(O_2)} = 6.12 \times 10^{-3} \times 74}{\ell n \frac{(2000)}{p_2(\text{unknown})} = \frac{3.462 \times 10^{-2}}{79} \times 74} = 1.523 : 1$$

***Illustration 15.*** One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 s to diffuse through the same hole. Determine the molecular formula of the compound.

**Solution.** Rate of diffusion, $r \propto p$

$$r \propto \sqrt{1/M} \text{ or } r \propto \frac{p}{\sqrt{M}}$$

or $\frac{r_2}{r_1} = \frac{p_2}{p_1}\left(\frac{M_1}{M_2}\right)^{1/2}$ $\qquad$ Again, $r \propto \frac{1}{t}$

or $\frac{t_1}{t_2} = \left(\frac{p_2}{p_1}\right)\left(\frac{M_1}{M_2}\right)^{1/2}$

or $M_2 = \left(\frac{p_2 t_2}{p_1 t_1}\right)^2 M_1 = \left(\frac{1.6}{0.8} \times \frac{57}{38}\right)^2 \times 28 = 252 \text{ g mol}^{-1}$

Let the molecular formula of the unknown compound be $XeF_n$.

$M_{xe} + nM_F = 252$

or $131 + 19\,n = 252$

$$n = \frac{252 - 131}{19} = 6.36 \simeq 6$$

Hence, the molecular formula of the gas is $XeF_6$.

***Illustration 16*.*** At 1200ºC, mixture of $Cl_2$ and Cl atoms (both in gaseous state) effuses 1.16 times as fast as krypton effuses under identical conditions. Calculate the fraction of chlorine molecules dissociated into atom M (Kr) = 83.8 g mol$^{-1}$.

**Solution.** $Cl_2 \rightleftharpoons 2Cl$

$$\frac{r(Cl_2 \text{ and } Cl \text{ mix})}{r(Kr)} = 1.16 = \sqrt{\frac{M(Kr)}{M_{av}(Cl_2 + Cl)}} = \sqrt{\frac{83.8}{M_{av}}}$$

$$\therefore \quad M_{av} = \frac{83.8}{(1.16)^2} = 62.28 \text{ g mol}^{-1}$$

| | $Cl_2$ | $\rightleftharpoons$ 2Cl |
|---|---|---|
| Initial mole | 1 | 0 |
| After dissociation | (1 – x) | 2x |

(x = degree of dissociation)

Total moles after dissociation = 1 – x + 2x = (1 + x)

$$\therefore \quad \frac{(1-x)M(Cl_2) + 2x\,M(Cl)}{(1+x)} = 62.28$$

$$\frac{(1-x)\times 71 + 2x \times 35.5}{1+x} = 62.28$$

$$\frac{(1-x+x)71}{1+x} = 62.28$$

$$\frac{1}{1+x} = \frac{62.28}{71} = 0.88$$

$$1 + x = 1.14$$

$$x = 0.14$$

$\therefore$ % dissociation = 14%

Alternately, following formula can also be used to determine degree of dissociation when there is equilibrium mixture.

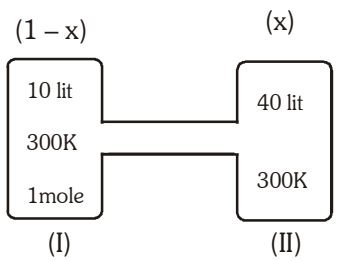
$$x = \frac{m(\text{normal}) - m(\text{average})}{m(\text{average})} = \frac{71 - 62.28}{62.28} = 0.14$$

***Illustration 17.*** A 10 liter container consist of 1 mole of gas at 300 K. It is connected to another container having volume 40 liter and is initially at 300 K. The nozzle connecting two containers is opened for a long time and once the movement of gas stopped, the larger container was heated to a temperature of 600 K. Calculate

***(a)*** Moles and pressure of gas in both the containers before heating.

***(b)*** Moles and pressure in two containers after heating. (assume that initially the larger container is completely evacuated.)

**Solution.** ***(a) Before heating :***




PV = nRT

$$\frac{(1-x)R \times 300}{10} = \frac{x \times R \times 300}{40}$$

x = 0.8 moles

$$\text{Pressure} = \frac{x \times R \times T}{V} = \frac{0.8 \times R \times 300}{40} = 0.492 \text{ atm}$$

**(b)** ***After heating :***

$$\frac{(1-x_1)R\times 300}{10}=\frac{x_1\times R\times 600}{40}$$

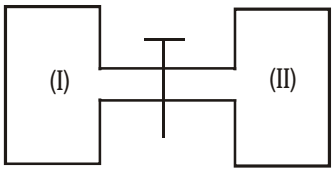
$x_1$ = 0.67 moles, Given $T_1$ = 600 K

$$\text{Pressure} = \frac{x_1\times R\times T_1}{V}=\frac{0.67\times .0821\times 600}{40} = 0.821 \text{ atm}$$

***Illustration 18*.*** 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 weight of the gases in second bulb.

***Solution.*** At STP

Before diffusion $\left.\begin{array}{l} D_2 = 1.12\,\text{lit.at STP} = 0.2\,\text{g} = 0.05\,\text{mole} \\ H_2 = 2.24\,\text{lit. at STP} = 0.2\,\text{g} = 0.1\,\text{mole}\end{array}\right\}$ in I bulb




When these moles are placed in the bulb, the partial pressure of gas will be different because Vand 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 g

Now for diffusion of $D_2$ and $H_2$

$$\frac{r_{D_2}}{r_{H_2}}=\sqrt{\frac{M_{H_2}}{M_{D_2}}}\times\frac{P_{D_2}}{P_{H_2}}$$

$$\because \frac{w_{D_2}}{t_{D_2}}\times\frac{t_{H_2}}{w_{H_2}}=\sqrt{\frac{M_{D_2}}{M_{H_2}}}\times\frac{P_{D_2}}{P_{H_2}}$$

$$\therefore \frac{0.1}{t}\times\frac{t}{w_{H_2}}=\sqrt{\left(\frac{4}{2}\right)}\times\frac{1}{2}$$

$\therefore$ $w_{H_2}$ = 0.14 g

$\therefore$ Wt. of gases in II bulb = wt. of $D_2$ + wt. of $H_2$

= 0.10 g + 0.14 g = 0.24 g

$\because$ % $D_2$ by wt. $=\frac{0.10}{0.24}\times 100 = 41.66$ %

% $H_2$ in bulb II = 58.33%

## BEGINNER'S BOX–4

***Graham's law of diffusion and effusion***

**1.** If a mixture containing 3 moles of hydrogen and 1 mole of nitrogen is converted completely into ammonia, the ratio of initial and final volume under the same temperature and pressure would be :

(A) 3 : 1 (B) 1 : 3 (C) 2 : 1 (D) 1 : 2

**2.** If the pressure of a gas contained in a closed vessel is increased by 0.4 % when heated by 1°C its initial temperature must be :

(A) 250 K (B) 250°C (C) 25°C (D) 25 K

**3.** $SO_2$ at STP contained in a flask was replaced by $O_2$ under identical conditions of pressure, temperature and volume. Then the weight of $O_2$ will be _____ of $SO_2$ :

(A) half (B) one fourth (C) twice (D) four times

**4.** A sample of gas at 35°C & 1 atm pressure occupies a volume of 3.75 litres. At what temp. should the gas be kept if it is required to reduce the volume to 3 litres at the same pressure :

(A) –26.6°C (B) 0°C (C) 3.98°C (D) 28°C

**5.** A cylinder contains acetylene gas at 27°C and 4.05 M Pa. The pressure in the cylinder after half the mass of gas is used up and temperature has fallen to 12°C will be :

(A) 4.05 M Pa (B) 2.025 M Pa (C) 3.84 M Pa (D) 1.92 M Pa

**6.** 32 cc of hydrogen diffuses through a fine hole in 1 minute. What volume of $CO_2$ will diffuse in 1 minute under the same conditions ?

**7.** 180 mL of a hydrocarbon diffuses through a porous membrane in 15 minutes while 120 mL of $SO_2$ under identical conditions diffuses in 20 minutes. What is the molecular mass of the hydrocarbon ?

**8*.** At room temperature, ammonia gas at one atmospheric pressure and hydrogen chloride at P atmospheric pressure are allowed to effuse through identical pinholes from opposite ends of a glass tube of one metre length and of uniform cross reaction. $NH_4Cl$ 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 ?

**9*.** The rate of effusion of an unknown gas (X) through a pin hole is found to be 0.279 times the rate of effusion of hydrogen gas through the same pinhole, if both are at STP. What is the molecular mass of the unknown gas

**10*.** If a 2 m long narrow tube, HCl is allowed to diffuse in the tube from one end and $NH_3$ from the other end. If diffusion is started at the same time, predict at what point the white fumes of $NH_4Cl$ will form?

## 7.0 KINETIC THEORY OF GASES

SL AL

The theoretical model for all the experimental gas laws can be analys with the help of kinetic theory of gases which is based on following assumptions :

***(a)*** All the gases consists of very small molecules or atoms whose volume is negligible compared to volume of container (in case volume of container is very small, then this assumption will be violated)

***(b)*** There is no interaction between gaseous particles (the interaction may appreciably affected under certain conditions of temperature and pressure).

***(c)*** The gaseous molecules are under a continuous state of motion which is unaffected by gravity (the random straight line motion is known as brownian motion)

***(d)*** Due to the continuous motion, collision between gaseous molecules with the wall of cantainer occurs. The collision with the wall of container are responsible for pressure exerted by the gas on the wall of container.

***(e)*** The molecule moves with different speed, however the speed of each molecule keep on changing as the collision occur.

***(f)*** All the collision occuring are considered to be perfectely elastic which implies that there is no loss of energy.

***(g)*** The average kinetic energy of gas will depends on absolute temperature only.

***Translational kinetic energy of n moles*** $\frac{1}{2}Mu^2 = \frac{3}{2}PV = \frac{3}{2}nRT$

***Average translational kinetic energy per molecule*** $= \frac{3}{2}\frac{RT}{N_0} = \frac{3}{2}KT$

Where $K\left(=\frac{R}{N_0}\right)$ is called Boltzmann's constant.

Its numerical value is $1.38 \times 10^{-16}$ erg $K^{-1}$ molecule$^{-1}$

Thus average K.E. is proportional to absolute temperature.

If T = 0 K (i.e., – 273.15°C), then average KE = 0

Thus, absolute zero (0 K) is the temperature at which molecular motion ceases.

## 7.1 Different types of molecular velocities

SL AL

$$PV = \frac{1}{3}MU_{rms}^2$$

***(i)*** ***Root mean square velocity ($U_{rms}$) :*** It is defined as the square root of the mean of the squares of the velocities possessed by all the molecules present in the given sample of gas

$$U_{rms} = \sqrt{\frac{U_1^2 + U_2^2 + ...U_n^2}{N}}$$

$\therefore$ $U_{rms}$ (root mean square velocity) $= \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$

Where d is the density.

If $N_1$ molecules have velocity $u_1$ and $N_2$ molecules have velocity $u_2$, then

$$u_{rms} = \sqrt{\frac{N_1u_1^2 + N_2u_2^2}{N_1 + N_2}}$$

***(ii)*** ***Average velocity ($U_{av}$) :*** It is given by the arithmetic mean of the different velocities possessed by the molecules of the gases at a particular temperature.

$$u_{av} = \frac{U_1 + U_2 + ...U_n}{n}$$

$u_{av}$ (average velocity) $= \sqrt{\frac{8RT}{\pi M}}$

***(iii) Most probable velocity ($u_{mp}$) :*** It is defined as the velocity possessed by the maximum number of molecules of a gas at a given temperature.

$$u_{mp} \text{ (most probable velocity)} = \sqrt{\frac{2RT}{M}}$$

If P and T both are given, use equation in terms of temperature i.e. use

$$u_{rms} = \sqrt{\frac{3RT}{M}} \text{ and not } \sqrt{\frac{3PV}{M}}$$

To have velocity in $ms^{-1}$ (MKS) take R = 8.314 J $mol^{-1}K^{-1}$, M in kg.

If density is in kg $m^{-3}$ and P in N $m^{-2}$, velocity will be in $ms^{-1}$.

***Note :*** *Relation between rms velocity, average velocity and most probable velocity.*

$$u_{rms} : u_{av} : u_{mp} = \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{2RT}{M}} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2}$$

$$= 1.2248 : 1.1284 : 1$$

## 7.2 Distribution of molecular speeds

SL AL

***(a)*** The speed of a molecule of a gas changes continuously as a result of collisions with other molecules and with the walls of the container. Thus, the net result is that we cannot speak of the speed of individual molecule; hence must consider the statistical averages of the speeds of the whole collection of gas molecules.

***(b)*** The manner in which the molecules of a gas are distributed over the possible speed ranges, from zero to very high values, was first investigated by Maxwell using the theory of probability. His results are expressed as the law of distribution of molecular speeds, one form of which is

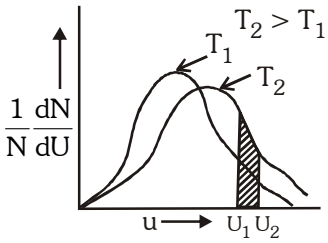
$$dN = 4\pi N \left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{mu^2}{2KT}} u^2 du$$

***(c)*** The above expression gives the no. of molecules dN having speeds between U and U + du in terms o f total no. of molecules, N present in the gas m is mass of single gas molecule and T is the absolute temperature of gas.

***(d)*** The Maxwell distribution of speeds is customarily plotted with the fraction

$\frac{1}{N}\left(\frac{dNu}{du}\right)$ as the ordinate and u as the abscissa.

$$\frac{1}{N}\left(\frac{dN}{du}\right) = \frac{1}{du}\left(\frac{dN}{du}\right)$$




So, the term, $\frac{1}{N}\frac{dN}{du}$ represents the fraction of molecules in the speed range of u to u + du per unit interval of speed. Roughly speaking, this gives the probability of finding a molecule with a speed between u and (u + du). The distribution of two temperatures is shown in the fig.

***(e)*** The curve at any temperature is parabolic near the origin, since the factor $u^2$ is dominant in this region, the exponential function being approximately equal to unity. At high values of u, however, the exponential factor dominates the behaviour of the function, causing it to decrease rapidly in value. As a consequence of the contrasting behaviour of two factors, the product function passes through a maximum at a speed known as the most probable speed ($u_{mps}$). Thus, the most probable speed is the speed possessed by the maximum fraction of the molecules.

***(f)*** It can be seen from the given figure, that the fraction of molecules having either very low speeds or very high speeds are small in numbers. The total area under the curve gives the total no. of molecules in the collection i.e. the no. of molecules comprising of all speeds. The area under the curve between any two speeds, for example, $U_1$ and $U_2$, gives the total no. of molecules having speed between these two values.

***(g)*** The given figure illustrates the distribution of speeds at two temperatures $T_1$ and $T_2$. Since the total no. of molecules is the same at both temperatures, increases the K.E. of the molecules, it follows that fraction of molecules having lower speed range decreases whereas fraction of molecules having higher speed range increases on increasing the temperature.

***(h)*** Also the curve at the higher temperature $T_2$ has its $U_{mps}$ shifted to a higher value compared with that corresonponding fraction of molecules has decreased. But at the same time for the $T_1$ curve near whereas $u_{mps}$ has become broader at the higher temperature indicating the more molecules possess speeds near to most probable speed.

## 7.3 Collision frequency & mean free path

AL

***Assumption***

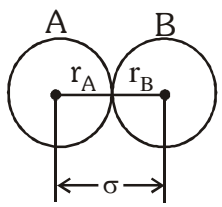
(i) All the particles (molecules or atoms) have rigid , similar shape and size and are spherical in nature that will not change after collision.

(ii) All the molecules move with the same speed i.e., average speed $u_{avg}$.

***Collision diameter***

It is the closest distance between the centres of two molecules taking part in collision.

Collision diameter $(\sigma) = r_A + r_B$



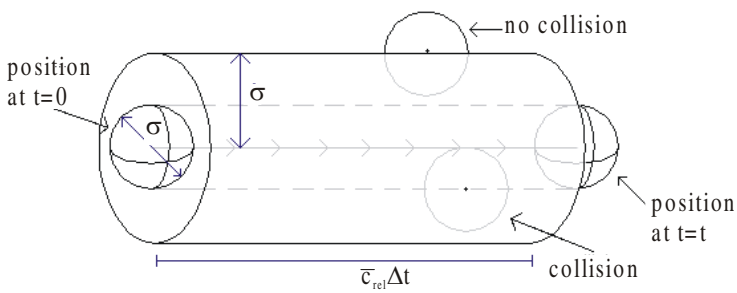

***Collision Frequency***

It is the number of molecular collisions taking place per second per unit volume of the gas.

***Determination of number of bimolecular collisions***

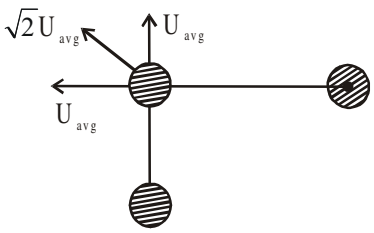
(a) While considering the molecules among themselves the molecules to be rigid, non-interacting and spherical with diameter σ. It is also assumed that all the molecules move with the same speed. The arithmetic mean of speed is $U_{avg}$.

(b) Two identical molecules of diameter σ will just touch each other when the distance separating their centres is σ. Thus, a moving molecule will collide with other molecules whose centres come within a distance of σ from its centre. The quantity $\pi\sigma^2$ is called the collision cross-section for the rigid spherical molecule. It is obvious that this collision cross-section is an area of an imaginary sphere of radius σ around the molecule within which the centre of another molecule cannot penetrate.



(c) If the molecule is moving with an average speed $U_{avg}$, then in a unit time area swept out by a single molecule is $\pi\sigma^2 U_{avg}$. If N* is the no. of molecules with in the volume $\pi\sigma^2 U_{avg}$, the no. of collisions by a single molecule in a unit time will be $\pi\sigma^2 U_{avg} N^*$.

(d) So, far, we have assumed that only one molecule is moving and all other are stationary. In practice however, this is not true. In order to account for the movements of all molecules, we must consider the average velocity along the line of centres of two colliding molecules instead of average velocity of a single molecule. If it is assumed that, on an average, molecules collide while approaching each other perpendicularly, then the average velocity along their centre is $\sqrt{2}\, U_{avg}$ as shown below.




∴ The no. of collisions made by a single molecule with other molecules per unit time (collision number) are given by

$$Z_1 = \sqrt{2}\,\pi\sigma^2\, U_{avg} N^*$$

(e) The total number of bimolecular collision per unit time is given as $Z_{11}$ (collision frequency)

$$Z_{11} = \frac{1}{2}(Z_1 N^*)$$

$$= \frac{1}{2} \times N^* \times \sqrt{2}\,\pi\sigma^2\, U_{avg} N^*$$

$$Z_{11} = \frac{1}{\sqrt{2}}\pi\sigma^2\, U_{avg} N^{*2}$$

(f) If the collisions involve two unlike molecules, the no. of bimolecular collision is given as $Z_{12}$.

$$Z_{12} = \pi\sigma_{12}^2 \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}} N_1^* N_2^*$$

Where $N_1^*$ and $N_2^*$ are the no. of molecules per unit volume of the two types of gases, $\sigma_{12}$ is the average diameter of two molecules, that is $\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}$ & $\mu$ is the reduced mass, that is $\mu = \frac{m_1 m_2}{(m_1 + m_2)}$, $m_1$ & $m_2$ are the mass of single molecule respectively 1 and 2.

***Determination of mean free path***

(a) The mean free path is the average distance travelled by a molecule between two successive collisions. We can express it as follows :

$$\lambda = \frac{\text{Average distance travelled per unit time}}{\text{No. of collsions made by single molecule per unit time}}$$

$$= \frac{U_{avg}}{Z_1} = \frac{U_{avg}}{\sqrt{2}\pi\sigma^2 U_{avg} N^*} = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$$

## 8.0 BAROMETRIC FORMULA

The following relation explains how atmospheric pressure varies with height.

$$\ell n\frac{P}{P^o} = -\frac{Mgz}{RT}$$

$P^o$ = 1 atm

P = Pressure at height z from sea level.

M = Average molar mass of air.

In the above relation, temperature is assumed not to vary with height.

## Illustrations

***Illustration 19.*** ***(a)*** Calculate the pressure exerted by $10^{23}$ gas molecules, each of mass $10^{-25}$ kg, in a container of volume $1\times 10^{-3}$ $m^3$ and having root mean square velocity of $10^3$ $ms^{-1}$.

***(b)*** Also calculate total kinetic energy and

***(c)*** temperature of the gas.

***Solution*** (a) By kinetic theory

$$P = \frac{1}{3}\frac{mNu^2}{V} = \frac{1\times 10^{-25}\times 10^{23}\times (10^3)^2}{3\times 10^{-3}} = 3.33 \times 10^6 \text{ N m}^{-2}$$

(b) Total KE $= \left(\frac{1}{2}mu^2\right)\times N$

$$= \frac{1}{2}\times 10^{-25}\times (10^3)^2\times 10^{23} = \frac{1}{2}\times 10^4 = 0.5\times 10^4 \text{ J}$$

(c) Also total KE $= \frac{3}{2}nRT$, where n (mole) $= \frac{10^{23}}{N_A} = \frac{10^{23}}{6.023\times 10^{23}}$

$$0.5\times 10^4 = \frac{3}{2}\times\frac{10^{23}}{6.023\times 10^{23}}\times 8.314\times T$$

$$\therefore\ T = \frac{0.5\times 10^4\times 2\times 6.023}{3\times 8.314} = 2415 \text{ K}$$

***Illustration 20****. A gas bulb of 1 litre capacity contains $2.0\times 10^{21}$ molecules of nitrogen exerting a pressure of $7.57\times 10^3$ $Nm^{-2}$. Calculate the root mean square velocity of the gas molecules.

***Solution*** No. of gas molecules = $2\times 10^{21}$

$6.023\times 10^{23}$ molecules of nitrogen weight = 28 g

$2\times 10^{21}$ molecules of $N_2$ weights $= \frac{28\times 2\times 10^{21}}{6.023\times 10^{23}}$ g = 0.093 g

$$\therefore \text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{0.093}{1}\text{ g/L} = \frac{0.093\times 10^{-3}}{10^{-3}} = 0.093 \text{ kg/m}^3$$

$$u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}} = U_{rms} = \sqrt{\frac{3\times 7.57\times 10^3}{0.093}} = 494.16 \text{ m/s}$$

***Illustration 21*.*** Calculate $\lambda$, $Z_1$ and $Z_{11}$ for oxygen at 298 K and $10^{-3}$ mm Hg. Given $\sigma = 3.61 \times 10^{-8}$ cm.

***Solution***

$$N^* = \frac{P}{kT} = \frac{10^{-3} \times 101325}{760 \times 1.38 \times 10^{-23} \times 298} = 0.324 \times 10^{20}$$

$$U_{avg} = \sqrt{\frac{8}{\pi}\frac{RT}{M}} = \sqrt{\frac{8}{3.14} \times \frac{8.314 \times 298}{32 \times 10^{-3}}} = 444.138 \text{ m/sec}$$

$$Z_1 = \sqrt{2}\,\pi\,\sigma^2\,U_{avg}N^* = \sqrt{2} \times 3.14 \times 3.61 \times 10^{-10}\text{ m} \times 444.138 \text{ m} \times 0.324 \times 10^{20}$$
$$= 8.326 \times 10^3 \text{ sec}^{-1}$$

$$Z_{11} = \frac{1}{2}Z_1N^* = \frac{1}{2} \times 8.326 \times 10^3 \text{ sec}^{-1} \times 0.324 \times 10^{20} = 13.488 \times 10^{22} \text{ m}^{-3}\text{ sec}^{-1};$$

$$\lambda = \frac{U_{avg.}}{Z_1} = \frac{444.138 \text{ m/sec}}{8.326 \times 10^3 \text{ sec}^{-1}} = 5.334 \times 10^{-2} \text{ m}$$

## BEGINNER'S BOX–5

### *Kinetic Theory of Gases*

**1.** The r.m.s. velocity of hydrogen at 27°C, R = 8.314 J $mol^{-1}$ $K^{-1}$ is :
(A) 1.934 m/s (B) 19.34 m/s (C) 193.4 m/s (D) 1934 m/s

**2.** Temperature at which r.m.s. speed of $O_2$ is equal to that of neon at 300 K is :
(A) 280 K (B) 480 K (C) 680 K (D) 180 K

**3.** The most probable velocity of a neutron at 20°C is nearby : ***[Assume its follows KTG]***
(A) 220 m/s (B) 2200 m/s (C) 22200 m/s (D) 22 m/s

**4.** The R.M.S. speed of the molecules of a gas of density 4 kg $m^{-3}$ and pressure $1.2 \times 10^5$ N $m^{-2}$ is :
(A) 120 m $s^{-1}$ (B) 300 m $s^{-1}$ (C) 600 m $s^{-1}$ (D) 900 m $s^{-1}$

**5.** The R.M.S. velocity of a gas whose each molecule weighs $10^{-12}$ g and at temperature 27°C is :
(A) 0.70 cm/s (B) 0.35 cm/s (C) 0.35 m/s (D) 0.70 m/s

**6.** The average speed of an ideal gas molecule at 27°C is 0.3 m $sec^{-1}$. The average speed at 927°C :
(A) 0.15 m $sec^{-1}$ (B) 0.6 m $sec^{-1}$ (C) 1.2 m $sec^{-1}$ (D) 0.6 cm $sec^{-1}$

**7.** The temperature at which $CO_2$ has the same R.M.S. speed to that of $O_2$ at S.T.P. is/are :
(A) 375.38 K (B) 102.38 °C (C) 275.38 K (D) 202.38 °C

**8.** The temperature at which the most probable speed of $CO_2$ molecules be twice as that of 50°C is :
(A) 200°C (B) 1292 K (C) 100°C (D) 646 K

**9.** What is the total translational and rotational energy of 1 mole of oxygen at 300 K.
R = 8.314 J $mol^{-1}$ $K^{-1}$ : ***(Given rotational energy/mole = RT)***
(A) 6235.5 J (B) 623.25 J (C) 62.325 J (D) 6.2325 J

**10*.** The kinetic energy of N molecules of $O_2$ is x joule at –123°C. Another sample of $O_2$ at 27°C has a kinetic energy of 2 x. The later sample contains _____ molecules of $O_2$ :
(A) N (B) N/2 (C) 2 N (D) 3 N

## 9.0 REAL GAS

SL AL

An ideal gas is a hypothetical gas whose pressure, volume and temperature behaviour is completely described by the ideal gas equation. Actually no gas is ideal or perfect in nature. All gases are real gases.

Real gases do not obey the ideal gas laws exactly under all conditions of tamperature and pressure.

Real gases deviates from ideal behaviour because of mainly two assumptions of "Kinetic theory of gases".

***(i)*** The volume of gas particle is negligible compared to volume of container (while the real gas particle have some significant volume).

***(ii)*** There is no interaction between gaseous particles (while attraction forces exist between real gas particles).

***Compressibility factor :*** The extent to which a real gas departs from the ideal behaviour may be expressed in terms of compressibility factor (Z), where Z is

$$Z = \frac{V_m}{V_{m(ideal)}} = \frac{PV_m}{RT} \quad [V_m = \text{molar volume}]$$

When $Z > 1$, $V_m > 22.4$ lit at STP ; When $Z < 1$, $V_m < 22.4$ lit at STP

***Plots of compressibility factor vs pressure***

***(i)*** For an ideal gas Z = 1 and is independent of temperature and pressure.

***(ii)*** Exceptional behaviour of $H_2$ and He :

for these gases Z > 1. For such gases repulsive forces predominants.

***(iii)*** ***Effect of pressure :***

At very low P, $PV \approx RT$ i.e. $Z \approx 1$

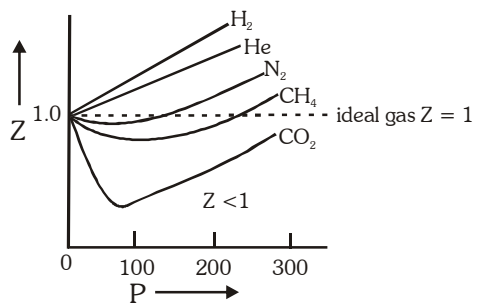
At low P, $PV < RT$ i.e. $Z < 1$

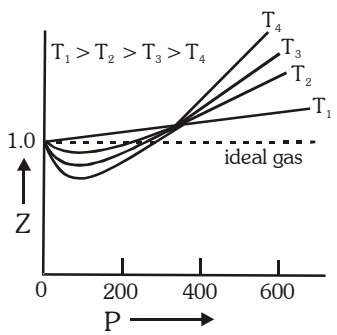
At moderate P, $PV \approx RT$ i.e. $Z \approx 1$

At high P, $PV > RT$ i.e. $Z > 1$

***(iv)*** For the gases which are easily liquefied (e.g. $CO_2$) Z dips sharply below the ideal line in the low pressure region.

***(v)*** Effect of temperature : An increase in temperature shows a decrease in deviation from ideal behaviours i.e. PV approaches unity or Z approaches unity with increase in temperature.




## 9.1 Volume Correction

SL AL

In the ideal gas equation, $P_iV_i = nRT$, $V_i$ represents the ideal volume where the molecules can move freely. In real gases, a part of the total volume is occupied by the gas molecules. Hence the free volume $V_i$ is the total volume V minus the volume occupied by the gas molecules.

i.e. Real volume of gas = Actual volume of container – volume occupied by N molecules in motion.

$V_i = V - b$ for one mole of gas

$V_i = V - nb$ for n mole of gas

Where b is termed the 'excluded volume' or 'co-volume'.

It is constant and characteristic for each gas.

$$b = \left(\frac{4}{3}\pi r^3\right) \times 4N$$

[where r = radius of gas molecule, N = Avogadro's number]

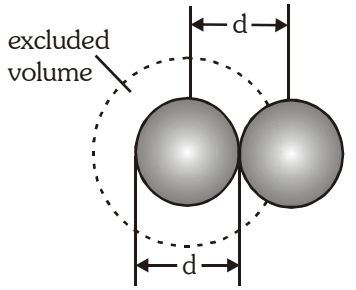


Illustration of excluded volume

## 9.2 Pressure Correction

SL AL

In order to take account the effect of intermolecular forces of attraction, let us consider a molecule A is the midst of the vessel.

This molecule is surrounded by other molecules in a symmetrical manner and is being attracted uniformly on all sides by the neighbouring molecules with the result that this molecule on the whole experiences no net force of attraction. Now, consider a molecule B near the side of the vessel, which is about to strike one of its sides, thus contributing towards the total pressure of the gas. There are molecules only on one side of the vessel, i.e. towards its centre, with the result that this molecule experiences a net force of attraction towards the centre of the vessel. This results in decreasing the velocity of the molecule, and hence its momentum. Thus, the molecule does not contribute as much force as it would have, had there been no force of attraction. Thus, the pressure of a real gas would be smaller than the corresponding pressure of an ideal gas. Van der Walls noted that the total force of attraction on any molecule about to hit a wall is proportional to the concentration of neighbouring molecules, n/V. However, the number of molecules about to hit the wall per unit wall area is also proportional to the concentration n/V. Therefore, the force per unit wall area, or pressure, is reduced from that assumed in the ideal gas wall by a factor proportional to $n^2/V^2$. Letting a be the proportionality constant, we can write P (actual) = P(ideal) – $n^2a/V^2$ or P (ideal) = P(actual) + $n^2a/V^2$ 'a' is a constant which depends upon the nature of the gas, V is the volume of 1 mole of gas.

Combining the two corrections, for 1 mole of gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

For n mole of gas $\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$

## 9.3 Characteristics of 'a' and 'b'

Van der Waals constant for attraction 'a' and volume 'b' are characteristic constants for a given gas.

***(i)*** The 'a' values for a given gas are measure of intermolecular forces of attraction. More are the intermolecular forces of attraction, more will be the value of a.

***(ii)*** For a given gas van der Waals constant of attraction 'a' is always greater than van der Waals constant of volume 'b'.

***(iii)*** The gas having higher value of 'a' can be liquefied easily and therefore $H_2$ and He are not liquefied easily.

***(iv)*** Unit of 'a' is $lit^2\ mole^{-2}$ atm or $cm^4\ mole^{-2}$ dyne.

***(v)*** Unit of 'b' is lit $mole^{-1}$ or $cm^3$ $mole^{-1}$.

***(vi)*** At low pressure, volume correction for 1 mole of gas is negligible, $\therefore$ b = 0

The gas equation can be written as

$$\left(P+\frac{a}{V^2}\right)V = RT \quad \text{or} \quad Z = \frac{PV_m}{RT} = 1 - \frac{a}{V_m RT}$$

where $V_m$ = molar volume

where Z is known as the compressibility factor.

***(vii)*** At higher pressures, the pressure correction for 1 mole of gas is negligible

$$\therefore \frac{a}{V^2} = 0$$

or $(P + 0)(V - b) = RT$ or $P(V_m - b) = RT$

or $PV_m = RT + Pb$ or, $Z = \frac{PV_m}{RT} = 1 + \frac{Pb}{RT}$

***The van der Walls constants for some common gases***

| ***Gas*** | ***a ($dm^6$ atm $mol^{-2}$)*** | ***b ($dm^3 mol^{-1}$)*** |
|---|---|---|
| Ammonia | 4.17 | 0.0371 |
| Carbon dioxide | 3.59 | 0.0427 |
| Chlorine | 6.49 | 0.0562 |
| Helium | 0.034 | 0.0237 |
| Hydrogen | 0.024 | 0.0266 |
| Hydrogen chloride | 3.67 | 0.0408 |
| Methane | 2.25 | 0.0428 |
| Nitrogen | 1.39 | 0.0319 |
| Oxygen | 1.36 | 0.0318 |
| Sulphur dioxide | 3.71 | 0.0564 |
| Water | 5.44 | 0.0305 |

## BEGINNER'S BOX–6

### *Real Gases*

***1.*** The compressibility factor of real gas is usually greater than one (Z > 1) at high temperature and high pressure. This is because

(A) the constant a is negligible while b is not
(B) the constant b is negligible while a is not
(C) both a and b are negligible
(D) both a and b are no negligible

***2.*** What is not true about the vander waal constant 'b' among the statements given below ?

I. It is called excluded volume
II. It accounts for the interparticle forces
III. Its units are mol $dm^{-3}$
IV. Its value depends on molecular size

(A) I, II
(B) II, IV
(C) II, III
(D) I, IV

***3*.*** Among the four statements given below for real gases, which are incorrect :

(A) The molecules causes attractive interactions.
(B) They show deviation from ideal gas laws.
(C) The molecules are almost volume less points.
(D) The molecules have negligible mass.

**4*.** Consider an ideal gas contained in a vessel. If the intermolecular interaction suddenly begins to act, which of the following will happen :

(A) the observed pressure decreases
(B) the observed pressure increases
(C) the observed pressure remains same
(D) none of these

**5.** A real gas obeying Vander Waals equation will resemble ideal gas, if the :

(A) constants a & b are small
(B) a is large & b is small
(C) a is small & b is large
(D) constant a & b are large

**6** 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 :

(A) 0.40, $CO_2$ is more compressible than ideal gas
(B) 0.65, $CO_2$ is more compressible than ideal gas
(C) 0.55, $CO_2$ is more compressible than ideal gas
(D) 0.62, $CO_2$ is more compressible than ideal gas

**7*.** Calculate the radius of He atoms if its Vander Waal's constant 'b' is 24 ml $mol^{-1}$ :

(Note ml = cubic centimeter)

(A) 1.355 Å
(B) 1.314 Å
(C) 1.255 Å
(D) 0.355 Å

## 10.0 LIQUEFACTION OF GASES AND CRITICAL POINTS

SL AL

The phenomenon of converting a gas into liquid is known as liquefaction. The liquefaction of a gas takes place when the intermolecular forces of attraction become so high that exist in the liquid. A gas can be liquefied by :

(a) ***Increasing pressure :*** An increase in pressure results in an increase in attraction among molecules.

(b) ***Decreasing temperature*** : A decrease in temperature results in a decrease in kinetic energy of molecules.

### 10.1 Andrews Isotherms

SL AL

The essential conditions for liquefaction of gases were discovered by Andrews (1869) as a result of his study of P–V–T relationship for $CO_2$.The types of isotherms are shown in figure.

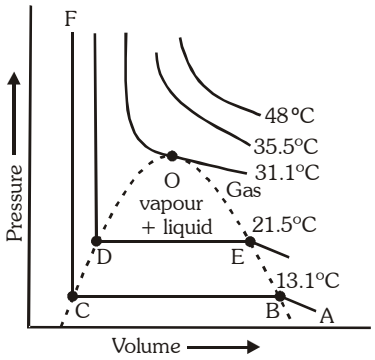



Fig : Isotherms for carbon dioxide showing critical region

***Observations from figure***

***(a)*** ***At low temperatures :*** For the curve ABCF, as the pressure increases, volume of the curve decreases (curve A to B).

At point B, at constant pressure, liquefaction commences and the volume decreases rapidly (because gas is converted to liquid with higher density).

At point C, liquefaction is complete. The line CF represents the variation of V with P of the liquid state. The steepness of the line CF indicates that the liquid cannot be easily compressed. Thus AB, represent gaseous state, BC represent liquid and vapour in equilibrium. CF represent liquid state.

The pressure corresponding to the line BC is there vapour pressure of the liquid.

**(b)** ***At higher temperatures*** : Similar type of curve as in case (a) is obtained but the width of the horizontal portion is reduced. The pressure corresponding to this portion is higher than at lower temperatures.

**(c)** ***At high temperatures*** : (like 48°C), the isotherms are like those of ideal gas.

**(d)** ***At temperature (31.1°C)*** : The horizontal portion is reduced to a point.

The isotherm at $T_C$ is called ***critical isotherm***.

At point O, $\frac{dP}{dV} = 0$.

The point O is called the ***point of inflection***.

***Critical temperature ($T_C$)*** : The maximum temperature at which gas can be liquefied by the application of pressure alone i.e. the temperature above which a liquid cannot exit is called the critical temperature$T_C$.

$$T_C = \frac{8a}{27Rb}$$

***Critical pressure ($P_C$)*** :The minimum pressure required to liquefy the gas at the temperature $T_C$ is called the critical pressure $P_C$.

$$P_C = \frac{a}{27b^2}$$

***Critical volume ($V_C$)*** :The volume occupied by one mole of the gas at critical temperature, $T_C$ and critical pressure, $P_C$ is called the critical volume ($V_C$) of the gas.

$V_C = 3b$

**(i)** Therefore the value of critical compressibility factor in terms of vander wall's constants is given by

$$Z = \frac{P_C V_C}{RT_C} = \frac{\frac{a}{27b^2} \times 3b}{R \times \frac{8b}{27Rb}}$$

$$= \frac{\frac{a}{9b}}{\frac{8Ra}{27Rb}}$$

$$= \frac{\frac{a}{9b}}{\frac{8a}{27b}}$$

$$Z = \frac{P_C V_C}{RT_C} = \frac{a}{9b} \times \frac{27b}{8a}$$

$$= \frac{3}{8} = 0.375$$

**(ii)** If we compart the value of $\frac{P_C V_C}{RT_C} = 0.375$, with the experimental values, it has been found that the agreement is very poor.

***Critical constants of gases***

| ***Gas*** | ***$P_C$ (atm)*** | ***$V_{m,c}$ ($cm^3mol^{-1}$)*** | ***$T_C$ (K)*** |
|---|---|---|---|
| He | 2.26 | 57.9 | 5.2 |
| Ne | 26.9 | 41.7 | 44.4 |
| $H_2$ | 12.8 | 65.5 | 33.3 |
| $O_2$ | 50.1 | 78.2 | 154.8 |
| $N_2$ | 33.5 | 90.1 | 126.2 |
| $CO_2$ | 72.8 | 94.0 | 304.2 |
| $H_2O$ | 218.0 | 55.6 | 647.3 |
| $NH_3$ | 111.5 | 72.5 | 405.0 |
| $CH_4$ | 45.6 | 98.7 | 190.6 |

***Virial Equation Of State For 1 Mole Of Gas***

$$z = \frac{PV}{RT} = 1 + B\frac{1}{V} + C\frac{1}{V^2} + D\frac{1}{V^3} + \ldots\ldots \text{ (B, C, D... are temp. dependent constant)}$$

$$\left.\begin{aligned} B &= \text{second virial coefficient} = b - \frac{a}{RT} \\ C &= \text{third virial coefficient} = b^2 . \end{aligned}\right] \text{gas dependent}$$

***Boyle's temperature***

The temperature at which a real gas behaves like an ideal gas over an appreciable range of pressure is known as Boyle's temperature ($T_B$). It means that at this temperature, the value of PV remains constant for an appreciable range of pressure, i.e. Boyle's Law is obeyed. Mathematically we may express the Boyle temperature or Boyle point as the temperature where $\frac{\partial(PV)}{\partial P} = 0$ when $P \to 0$.

So to use ideal gas equation for real gas, we will use some correction factor for volume as well as for pressure.

$$T_B = \frac{a}{Rb}$$

## Illustrations

***Illustration 22.*** Calculate the pressure exerted by 5 mole of $CO_2$ in one litre vessel at 47°C using van der waal's equation. Also report the pressure of gas if it behaves ideal in nature.

Given that a = 3.592 atm $lt^2$ $mol^{-2}$, b = 0.0427 L/mol. Also, if the volume occupied by $CO_2$ molecules is negligible, then calculate the pressure exerted by one mole of $CO_2$ gas at 273 K.

***Solution*** Vander waal's equation

$$\left[p + \frac{n^2a}{V^2}\right][V - nb] = nRT$$

$n_{CO_2} = 5$, V = 1 litre, T = 320 K, a = 3.592, b = 0.0427

$$\therefore \left[P + 25 \times \frac{3.592}{1}\right][1 - 5 \times 0.0427] = 5 \times 0.0821 \times 320$$

$\therefore$ P = 77.218 atm

For ideal behaviour of gas, PV = nRT

$\therefore P \times 1 = 5 \times 0.0821 \times 320$

$\therefore P = 131.36$ atm

For one mole $\left[P + \frac{a}{V^2}\right][V - b] = RT$

$$\therefore P = \frac{RT}{V} - \frac{a}{V^2}$$

$$\therefore P = \frac{0.0821 \times 273}{22.4} - \frac{3.592}{(22.4)^2}$$

$\therefore P = 0.9922$ atm

The volume occupied by 1 mole at 273 K is 22.4 litre if b is negligible.

***Illustration 23.*** Two moles of ammonia gas are enclosed in a vessel of 5 litre capacity at 27°C. Calculate the pressure exerted by the gas, assuming that

***(i)*** the gas behaves like an ideal gas (using ideal gas equation).

***(ii)*** the gas behaves like a real gas (using van der Waal's equation)

Given that for ammonia, a = 4.17 atm litre$^2$ mol$^{-2}$ and b = 0.037 litre mol$^{-1}$.

***Solution*** Given,

n = 2 moles

V = 5 litres

T = 27°C = (27 + 273) K = 300 K

a = 4.17 atm litre$^2$ mol$^{-2}$

b = 0.037 litre mol$^{-1}$

Also, we know that

R = 0.0821 litre atm K$^{-1}$ mol$^{-1}$

***(i)*** If the gas behaves like an ideal gas, we have

PV = nRT

$$\therefore P = \frac{nRT}{V} = \frac{2 \times 0.0821 \times 300}{5} = 9.85 \text{ atm}$$

***(ii)*** If the gas behaves like a real gas, we apply van der Waal's equation i.e.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\text{or } P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} = \frac{2 \times 0.0821 \times 300}{5 - 2 \times 0.037} - \frac{4.17 \times (2)^2}{(5)^2} = 9.33 \text{ atm.}$$

***Illustration 24*.*** One way of writing the equation of state for real gases is $PV = RT\left[1 + \frac{B}{V} + \ldots\right]$ where B is a constant. Derive an approximate expression for B in terms of van der Waal's constants a and b.

***Solution.*** According to van der Waal's equation

$$\left[P + \frac{a}{V^2}\right][V - b] = RT$$

$$\text{or } P = \frac{RT}{(V - b)} - \frac{a}{V^2}$$

Multiply by V, then

$$PV = \frac{RTV}{(V-b)} - \frac{a}{V}$$

or $$PV = RT\left[\frac{V}{V-b} - \frac{a}{VRT}\right] \quad \text{or} \quad PV = RT\left[\left(1-\frac{b}{V}\right)^{-1} - \frac{a}{VRT}\right]$$

$\because$ $$\left[1-\frac{b}{V}\right]^{-1} = 1 + \frac{b}{V} + \left(\frac{b}{V}\right)^2 + ....$$

$\therefore$ $$PV = RT\left[1+\frac{b}{V}+...-\frac{a}{VRT}\right]$$

$$PV = RT\left[1+\left(b-\frac{a}{RT}\right).\frac{1}{V}+...\right] \quad \therefore \quad B = b - \frac{a}{RT}$$

***Illustration 25*.*** The critical temperature and pressure of $CO_2$ gas are 304.2 K and 72.9 atm respectively. What is the radius of $CO_2$ molecule assuming it to behave as vander Waal's gas ?

***Solution.*** $T_C = 304.2$ K $\quad P_C = 72.9$ atm

$$T_C = \frac{8a}{27Rb} \qquad P_C = \frac{a}{27b^2}$$

$$\therefore \frac{T_C}{P_C} = \frac{\frac{8a}{27Rb}}{\frac{a}{27b^2}} = \frac{8a}{27Rb} \times \frac{27b^2}{a} = \frac{8b}{R}$$

$$\text{or } b = \frac{RT_C}{8P_C} = \frac{1}{8} \times \frac{0.082 \times 304.2}{72.9} = 0.04277 \text{ lit mol}^{-1}$$

$$b = 4\,N_A \times \frac{4}{3}\pi r^3 = 42.77 \text{ cm}^3$$

$$\therefore 4 \times N_A \times \frac{4}{3}\pi r^3 = 42.77$$

$$\text{or } r^3 = \frac{3 \times 42.77 \times 10^{-23}}{16 \times 6.023 \times 3.14}$$

or $r^3 = 0.424 \times 10^{-23} = 4.24 \times 10^{-24}$

or $r = (4.24)^{1/3} \times 10^{-8}$ cm $= 1.62 \times 10^{-8}$ cm

$\therefore$ radius of $CO_2$ molecule = 1.62 Å

## BEGINNER'S BOX–7

### *Liquification and Critical Phenomena*

***Identify True or False for Q.1 to Q.4.***

**1.** A gas with a = 0 can be very easily liquefied.

**2.** Mean free path increases with the increase in temperature at constant pressure.

**3.** The behaviour of a real gas approach ideal gas at high temperature & low pressure.

**4.** Real gases deviate form ideal behaviour because their molecules cause attractive interaction on one another.

**5*.** For three different gases values of vander Waal's constant 'a' and 'b' are given. What is the correct order of liquefaction of gases :

| Gases | a | b |
|---|---|---|
| $X_2$ | 1.3 | 0.090 |
| $Y_2$ | 4.1 | 0.023 |
| $Z_2$ | 2.,2 | 0.075 |

(A) $X_2 > Y_2 > Z_2$ (B) $Y_2 > Z_2 > X_2$ (C) $Z_2 > Y_2 > X_2$ (D) $X_2 > Z_2 > Y_2$

**6.** The value of vander Waal's constant 'a' for the gases $O_2$, $N_2$, $NH_3$ and $CH_4$ are 1.36 , 1.39, 4.17 and 2.253 $l^2$ atm, $m^{-2}$, respectively. The gas which can most easily be liquefied is

(A) $O_2$ (B) $N_2$ (C) $NH_3$ (D) $CH_4$

**7.** Vander Waal's constant for three different gases are given

| Gas | a | b |
|---|---|---|
| X | 3.0 | 0.025 |
| Y | 10.0 | 0.030 |
| Z | 6.0 | 0.035 |

Which is correct ?

(A) Maximum critical temperature - Y (B) Most ideal behaviour - X

(C) Maximum molecular volume - Z (D) All are correct

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

(A) a=1.095 litre$^2$ atm $mol^{-2}$, b=0.0185 litre $mol^{-1}$ (B) a=1.92 litre$^2$ atm $mol^{-2}$, b=0.185 litre $mol^{-1}$

(C) a = 2.095 litre$^2$ atm $mol^{-2}$,b=0.0189 litre $mol^{-1}$ (D) a=2.95 litre$^2$ atm $mol^{-2}$,b=0.1185 litre $mol^{-1}$

**9.** 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.

## 11.0 EUDIOMETRY

Eudiometry or gas analysis involves the calculations based on gaseous reactions or the reactions in which at least two components are gaseous, in which the amounts of gases are represented by their volumes, measured at the same pressure and temperature. Some basic assumptions related with calculations are:

**1.** Gay-Lussac's law of volume combination holds good. According to this law, the volumes of gaseous reactants reacted and the volumes of gaseous products formed, all measured at the same temperature and pressure, bear a simple ratio.

$$N_2\,(g) + 3H_2\,(g) \longrightarrow 2NH_3\,(g)$$

1 vol. 3 vol. 2 vol.

Problem may be solved directly is terms of volume, in place of mole. The stoichiometric coefficients of a balanced chemical reactions gives the ratio of volumes in which gaseous substances are reacting and products are formed, at same temperature and pressure.

**2.** The volumes of solids or liquids is considered to be negligible in comparison to the volume of gas. It is due to the fact that the volume occupied by any substance in gaseous state is even more than thousand times the volume occupied by the same substance in solid or liquid states.

$$2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(l)$$

2 mole 1 mole 2 mole

2 vol. 1 vol. 0 vol.

**3.** Air is considered as a mixture of oxygen and nitrogen gases only. It is due to the fact that about 99% volume of air is composed of oxygen and nitrogen gases only.

**4.** Nitrogen gas is considered as a non- reactive gas. It is due to the fact that nitrogen gas reacts only at very high temperature due to its very high thermal stability. Eudiometry is performed in an eudiometer tube and the tube can not withstand very high temperature. This is why, nitrogen gas can not participate in the reactions occurring in the eudiometer tube.

**5.** The total volume of non-reacting gaseous mixture is equal to sum of partial volumes of the component gases ***(Amagat's law)***.

$V = V_1 + V_2 + .....$

Partial volume of gas in a non-reacting gasesous mixture is its volume when the entire pressure of the mixture is supposed to be exerted only by that gas.

**6.** The volume of gases produced is often given by certain solvent which absorb contain gases.

| ***Solvent*** | ***Gases absorb*** |
|---|---|
| KOH | $CO_2$, $SO_2$, $Cl_2$ |
| Ammonical $Cu_2Cl_2$ | CO |
| Turpentine oil | $O_3$ |
| Alkaline pyrogallol | $O_2$ |
| water | $NH_3$, HCl |
| $CuSO_4/CaCl_2$ | $H_2O$ |

***Illustration 26. 10 ml of CO is mixed with 25 ml air (20% $O_2$ by volume) in a container at 1 atm. Find final volume (in ml) of container at 1 atm after complete combustion. (Assume that temperature remain constant).***

**Sol.** $$\overset{10\,ml}{CO} + \overset{5ml}{\frac{1}{2}O_2} \longrightarrow \underset{10ml}{CO_2}$$

$V_f = V_{CO_2}$ + Volume of remaining air = 10 + 20 = 30 ml

***Illustration 27. A 3 L gas mixture of propane ($C_3H_8$) and butane ($C_4H_{10}$) on complete combustion at 25°C produced 10 L $CO_2$. Assuming constant P and T conditions what was volume of butane present in initial mixture ?***

**Sol.** $C_3H_8(g) + 5O_2 \longrightarrow 3CO_2(g) + 4H_2O(l)$

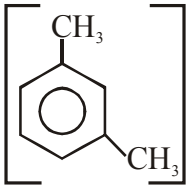
x L 3x L

$C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$

(3-x) L 4(3 – x) L

from question 3x + 4 (3 –x) = 10 Þ x = 2

∴ Volume of butane , $C_4H_{10}$ = (3 – x) = 1 L

***Illustration 28.*** ***100 ml gaseous meta Xylene***  ***undergoes combustion with excess of oxygen at room temperature and pressure. Volume contraction / expansion (in ml) during reaction is :***

**Sol.** $C_8H_{10}(g) + \frac{21}{2}O_2(g) \longrightarrow 8CO_2(g) + 5H_2O(l)$

100 ml $\quad \frac{21}{2} \times 100 = 1050\text{ml} \quad$ 800 ml $\quad$ 0

Conctraction in volume = (100 + 1050) – 800 = 350 ml

***Illustration 29. An alkene upon combustion produces $CO_2(g)$ and $H_2O(g)$. In this combustion process if there is no volume change occurs then the no. of C atoms per molecule of alkene will be :***

**Sol.** $C_nH_{2n}(g) + \frac{3n}{2}O_2(g) \rightarrow nCO_2(g) + nH_2O(g)$

if there no volume changes i.e. $D_{ng} = 0$

$$(n + n) - \left(1 + \frac{3n}{2}\right) = 0 \Rightarrow n = 2$$

***Illustration 30. A gaseous hydrocarbon ($C_xH_y$) requires 6 times of its own volume of $O_2$ for complete oxidation and produces 4 times of its volume of $CO_2$. Find out the volume of x + y.***

**Sol.** $C_xH_y + (x + \frac{y}{4})O_2 \longrightarrow XCO_2 + \frac{y}{2}H_2O(l)$

Vol a $\quad a\left(x + \frac{y}{4}\right) \quad$ ax

Given that : a(x + y/4) = 6a

vol of $CO_2$ = 4 vol of $C_xH_y$

ax = 4 (a)

x = 4 ...(2)

from (1) $x + \frac{y}{4} = 6$

$\therefore$ x + y = 4 + 8 = 12

## GOLDEN KEY POINTS

- ***Volume coefficient ($\alpha_v$) of a gas***

  The ratio of increase in volume of a gas at constant pressure per degree rise of temperature to its volume at 0°C is the volume coefficient of the gas.

  $$\alpha_v = \frac{V_t - V_0}{V_0 \times t} \quad \text{or} \quad V_t = V_0(1 + \alpha_v t)$$

  For all gases, $\alpha_v = \frac{1}{273}$

- ***Pressure coefficient ($\alpha_p$) of a gas***

  The ratio of increase in pressure of the gas at constant volume per degree rise of temperature to its pressure at 0°C is the pressure coefficient of the gas.

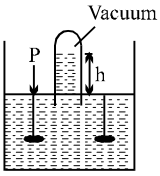
  $$\alpha_p = \frac{P_t - P_0}{P_0 \times t} \quad \text{or} \quad P_t = P_0(1 + \alpha_p t)$$

  For all gases, $\alpha_p = \frac{1}{273}$

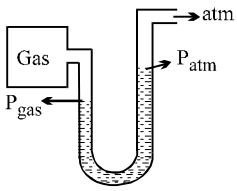
- ***Barometer :*** $P = \frac{A \times h \times d \times g}{A}$ where d = density of fluid

  h = vertical height

  g = acceleration due to

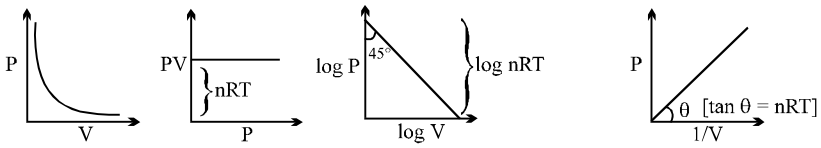



- ***Manometer :*** $P_{gas} = P_{atm} + hdg$



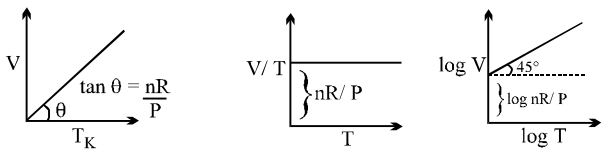

- ***Boyle's law :*** $V \propto \frac{1}{P}$ $\begin{pmatrix} T, \text{constant} \\ n \text{ constant} \end{pmatrix}$ $P_1V_1 = P_2V_2$

  ***Graphs are Isotherms :***



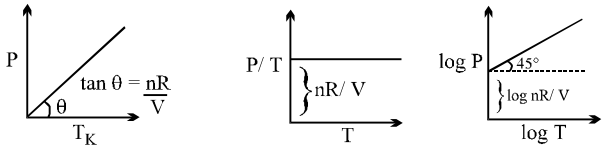

- ***Charle's law :*** $V \propto T$ $\begin{pmatrix} P, \text{constant} \\ n \text{ constant} \end{pmatrix}$ $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

- ***Graphs are Isobars :***

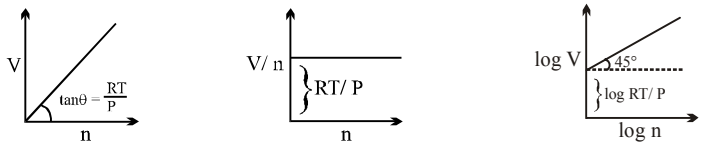



- ***Gay Lussac's law :*** $P \propto T$ $\begin{pmatrix} V, \text{constant} \\ n \text{ constant} \end{pmatrix}$ $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

- ***Graphs are Isochor***




- ***Avogadro's law :*** $V \propto n$ (T, P constant) $\frac{V_1}{n_1} = \frac{V_2}{n_2}$




- ***Combined Gas Law :*** $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

- ***Equation Of State :*** $PV = nRT$

  $d$ = density of gas

  $\Rightarrow PV = \frac{w}{M} RT$ R = Universal Gas constant = 0.0821 atm litres kelvin$^{-1}$ mol$^{-1}$

  $\Rightarrow PM = dRT$ = 8.314 joule / kelvin = 2cal kelvin$^{-1}$ mol$^{-1}$

- ***Dalton's law of partial pressure :***

  $P_{total} = P_A + P_B + .....$ ; $P_{wet\ gas} = P_{dry\ gas} + P_{H_2O\ vapour}$ ( i.e. aq. tension.)

  $P_A$, $P_B$ are partial pressures ; $P_A$ = mole fraction$_A$ × Total pressure

  and % of gas in mixture $= \frac{\text{Partial pressure}}{\text{Total pressure}} \times 100$ .

- ***Amagat's Law :***

  The total volume of a mixture of gases is equal to the sum of the partial volumes of the constituent gases, at same Temperature & Pressure.

- ***Graham's law of Diffusion or Effusion :***

  $r \propto \frac{1}{\sqrt{d}}$ or $r \propto \frac{1}{\sqrt{M}}$ $r \propto \frac{P}{\sqrt{M}}$ [For gases effusing at different pressures]

  ***r*** is rate of diffusion of any gas.

  $$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \ ; \ \frac{\text{volume / time}}{\text{volume / time}} = \sqrt{\frac{M_2}{M_1}}$$

  ***d*** is density at some temperature.

  $$r = \frac{\text{moles diffused}}{\text{time taken}} = \frac{\text{distance travelled in a narrow tube}}{\text{time taken}} = \frac{\text{Pressure drop I}}{\text{Pressure drop II}}$$

- ***Kinetic theory of gases***

$$PV = \frac{1}{3} m N u^2 = \frac{1}{3} M u^2 \text{ (For 1 mole)}$$

- ***Types of velocities***

$$u^2 = \frac{u_1^2 + u_2^2 + \ldots\ldots + u_N^2}{N} \quad ; \quad u = \textbf{\textit{root mean square speed}}.$$

$$u = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}} \quad ;$$

$$\textbf{\textit{Average speed}} = \frac{u_1 + u_2 + \ldots\ldots + u_N}{N} = \sqrt{\frac{8RT}{\pi M}}$$

$$\textbf{\textit{most probable speed}} = \sqrt{\frac{2RT}{M}}$$

most probable : average : r. m. s. = 1 : 1.13 : 1.22

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$ ] Relationship between three types of speeds

$$u_{rms} > u_{av} > u_{mp}$$

Average kinetic energy of a single molecule $= \frac{3}{2} \cdot \frac{R}{N} \cdot T = \frac{3}{2} kT$

$k$ = Boltzman constant $= 1.3806 \times 10^{-16}$ erg deg$^{-1}$.

Total kinetic energy for ***one mole*** of a gas $= \frac{3}{2} RT$.

kinetic energy of ***n moles*** of a gas $= n \times \frac{3}{2} RT$

- ***Vander Waals equation of state***

$$\left(P + \frac{a}{V^2}.n^2\right)(V - nb) = nRT.$$

a, b are Vander Waals constants ; different for each gas

unit of a $\longrightarrow$ atm L$^2$ mol$^{-2}$ ; S.I. unit $\longrightarrow$ Pa m$^6$ mol$^{-2}$

unit of b $\longrightarrow$ L mol$^{-1}$; S.I. unit $\longrightarrow$ m$^3$ mol$^{-1}$

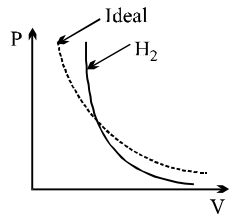
greater the value of 'a' more easily the gas is liquefiable ;

greater the value of 'b' greater the molecular size ,

- ***Real gases : Deviation from ideal behaviour***

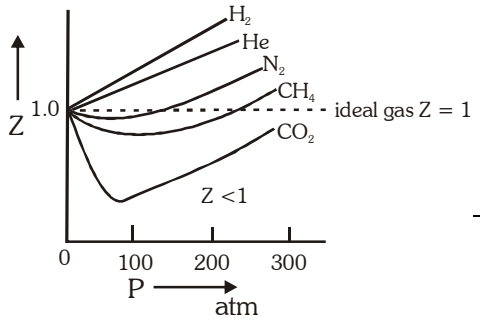
The curve for the real gas has a tendency to coincide with that of an ideal gas at low pressures when the volume

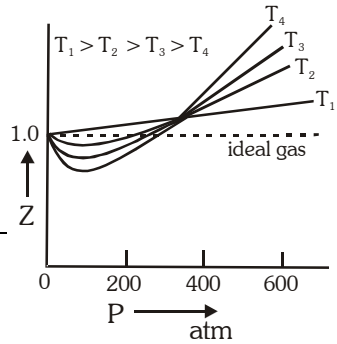
is large. At higher pressures, however deviations are observed.



- ***Compressibility factor***

$$z = \frac{PV}{nRT} = \frac{\text{volume observed}}{\text{volume ideal}}$$




- ***Boyle Temperature***

$$T_B = \frac{a}{bR}$$

- ***Inversion Temperature***

$$T_i = \frac{2a}{bR}$$

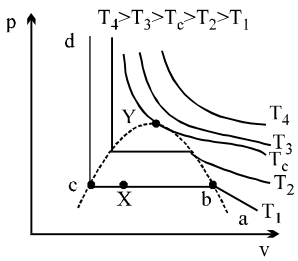
- ***Interpretation Of Deviation From Vander Waals Equation***

***(i)*** At low pressure $z = \frac{PV}{RT} = 1 - \frac{a}{VRT}$

***(ii)*** At high pressure $z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}$

***(iii)*** At extremely low pressure $z = \frac{PV}{RT} = 1$ ; $Pb = \frac{a}{V}$

- ***Critical Phenomenon : Critical Temp, Critical pressure, Critical volume***




$$T_c = \frac{8a}{27Rb} \; ; \quad P_c = \frac{a}{27b^2} \; ; \quad V_c = 3b$$

# SOME WORKED OUT EXAMPLES

***Illustration 1.***

A gas is present at a pressure of 2 atm. What should be the increase in pressure so that the volume of the gas can be decreased to 1/4$^{th}$ of the initial value if the temperature is maintained constant.

***Solution.***

PV = constant for a given mass of gas at constant pressure

$\Rightarrow \quad P_1V_1 = P_2V_2 \qquad P_1V_1 = P_2V_2 \qquad V_1 = V \qquad V_2 = V/4 \qquad P_2 = ?$

Now, $2 \times V = P_2 \times \frac{V}{4} \Rightarrow \quad P_2 = 8$ atm

$\therefore$ Pressure should be increased from 2 to 8 atm

$\therefore$ total increase = 8 – 2 = 6 atm.

***Illustration 2.***

A sample of gas occupies 10 litre under a pressure of 1 atmosphere. What will be its volume if the pressure is increased to 2 atmospheres? Assume that the temperature of the gas sample does not change.

***Solution.***

Mass and temperature is constant hence we can use Boyle's law

$P_1V_1 = P_2V_2$

Given $P_1 = 1$ atm, $V_1 = 10$ litre, $P_2 = 2$ atm, $V_2 = ?$

$1 \times 10 = 2 \times V_2 \Rightarrow V_2 = 5$ litre

***Illustration 3.***

1 mole of an ideal gas at constant atmospheric pressure is heated to increase its volume by 50% of initial volume. The change in temperature made was 300 K to T K. Than calculate final temperature.

***Sol.*** At constant pressure for a given amount of gas

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \Rightarrow \frac{V}{300} = \frac{1.5V}{T} \quad (V_1 = V, \quad T_1 = 300\text{ K}, \quad V_2 = 1.5V)$$

T = 450 K

***Illustration 4.***

A balloon of diameter 20 m weights 100 kg. Calculate its pay-load, if it is filled with He at 1.0 atm and 27°C. Density of air is 1.2 kg m$^{-3}$. [R = 0.0082 dm$^3$ atm K$^{-1}$ mol$^{-1}$]

***Solution.***

Weight of balloon = 100 kg = $10 \times 10^4$ g

$$\text{Volume of balloon} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times \left(\frac{20}{2} \times 100\right)^3 = 4190 \times 10^6 \text{ cm}^3 = 4190 \times 10^3 \text{ litre}$$

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

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

$\therefore$ Total weight of gas and balloon

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

Weight of air displaced $= \dfrac{1.2 \times 4190 \times 10^6}{10^3} = 502.8 \times 10^4$ g

$\therefore$ Pay load = wt. of air displaced – (wt. of balloon + wt. of gas)

$\therefore$ Pay load $= 502.8 \times 10^4 - 78.13 \times 10^4 =$ ***$424.67 \times 10^4$ g***

***Illustration 5.***

The temperature of a certain mass of a gas is doubled. If the initially the gas is at 1 atm pressure. Find the % increase in pressure ?

***Solution.***

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \; ; \; \frac{1}{T} = \frac{P_2}{2T}$$

$$\% \text{ increase} = \frac{2-1}{1} \text{ x } 100 = 100\%$$

***Illustration 6.***

Pressure of gas contained in a closed vessel is increased by 0.4%, when heated by 1°C. Calculate its final temperature. Assume ideal nature.

***Solution.***

Since no information is given about volume hence we can assume that volume is constant and use

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

given $P_1 = P$, $\quad T_1 = T$, $\quad P_2 = P + \dfrac{0.04P}{100} = 1.004\,P$, $\quad T_2 = T + 1$

$$\therefore \quad \frac{P}{T} = \frac{1.004P}{T+1} \Rightarrow T = 250 \text{ K}$$

***Illustration 7.***

The density of an unknown gas at 98°C and 0.974 atm is $2.5 \times 10^{-3}$ g/ml. What is the mol wt. of gas?

***Solution.***

Density $= 2.5 \times 10^{-3}$ g/ml = 2.5 g/L

$\therefore \quad PM = \rho RT$

$0.974 \times M = 2.5 \times 0.0821 \times 371 \Rightarrow M = 78.18.$

***Illustration 8.***

When 3.2 g of sulphur is vapourised at 450°C and 723 mm pressure, the vapours occupy a volume of 780 ml. What is the molecular formula of sulphur vapours under these conditions? Calculate the vapour density also.

***Solution.***

$$PV = nRT \Rightarrow \frac{723}{760} \times \frac{780}{760} = \frac{3.2}{M} \times 0.082 \times 723$$

$M = 255.9$

No. of catoms of sulpher in one molecule $= \dfrac{M}{32} = 8$

$\therefore$ Molecular formula of sulphur $= S_8$

$$\text{V. D.} = \frac{M}{2} = \frac{255.9}{2} \Rightarrow 127.99$$

***Illustration 9.***

Calculate the mean molar mass of a mixture of gases having 7 g of Nitrogen, 22 g of $CO_2$ and 5.6 litres of CO at STP.

***Solution.***

Moles of $N_2$ = 7/28 = 1/4

Moles of $CO_2$ = 22/44 = 1/2

Moles of CO = 5.6 / 22.4 = 1/4

$$\text{mean molar mass} = M_{min} = \frac{n_1M_1 + n_2M_2 + n_3M_3}{n_1 + n_2 + n_3} = (7 + 7 + 22) / 1 = 36$$

***Illustration 10.***

A gaseous mixture contains 55% $N_2$, 20% $O_2$, and 25% $CO_2$ by mass at a total pressure of 760 mm. Calculate the parital pressure of each gas.

***Solution.***

Total mass of the gases = 100 g

$W_{N_2}$ = 55g, $W_{O_2}$ = 20 g, $W_{CO_2}$ = 25g

$n_{N_2}$ = 55/28 = 1.964, $n_{O_2}$ = 20/32 = 0.625, $n_{CO_2}$ = 25/44 = 0.568

Total moles = 3.157

$$P_{N_2} = \frac{1.964 \times 760}{3.157} = 472.8 \text{ mm} \quad P_{O_2} = \frac{0.625 \times 760}{3.157} = 150.46 \text{ mm}$$

$$P_{CO_2} = \frac{0.568 \times 760}{3.157} = 136.74 \text{ mm}$$

***Illustration 11.***

A mixture containing 1.6 g of $O_2$, 1.4g of $N_2$ and 0.4 g of He occupies a volume of 10 litre at 27°C. Calculate the total pressure of the mixture and partial pressure of each compound.

***Solution.***

PV = nRT V = 10 litre T = 27°C = 300K

$$n_{He} = \frac{0.4}{4} = 0.1, \quad n_{N_2} = \frac{1.4}{28} = 0.05, \quad n_{D_2} = \frac{1.6}{32} = 0.05$$

Total no. of moles = 0.1 + 0.05 + 0.05 $\Rightarrow$ 0.2

PV = nRT $\Rightarrow$ P× 10 = 0.2 × 0.082 × 300 = 0.04926 $\Rightarrow$ P = 0.492 atm

Partial pressure = Total pressure × molefraction

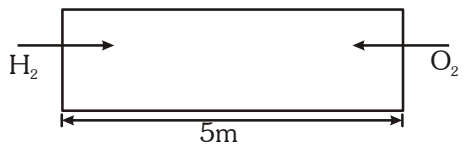
$$P_{He} = 0.492 \times \frac{0.1}{0.2} = 0.246 \text{ atm}$$

$$P_{N_2} = 0.492 \times \frac{0.05}{0.2} = 0.123 \text{ atm}$$

$$P_{O_2} = 0.492 \times \frac{0.05}{0.2} = 0.123 \text{ atm}$$

***Illustration 12.***

In a tube of length 5 m having 2 identical holes at the opposite ends. $H_2$ & $O_2$ are made to effuse into the tube from opposite ends under identical conditions. Find the point where gases will meet for the first time.



***Solution.***

$$\frac{r_1}{r_2} = \frac{dx}{dt} \times \frac{dt}{dx} = \sqrt{\frac{M_2}{M_1}}$$

$$\frac{dx_1}{dx_2} = \sqrt{\frac{32}{2}}$$

$$\frac{dx_1}{dx_2} = 4 \Rightarrow \frac{\text{distance travelled by } H_2}{\text{distance travelled by } O_2} = 4$$

$$\frac{x}{(5-x)} = 4$$

$x = (5 - x)\,4$ ; $\quad x = 20 - 4x$ ; $5x = 20$ ; $\quad x = 4$ from $H_2$ side

***Illustration 13.***

Assume that you have a sample of hydrogen gas containing $H_2$, HD and $D_2$ that you want to separate into pure components (H = $^1H$ and D = $^2H$). What are the relative rates of diffusion of the three molecules according to Graham's law ?

***Solution.***

Since $D_2$ is the heaviest of the three molecules, it will diffuse most slowly, and let we call its relative rate 1.00. We can then compare HD and $H_2$ with $D_2$.

Comparing HD with $D_2$, we have

$$\frac{\text{Rate of HD diffusion}}{\text{Rate of } D_2 \text{ diffusion}} = \sqrt{\frac{\text{Molecular mass of } D_2}{\text{Molecular mass of HD}}} = \sqrt{\frac{4.0\text{amu}}{3.0\text{amu}}} = 1.15$$

Comparing $H_2$ with $D_2$ we have

$$\frac{\text{Rate of } H_2 \text{ diffusion}}{\text{Rate of } D_2 \text{ diffusion}} = \sqrt{\frac{\text{Mass of } D_2}{\text{Mass of } H_2}} = \sqrt{\frac{4.0\text{ amu}}{2.0\text{ amu}}} = 1.41$$

Thus, the relative rates of diffusion are $H_2$(1.41) > HD (1.15) > $D_2$(1.00).

***Illustration 14.***

In a container of capacity 1 litre there are $10^{23}$ molecules each of mass $10^{-22}$ gms. If root mean square speed is $10^5$ cm/sec then calculate pressure of the gas.

***Solution.***

$$PV = \frac{1}{3} MN\,\overline{U^2}$$

$P = ?$

$V = 10^{-3}\ m^3$

$m = 10^{-25}$ kg

$N = 10^{23}$

$\sqrt{\overline{U^2}} = 10^5$ cm/sec $= 10^3$ m/sec

$\overline{U^2} = 10^6\ m^2/sec^2$

$$P \times 10^{-3} = \frac{1}{3} \times 10^{-25} \times 10^{23} \times 10^6$$

$$P = \frac{1}{3} \times 10^{-2} \times 10^6 \times 10^3$$

$$P = \frac{1}{3} \times 10^7 \text{ pascals}$$

***Illustration 15.***

The vander waals constant for HCI are a = 371.843 KPa.dm$^6$ mol$^{-2}$ and b = 40.8 cm$^3$ mol$^{-1}$ find the critical constant of this substance.

***Solution.***

The critical pressure, $P_C = \frac{a}{27b^2} = \frac{371.843 \times 10^3}{27 \times (40.8)^2 \times 10^{-6}} = \frac{371.843 \times 10^9}{27 \times (40.8)^2} = 8.273 \text{ x } 10^6$

$P_C = 8.273$ MPa

The critical pressure, $T_C = \frac{8a}{27Rb}$

R = 8.314 KPa dm$^3$ K$^{-1}$ mol$^{-1}$

$T_C = \frac{8a}{27Rb} = \frac{8 \times 371.843}{8.314 \times 27 \times 40.8 \times 10^{-3}} = 324.79 = 324.8$ K

The critical volume, $V_C = 3b = 3 \text{ x } 40.8 = 122.4$ cm$^3$

***Illustration 16.***

In a container of capacity 1 litre, air and some liquid water is present in equilibrium at total pressure of 200 mm of Hg. This container is connected to another one litre evacuated container. Find total pressure inside the container when equilibrium is again stablised (aqueous tension or vapour pressure at this temp. is 96 mm Hg).

***Solution.***

Total pressure = 200 mm of Hg = $P_{gas} + P_{vapour\ water}$

$\Rightarrow \quad P_{gas} + 96 = 200$

$P_{gas} = 104$ mm of Hg  Initially

when second container is connected

$P_1 = 104$ mm of Hg  $P_2 = ?$

$V_1 = 1$  $V_2 = 2$ litre

$P_1V_1 = P_2V_2$

$104 \times 1 = P_2 \times 2$

$52 = P_2$

After equilibrium is established

$P_{total} = 52 + 96 = P_{gas} + P_{water} = 148$ mm of Hg at equilibrium.

***Illustration 17.***

100 ml of hydrocarbon is mixed with excess of oxygen and exploded. On cooling, the mixture was reported to have a contraction of 250 ml. The remaining gas when passed through a solution of aqueous KOH, the mixture shows a further contraction of 300 ml. Find molecular formula of the hydrocarbon.

***Solution.***

$$C_xH_y + \left(x + \frac{Y}{4}\right) O_2 \longrightarrow x\,CO_2 + \frac{y}{2}H_2O$$

100 ml  $x$ 100  $\frac{y}{2}$ 100.

mixture contains $CO_2$ , $H_2O$ & excess $O_2$

on cooling, $H_2O$ is separated, volume of $H_2O$ = 250 ml

$\frac{y}{2} \times 100 = 250$ ; $y = 5$,

as KOH absorbs $CO_2$, hence 300 ml contraction is because of $CO_2$ that has been absorbed.

Volume of $CO_2$ = 100 x = 300 ; x = 3

Empirical formula = $C_3H_5$ ;  molecular formula = $C_6H_{10}$.

***Illustration 18.***

Assuming that $N_2$ molecules is spherical and its radius is $2 \times 10^{-10}$ meter, calculate the empty space in one mole of $N_2$ gas at NTP.

***Solution.***

Volume of one molecule of $N_2 = \frac{4}{3}\pi r^3$

$$= \frac{4 \times 3.14(2 \times 10^{-10})^3}{3} = 3.35 \times 10^{-29} m^3 = 3.35 \times 10^{-23} cm^3$$

Volume of one mole $N_2$ molecules $= 6.02 \times 10^{23} \times 3.35 \times 10^{-23} cm^3 = 20.167\ cm^3$

Volume of one mole $N_2$ at NTP = 22400 cc.

Hence empty space = 22400 – 22379.833 $cm^3$

$$\% \text{ empty space} = \frac{\text{Empty volume} \times 100}{\text{Total Volume}} = \frac{22379.833 \times 100}{22400} = 99.9\%$$

***Illustration 19.***

Under identical conditions of temperature, the density of a gas X is three times that of gas Y while molecular mass of gas Y is twice that of X. The ratio of pressures of X and Y will be

(A) 6 (B) 1/6 (C) 2/3 (D) 3/2.

***Ans. (A)***

***Solution.***

$$P\rho = \frac{PM}{RT} \Rightarrow P = \frac{\rho RT}{M} \Rightarrow P_x = \frac{\rho_x RT}{M_x},\ P_y = \frac{\frac{\rho_x RT}{3}}{2M_x},\quad 6P_y = \frac{\rho_x RT}{M_x} \quad \therefore P_y = P_x \Rightarrow \frac{P_x}{P_y} = 6$$

***Illustration 20.***

One mole of $N_2O_4(g)$ at 300 K is kept in a closed container under one atmosphere pressure. It is heated to 600 K when 20% by mass of $N_2O_4(g)$ decomposes to $NO_2(g)$. The resultant pressure is

(A) 1.2 atm (B) 2.4 atm (C) 2 atm (D) 1 atm

***Ans. (B)***

***Solution.***

Initial pressure of $N_2O_4$ at 600 K, $\Rightarrow P_{600\,k} = \frac{1}{300} \times 600 = 2atm$

$N_2O_4$ decomposes as follows $N_2O_4 \longrightarrow 2NO_2$

At equilibrium $1 - \alpha$ $2\alpha$

$\therefore$ Moles at equilibrium $= 1 - \alpha + 2\alpha = 1 + \alpha$

$\therefore$ The resultant pressure $= 2(1 + \alpha) = 2(1 + 0.2) = 2.4$ atm

# ANSWERS

## BEGINNER'S BOX-1

**1**. (B) **2.**(A) **3.**(A) **4.**(A) **5.**(B) **6.**(D)

**7.**(i) 10 cm of Hg (ii) 66 cm of Hg (iii) 86 cm of Hg

**8.**(i) 10132500 (ii) 76000 (iii) 1033.6 (iv) 76000 (v) 100

**9.** 67N

## BEGINNER'S BOX-2

**1**. 96g **2.** 262.2 ml **3.** 327.6 K

**4.**41.33 **5.**0.74 cm **6.** 1.57 $gL^{-1}$

**7.**(a) 0.37L (b) 181.55 (c) 2.27 atm (d) 0.418 L

**8.** 36.36g **9.**(C) **10.**(A)

## BEGINNER'S BOX-3

**1.**0.56 atm **2**. (a) $\frac{1}{3}$ (b) 73.89 atm **3.** 489.23 mm. 260.77 mm

**4.** Pm = 2.4 atm $P_{N_2} = 0.667$ atm $P_{O_2} = 0.733$ atm $P_{CO_2} = 1$ atm

**5.** $P_{CO} = 0.49$ atm $P_{CO_2} = 1.51$ atm

**6.**(B)

## BEGINNER'S BOX-4

**1**. (C) **2.**(A) **3.(**A) **4.**(A) **5.**(D)

**6.** 6.82 **7.** M = 16 **8.** 2.2 atm **9.** 25.7 atm

**10.** $NH_4Cl$ will form at 1.186 from the $NH_3$ and of the tube

## BEGINNER'S BOX-5

**1**. (D) **2.**(B) **3.**(B) **4.**(B) **5.**(B) **6.**(B)

**7.**(A) **8.**(B) **9.**(A) **10.**(A)

## BEGINNER'S BOX-6

**1.**(A) **2.**(C) **3.**(C,D) **4.**(A) **5.**(A) **6.**(B)

**7.**(A)

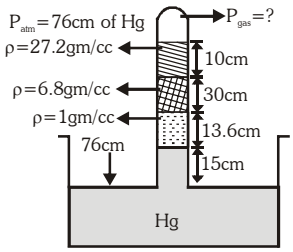
## BEGINNER'S BOX-7

**1**. (F) **2.**(T) **3.**(T) **4.**(T) **5.**(B) **6.**(C)

**7.**(D) **8.**(C) **9.**(D)

## EXERCISE – 1 MCQ (SINGLE CHOICE CORRECT)

**1.** In the following arrangement the pressure of the confined gas will be :




(A) 15 cm of Hg (B) 25 cm of Hg (C) 35 cm of Hg (D) 45 cm of Hg

**2.** If two moles of an ideal gas at 546 K occupies a volume of 44.8 litres, the pressure must be :
(A) 2 atm (B) 3 atm (C) 4 atm (D) 1 atm

**3.** At STP the order of root mean square velocity of molecules of $H_2$, $N_2$, $O_2$ and HBr is :
(A) $H_2 > N_2 > O_2 >$ HBr (B) HBr $> O_2 > N_2 > H_2$
(C) HBr $> H_2 > O_2 > N_2$ (D) $N_2 > O_2 > H_2 >$ HBr

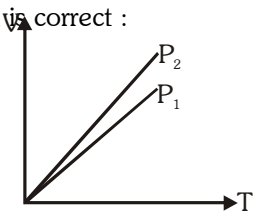
**4.** The density of a gas at 27°C and 1 atm is d. Pressure remaining constant at which of the following temperatures will its density become 0.75 d?
(A) 20 °C (B) 30 °C (C) 400 K (D) 300 K

**5.** At 27°C the ratio of rms velocities of ozone to oxygen is :
(A) $\sqrt{3/5}$ (B) $\sqrt{4/3}$ (C) $\sqrt{2/3}$ (D) 0.25

**6.** A real gas most closely approaches the behaviour of an ideal gas at :
(A) 15 atm and 200 K (B) 1 atm and 273 K (C) 0.5 atm and 500 K (D) 15 atm and 500 K

**7.** The temperature at which the second virial coefficient of a real gas is zero is called :
(A) Critical temperature (B) Boyle's temperature
(C) Boiling point (D) none of these

**8*.** V vs T curves at constant $P_1$ and $P_2$ for an ideal gas are shown in figure. Which is correct :
(A) $P_1 > P_2$
(B) $P_1 < P_2$
(C) $P_1 = P_2$
(D) all




**9.** At STP, 2.8 litres of hydrogen sulphide were mixed with 1.6 litres of sulphur dioxide and the reaction occurred according to the equation :
$2H_2S\ (g) + SO_2\ (g) \longrightarrow 2H_2O\ (l) + 3S\ (s)$
Which of the following shows the volume of the gas remaining after the reaction?
(A) 0.2 litres of $SO_2$ (g) (B) 0.4 litres of $H_2$ (g) (C) 1.2 litres of $H_2S$ (g) (D) 1.2 litres of $SO_2$ (g)

**10.** The rates of diffusion of $SO_3$, $CO_2$, $PCl_3$ and $SO_2$ are in the following order :

(A) $PCl_3 > SO_3 > SO_2 > CO_2$
(B) $CO_2 > SO_2 > PCl_3 > SO_3$
(C) $SO_2 > SO_3 > PCl_3 > CO_2$
(D) $CO_2 > SO_2 > SO_3 > PCl_3$

**11.** The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is :

(A) critical temperature
(B) Boyle temperature
(C) boiling temperature
(D) reduced temperature

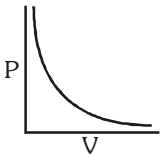
**12.** Helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom is :

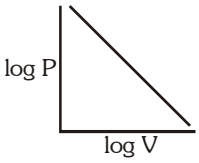
(A) two times that of a hydrogen molecules
(B) same as that of a hydrogen molecules
(C) four times that of a hydrogen molecules
(D) half that of a hydrogen molecules

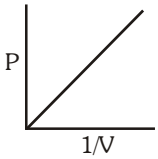
**13.** In vander Waal's equation of state for a non-ideal gas the term that accounts for intermolecular forces is :

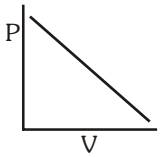
(A) (V – b)
(B) $\left(p + \frac{a}{v^2}\right)$
(C) RT
(D) $(RT)^{-1}$

**14.** Which of the following curves does not represent Boyle's law :

(A) 


(B) 


(C) 


(D) 


**15.** A closed vessel contains equal number of nitrogen and oxygen molecules at pressure of P mm. If nitrogen is removed from the system, then the pressure will be :

(A) P
(B) 2P
(C) P/2
(D) $P^2$

**16.** The ratio of average molecular kinetic energy of $PCl_5$ to that of $O_2$ both at 300 K is :

(A) 1 : 1
(B) 7 : 2
(C) 176 : 1
(D) 2 : 7

**17.** The correct order of normal boiling points of $O_2$, $N_2$, $NH_3$ and $CH_4$ for whom the values of vander waals constant 'a' are 1.360, 1.390, 4.170 and 2.253 $L^2.atm.mol^{-2}$ respectively, is :

(A) $O_2 < N_2 < NH_3 < CH_4$
(B) $O_2 < N_2 < CH_4 < NH_3$
(C) $NH_3 < CH_4 < N_2 < O_2$
(D) $NH_3 < CH_4 < O_2 < N_2$

**18*.** A molecule in a cube of length $\ell$ has a velocity $v_x$ in the x direction. The number of collisions with one face per second for this molecule with be given by which one of the following :

(A) $v_x/\ell$
(B) $v_x/2\ell$
(C) ½ $\ell$
(D) $N mv^2/3\ell$

**19.** The rate of diffusion of methane at a given temperature is twice that of gas X. The molecule weight of X is

(A) 64.0
(B) 32.0
(C) 4.0
(D) 8.0

**20.** For a fixed volume of a gas the pressure is increases when the temperature increases. This is due to :
(A) increase in the average molecular speed
(B) increase in the rate of collisions among molecules
(C) increase in the molecular attraction
(D) decrease in the mean free path

**21.** The ratio, $\frac{\text{rms velocity of } SO_2}{\text{rms velocity of He}}$, of sulphur dioxide and helium gases at 30°C is equal to :
(A) 4 (B) 0.25 (C) 0.10 (D) 8

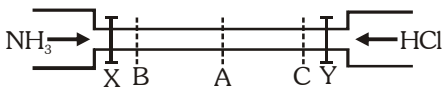
**22.** A chemist has synthesized a greenish yellow gaseous compound of chlorine and oxygen and finds that its density is 7.71 g/L at 36°C and 2.88 atm. Then the molecular formula of the compound will be :
(A) $ClO_3$ (B) $ClO_2$ (C) ClO (D) $Cl_2O_2$

**23.** The compressibility of a gas is less than unity at STP. Therefore :
(A) $V_m > 22.4$ L (B) $V_m < 22.4$ L (C) $V_m = 22.4$ L (D) $V_m \geq 44.8$ L

**24.** At what temperature will the total KE of 0.3 mol of He be the same as the total KE of 0.40 mol of Ar at 400 K :
(A) 533 K (B) 400 K (C) 346 K (D) 300 K

**25.** If molecules of the gas are spherical of radius 1 Å, the volume occupied by the molecules in 1 mol of a gas is :
(A) 22400 mL (B) 22.4 L (C) 2.52 mL (D) 4.22 mL

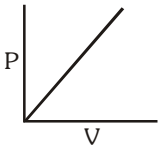
**26.** See the figure :

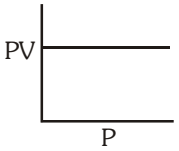


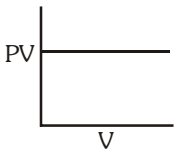

The valves of X and Y are opened simultaneously. The white fumes of $NH_4Cl$ will first form at :
(A) A (B) B
(C) C (D) A, B and C simultaneously

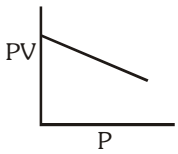
## EXERCISE – 2 MCQ (ONE OR MORE CHOICE CORRECT)

**1.** Which of the following graphs represent Boyle's law :

(A) 


(B) 


(C) 


(D) 


**2.** Which of the following statements are correct : ***(Assume ideal behaviour and identical conditions)***
(A) Helium diffuses at a rate 8.65 times as much as CO does.
(B) Helium escapes at a rate 2.65 times as fast as CO does.
(C) Helium escapes at a rate 4 times as fast as $CO_2$ does.
(D) Helium escapes at a rate 4 times as fast as $SO_2$ does.

**3.** When a fixed amount of 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 decreases

**4.** Which of the following are correct statements :
(A) vander waals constant 'a' is a measure of attractive force.
(B) vander waals constant 'b' is also called co-volume or excluded volume per mole.
(C) 'b' is expressed in L $mol^{-1}$
(D) 'a' is expressed in atm $L^2$ $mol^{-2}$

**5.** Which of the following statements are incorrect :
(A) Molar volume of every ideal gas at NTP is 22.4 L
(B) Under critical states compressibility factor is 1
(C) All gases will have equal value of average translational KE at a given temperature
(D) At absolute zero, KE is $\frac{3}{2}R$.

**6.** Which of the following quantities is the same for all ideal gases at the same temperature?
(A) The kinetic energy of 1 mol
(B) the kinetic energy of 1 g
(C) The number of molecules in 1 mol
(D) The number of molecules in 1 g

**7.** The value of the molar gas constant is
(A) $8.3145 \times 10^3$ J $(kmol)^{-1}K^{-1}$
(B) 1.987 cal mol $K^{-1}$
(C) $0.083145 \times 10^3$ $dm^3$ bar $mol^{-1}$ $K^{-1}$
(D) 0.083145 $dm^3$ bar $mol^{-1}$ $K^{-1}$

**8.** Which of the following expressions is correct on the basis of the ideal gas equation?
(A) $PV = \frac{N}{N_A}RT$
(B) $PV = Nk_BT$
(C) $PV = \frac{\rho}{w}RT$
(D) $PV = \frac{Mk_BT}{w}$

**9.** According to the kinetic theory of gases.
(A) the pressure exerted by fixed amount of a gas is proportional to the mean square speed of the molecules in a rigid vessel.
(B) the pressure exerted by fixed amount of a gas is proportional to the root mean square speed of the molecules in a rigid vessel.
(C) the root mean square speed is inversely proportional to the temperature.
(D) the mean translational kinetic energy of the molecule is directly proportional to the absolute temperature.

**10.** Indicate the correct statement for equal volumes of $N_2(g)$ and $CO_2(g)$ at 298 K and 1 atm.
***(Assume ideal behavour)***
(A) The average translational KE per molecule is the same for $N_2$ and $CO_2$
(B) The rms speed remains same for both $N_2$ and $CO_2$.
(C) The density of $N_2$ is less than that of $CO_2$.
(D) The total translational KE of both $N_2$ and $CO_2$ is the same.

**11.** Which of the following is correct for critical temperature?
(A) It is the highest temperature at which liquid and vapour can coexist.
(B) Beyond this temperature, there is no distinction between the two phases and a gas cannot be liquefied by compression.
(C) At this temperature, the surface tension of the system is zero.
(D) At this temperature, the gas and the liquid phases have different critical densities.

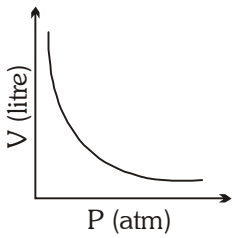
**12*.** According to Charles's law :
(A) $V \propto \frac{1}{T}$ (B) $\left(\frac{dV}{dT}\right)_P = K$ (C) $\left(\frac{dT}{dV}\right)_P = K$ (D) $\left(\frac{1}{T} - \frac{V}{T^2}\right) = 0$

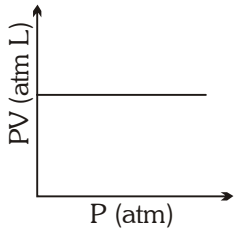
**13.** The temperature of ideal gas can be increased by
(A) decreasing the volume and pressure but keeping the amount constant
(B) increasing the pressure but keeping the volume and amount constant
(C) decreasing the amount but keeping the volume and pressure constant
(D) increasing the amount but keeping the volume and pressure constant

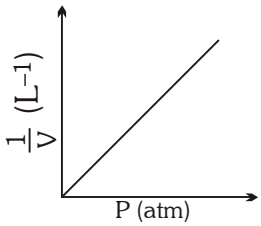
**14.** Four gas balloons A, B, C, D of equal volumes containing $H_2$, $H_2O$, CO, $CO_2$ respectively were pricked with needle and immersed in a tank containing $CO_2$. Which of them will shrink after some time.
(A) A (B) B (C) C (D) Both A and D

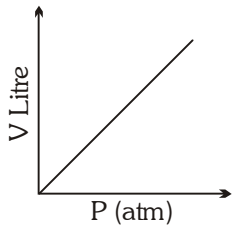
**15.** For a gaseous system, the pressure can be increased by
(A) increasing the volume of container but keeping the amount and temperature constant
(B) increasing the amount of gas at constant temperature and volume
(C) decreasing the volume of container but keeping the amount and temperature constant
(D) decreasing temperature but keeping amount and volume constant

**16.** Boyle's law is represented by -

(A) 


(B) 


(C) 


(D) 


**17*.** Three gases of densities A(0.82), B(0.25), C(0.51) are enclosed in a vessel of 4L capacity. Pick up the correct statement : ***(Assume ideal behaviour)***
(A) Gas A will tend to lie at the bottom
(B) The number of atoms of various gases A, B, C are same
(C) The gases will diffuse to form homogeneous mixture.
(D) The average kinetic energy of each gas is same.

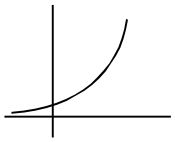
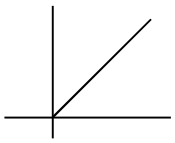
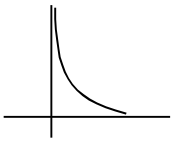
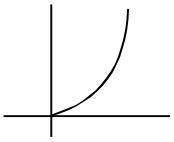
**18.** Which of the following pair of gases will have same rate of diffusion under similar condition
(A) $H_2$ & He (B) $CO_2$ & $N_2O$ (C) CO & $C_2H_4$ (D) NO & CO

**Match the column**

**19*.**

| **Column-I** | **Column-II** |
|---|---|
| (A) $P_1V_1 = P_2V_2 = P_3V_3 = .....$ | (p) Dalton's law of partial pressures at constant temperature. |
| (B) $\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} = .....$ at constant pressure. | (q) Kinetic equation of ideal gases. |
| (C) $r \propto \sqrt{\frac{1}{d}}$ | (r) 22.4 litre |
| (D) $P = P_1 + P_2 + P_3 + .....$ | (s) Isotherm |
| (E) $(V - b)\left(P + \frac{a}{V^2}\right) = RT$ | (t) Isobar |
| (F) R/N | (u) Charles' law |
| (G) Molar volume | (v) Graham's law |
| (H) $PV = \frac{1}{3}mnc^2$ | (w) Boyle's law |
| (I) Graph between P and V at constant temperature. | (x) Equation for real gases. |
| (J) Graph between V and T at constant pressure. | (y) Boltzmann's constant |

**20.** Match the description in ***Column I*** with graph provided in ***Column II***. For n moles of ideal gas at temperature 'T'.

| **Column I** | **Column II** |
|---|---|
| (A) $\frac{P}{V}$ vs P | (p)  |
| (B) $\frac{P}{V}$ vs V | (q)  |
| (C) $\frac{V}{P}$ vs $P^{-2}$ | (r)  |
| (D) $\frac{P}{V}$ vs *log* P | (s)  |

## EXERCISE – 3 SUBJECTIVE

**1.** 3.6 g of an ideal gas was injected into a bulb of internal volume of 8 L at pressure P atm and temp T K. The bulb was then placed in a thermostat maintained at (T + 15)K 0.6 g of the gas was let off to keep the original pressure. Find P and T if mol weight of is 44.

**2.** A toy balloon originally held 1.0 g of He gas and had a radius 10 cm. During the night, 0.25 g of the gas effused from the balloon. Assuming ideal gas behaviour, under these constant P and T conditions, what was the radius of the balloon the next morning.

**3.** If a scuba diver is to remain submerged for 1 hr, what pressure must be applied to force sufficient air into the tank to be used. Assume 0.5 $dm^3$ of air per breath at standard atmospheric pressure, a respiration rate of 38 breaths per minute, and a tank capacity of 30 $dm^3$.

**4*.** While resting, the average human male use 0.2 $dm^3$ of $O_2$ per hour at STP for each kg of body mass. Assume that all this $O_2$ is used to produce energy by oxidising glucose in the body. What is the mass of glucose required per hour by a resting male having mass 60 kg. What volume, at STP of $CO_2$ would be produced.

**5.** 12 g $N_2$, 4 g $H_2$ and 9 g $O_2$ are put into a one litre container at 27°C. What is the total pressure.

**6.** $1.0 \times 10^{-2}$ kg of hydrogen and $6.4 \times 10^{-2}$ kg of oxygen are contained in a $10 \times 10^{-3}$ $m^3$ flask at 473 K. Calculate the total pressure of the mixture. If a spark ignities the mixture, What will be the final pressure.

**7*.** At room temp, $NH_3$ gas at one atm & HCl gas at "P" atm are allowed to effuse through identical pin holes to the opposite ends of a glass tube 1 m long & uniform cross-section. A white deposit is observed at a distance of 60 cm from the HCl end. What is "P".

**8.** A gas mixture contains equal number of molecules of $N_2$ and $SF_6$, some of it is passed through a gaseous effusion apparatus. Calculate how many molecules of $N_2$ are present in the product gas for every 100 molecules of $SF_6$.

**9.** Two gases NO and $O_2$ were introduced at the two ends of a one metre long tube simultaneously (tube of uniform cross-section). At what distance from NO gas end, Brown fumes will be seen.

**10*.** At 20°C two balloons of equal volume and porosity are filled to a pressure of 2 atm, one with 14 kg $N_2$ & other with 1 kg $H_2$. The $N_2$ balloon leaks to a pressure of $\frac{1}{2}$ atm in one hour. How long will it take for $H_2$ balloon to leaks to a pressure of $\frac{1}{2}$ atm.

**11.** Pure $O_2$ diffuses through an aperture in 224 sec, where as mixture of $O_2$ and another gas containing 80% $O_2$ diffuses from the same in 234 sec. What is molecular weight of the gas.

**12*.** A space capsule is filled with neon gas 1.00 atm and 290 K. The gas effuses through a pin - hole into outer space at such a rate that the pressure drops by 0.3 torr/sec.

(a) If the capsule were filled with ammonia at the same temperature and pressure, what would be the rate of pressure drop.

(b) If the capsule were filled with 30.0 mol % helium, 20.0 mol% oxygen & 50.0 mol% nitrogen at a total pressure of 1.00 atm & a temp of 290 K, what would be the corresponding rate of pressure drop.

**13.** An iron cylinder contains helium at a pressure of 250 kPa and 27°C. The cylinder can withstand a pressure of $1 \times 10^6$ Pa. The room in which cylinder is placed catches fire. Predict whether the cylinder will blow up before it metls or not. [melting point of cylinder = 1800 K]

**14*.** The time taken for a given volume of gas E to effuse through a hole is 75 sec. Under identical conditions the same volume of a mix of CO & $N_2$ (containing 40% of $N_2$ by volume) effused in 70 sec. Calculate
(i) the relative mol mass of E, and
(ii) the RMS velocity (in $ms^{-1}$ units) of E at 0°C.

**15.** At what temperature in °C, the $U_{rms}$ of $SO_2$ is equal to the average velocity of $O_2$ at 27°C.

**16.** The density of CO at 273 K and 1 atm is 1.2504 kg $m^{-3}$. Calculate (a) root mean square speed (b) the average speed and (c) most probable speed.

## EXERCISE – 4 RECAP OF AIEEE/JEE (MAIN)

**1.** The no. of moles per litre in the equation PV = nRT is expressed by : ***[AIEEE-2002]***

(A) $\frac{P}{RT}$ (B) $\frac{PV}{RT}$ (C) $\frac{RT}{PV}$ (D) None

**2.** The correct value of R is ***[AIEEE-2002]***

(A) R = 0.082 litre atm (B) R = $8.314 \times 10^7$ erg $-K^{-1}$ $mol^{-1}$

(C) R = $2K^{-1}$ $mol^{-1}$ (D) None of these

**3.** According to the kinetic theory of gases, in an ideal gas, between two successive collisions a gas molecule travels- ***[AIEEE-2003]***

(A) In a straight line path (B) with an accelerated velocity

(C) In a circular path (D) In a wavy path

**4.** What volume of hydrogen gas, at 273K and 1 atm, pressure will be consumed in obtaining 21.6g of elemental boron (atomic mass = 10.8) from the reduction of boron trichloride by hydrogen ? ***[AIEEE-2003]***

(A) 44.8 L (B) 22.4 L (C) 89.6 L (D) 67.2 L

**5.** As the temperature is raised from 20°C to 40°C, the average kinetic energy of neon atoms changes by factor of which of the following ? ***[AIEEE-2004]***

(A) 1/2 (B) $\sqrt{(313/293)}$ (C) 313/293 (D) 2

**6.** In vanderwaals equation of state of the gas law, the constant 'b' is a measure of : ***[AIEEE-2004]***

(A) intermolecular repulsions (B) intermolecular attraction

(C) volume occupied by the molecules (D) intermolecular collisions per unit volume

**7.** For which of the following parameters the structural isomers $C_2H_5OH$ and $CH_3OCH_3$ would be expected to have the same values ? (Assume ideal behavior) ***[AIEEE-2005]***

(A) Heat of vaporization

(B) vapour pressure at the same temperature

(C) Boiling points

(D) Gaseous densities at the same temperature and pressure

**8.** 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 - ***[AIEEE-2006]***

(A) 2/3 (B) $\frac{1}{3} \times \frac{273}{298}$ (C) $\frac{1}{3}$ (D) $\frac{1}{2}$

**9.** For gaseous state, if most probable speed is denoted by C*, average speed $\overline{C}$ and mean square speed by C, then for a large number of molecules the ratio of these speeds are : ***[AIEEE - 2013]***

(A) $C^* : \overline{C} : C = 1.225 : 1.128 : 1$ (B) $C^* : \overline{C} : C = 1.128 : 1.225 : 1$

(C) $C^* : \overline{C} : C = 1 : 1.128 : 1.225$ (D) $C^* : \overline{C} : C = 1 : 1.225 : 1.128$

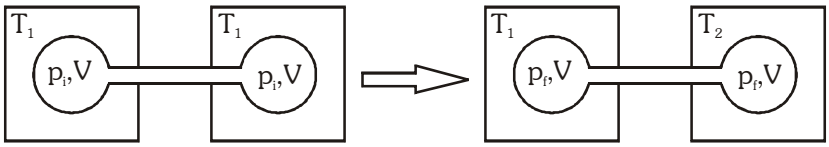
**10*.** If Z is a compressibility factor, van der Waals equation at low pressure can be written as: ***[JEE MAIN - 2014]***

(A) $Z = 1 + \frac{RT}{Pb}$ (B) $Z = 1 - \frac{a}{VRT}$ (C) $Z = 1 - \frac{Pb}{RT}$ (D) $Z = 1 + \frac{Pb}{RT}$

**11*.** Which one has the highest boiling point ? **[JEE MAIN - 2015]**

(A) He (B) Ne (C) Kr (D) Xe

**12*.** Two closed bulbs of equal volume (V) containing an ideal gas initially at pressure $p_i$ and temperature $T_1$ are connected through a narrow tube of negligible volume as shown in the figure below. The temperature of one of the bulbs is then raised to $T_2$. The final pressure $p_f$ is **[JEE MAIN - 2016]**




(A) $p_i\left(\frac{T_1T_2}{T_1+T_2}\right)$ (B) $2p_i\left(\frac{T_1}{T_1+T_2}\right)$ (C) $2p_i\left(\frac{T_2}{T_1+T_2}\right)$ (D) $2p_i\left(\frac{T_1T_2}{T_1+T_2}\right)$

**13.** At 300 K, the density of a certain gaseous molecule at 2 bar is double to that of dinitrogen ($N_2$) at 4 bar. The molar mass of gaseous molecule is:- **[JEE MAIN - 2017]**

(A) 28 g $mol^{-1}$ (B) 56 g $mol^{-1}$ (C) 224 g $mol^{-1}$ (D) 112 g $mol^{-1}$

**14.** Among the following, the incorrect statement is : **[JEE MAIN - 2017]**

(A) At low pressure, real gases show ideal behaviour

(B) At very large volume, real gases show ideal behaviour

(C) At Boyle's temperature, real gases show ideal behaviour

(D) At very low temperature, real gases show ideal behaviour

**15.** Assuming ideal gas behaviour, the ratio of density of ammonia to that of hydrogen chloride at same temperature and pressure is : **[JEE MAIN - 2018]**

(Atomic wt. of Cl = 35.5 u)

(A) 0.64 (B) 1.64 (C) 1.46 (D) 0.46

**16.** 0.5 moles of gas A and x moles of gas B exert a pressure of 200 Pa in a container of volume 10 $m^3$ at 1000 K. given R is the gas constant in $JK^{-1}$ $mol^{-1}$, x is : **[JEE MAIN - 2019]**

(A) $\frac{2R}{4+12}$ (B) $\frac{2R}{4-12}$ (C) $\frac{4-R}{2R}$ (D) $\frac{4+R}{2R}$

**17.** An open vessel at 27°C is heated until two fifth of the air (assumed as an ideal gas) in it has escaped from the vessel. Assuming that the volume of the vessel remains constant, the temperature at which the vessel has been heated is : **[JEE MAIN - 2019]**

(A) 750°C (B) 500°C (C) 750 K (D) 500 K

**18.** The volume of gas A is twice than that of gas B. The compressibility factor of gas A is thrice than that of gas B at same temperature. The pressures of the gases for equal number of moles are : **[JEE MAIN - 2019]**

(A) $2P_A = 3P_B$ (B) $P_A = 3P_B$ (C) $P_A = 2P_B$ (D) $3P_A = 2P_B$

**19.** Consider the van der Waals constants, a and b, for the following gases. **[JEE MAIN - 2019]**

| Gas | Ar | Ne | Kr | Xe |
|---|---|---|---|---|
| a/ (atm $dm^6$ $mol^{-2}$) | 1.3 | 0.2 | 5.1 | 4.1 |
| b/ ($10^{-2}$ $dm^3$ $mol^{-1}$ | 3.2 | 1.7 | 1.0 | 5.0 |

Which gas is expected to have the highest critical temperature?

(A) Kr (B) Ne (C) Ar (D) Xe

**20.** At a given temperature T, gases Ne, Ar, Xe and Kr are found to deviate from ideal gas behaviour. Their equation of state is given as $p = \frac{RT}{V-b}$ at T.

Here, b is the van der Waals constant. Which gas will exhibit steepest increase in the plot of Z (compression factor) vs p? ***[JEE MAIN - 2019]***

(A) Ne (B) Ar (C) Xe (D) Kr

**21.** Consider the following table : ***[JEE MAIN - 2019]***

| Gas | a/(k Pa $dm^6$ $mol^{-1}$) | b/($dm^3$ $mol^{-1}$) |
|---|---|---|
| A | 642.32 | 0.05196 |
| B | 155.21 | 0.04136 |
| C | 431.91 | 0.05196 |
| D | 155.21 | 0.4382 |

a and b are vander waals constant. The correct statement about the gases is :

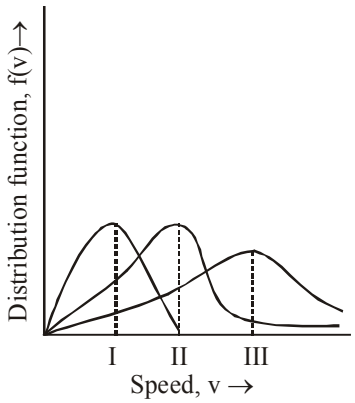
(A) Gas C will occupy lesser volume than gas A; gas B will be lesser compressible than gas D

(B) Gas C will occupy more volume than gas A; gas B will be lesser compressible than gas D

(C) Gas C will occupy more volume than gas A; gas B will be more compressible than gas D

(D) Gas C will occupy lesser volume than gas A; gas B will be more compressible than gas D

**22.** Points I, II and III in the following plot respectively correspond to ($V_{mp}$ : most probable velocity) ***[JEE MAIN - 2019]***



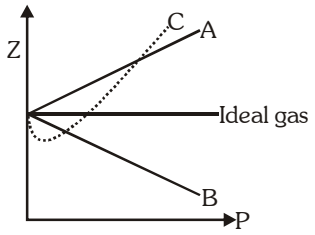

(A) $V_{mp}$ of $N_2$ (300K); $V_{mp}$ of $H_2$(300K);$V_{mp}$ of $O_2$(400K)

(B) $V_{mp}$ of $H_2$ (300K); $V_{mp}$ of $N_2$(300K);$V_{mp}$ of $O_2$(400K)

(C) $V_{mp}$ of $O_2$ (400K); $V_{mp}$ of $N_2$(300K);$V_{mp}$ of $H_2$(300K)

(D) $V_{mp}$ of $N_2$ (300K); $V_{mp}$ of $O_2$(400K);$V_{mp}$ of $H_2$(300K)

## EXERCISE – 5 RECAP OF IIT-JEE/JEE (ADVANCED)

**1*.** 


where $Z = \frac{PV}{nRT}$,

a = Vander Waal's constant for pressure correction

b = Vander Waal's constant for volume correction **[JEE 2006]**

Pick the only incorrect statement

(A) for gas A, if a = 0, the compressibility factor is linearly dependent on pressure

(B) for gas B, if b = 0, the compressibility factor is linearly dependent on pressure

(C) for gas C, $a \neq 0$, $b \neq 0$, it can be used to calculate a and b by giving lowest P value and its intercept with Z = 1.

(D) slope for all three gases at high pressure is positive.

**2*.** Match gases under specified conditions listed in Column-I with their properties / laws in Column-II. **[JEE-2007]**

| ***Column-I*** | ***Column-II*** |
|---|---|
| (A) Hydrogen gas (P = 200 atm, T = 273 K) | (p) compressibility factor $\neq 1$ |
| (B) Hydrogen gas (P ~ 0, T = 273 K) | (q) attractive forces are dominant |
| (C) $CO_2$ (P = 1 atm, T = 273 K) | (r) PV = nRT |
| (D) Real gas with very large molar volume | (s) P (V – nb) = nRT |

**3.** A gas described by van der Waals equation **[JEE-2008]**

(A) behaves similar to an ideal gas in the limit of large molar volumes

(B) behaves similar to an ideal gas is in limit of large pressures

(C) is characterised by van der Waals coefficients that are dependent on the identity of the gas but are independent of the temperature.

(D) has the pressure that is lower than the pressure exerted by the same gas behaving ideally

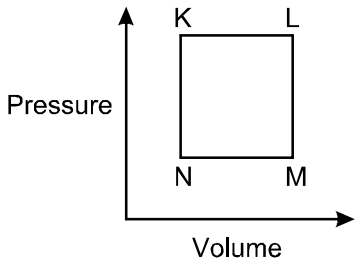
**4.** The term that corrects for the attractive forces present in a real gas in the vander Waals equation is : **[JEE-2009]**

(A) nb (B) $\frac{an^2}{V^2}$ (C) $-\frac{an^2}{V^2}$ (D) –nb

**5.** At 400 K, the root mean square (rms) speed of a gas **X** (molecular weight = 40) is equal to the most probable speed of gas **Y** at 60 K. The molecular weight of the gas **Y** is. **[JEE-2009]**

***Paragraph for Question Nos. 6 to 7***

A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure. ***[JEE-2013]***




**6.** The pair of isochoric processes among the transformation of states is :

(A) K to L and L to M (B) L to M and N to K (C) L to M and M to N (D) M to N and N to K

**7.** The succeeding operations that enable this transformation of states, are :

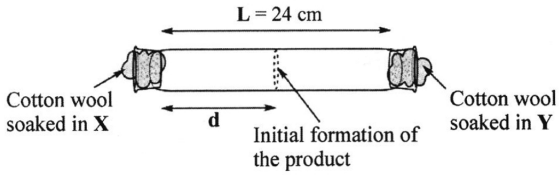
(A) Heating, cooling, heating, cooling (B) Cooling, heating, cooling, heating

(C) Heating, cooling, cooling, heating (D) Cooling, heating, heating, cooling

**8.** If the value of Avogadro number is $6.023\times10^{23}$ $mol^{-1}$ and the value of Boltzmann constant is $1.380\times10^{-23}$ J $K^{-1}$, then the number of significant digits in the calculated value of the universal gas constant is ***[JEE-2014]***

***Paragraph For Question (Q.9 to 10)***

***X*** and ***Y*** are two volatile liquids with molar weights of 10 g $mol^{-1}$ and 40 g $mol^{-1}$ respectively. Two cotton plugs, one soaked in ***X*** and the other soaked in ***Y***, are simultanesouly placed at the ends of a tube of length ***L*** = 24 cm, as shown in the figure. The tube is filled with an inert gas at 1 atmosphere pressure and a temperature of 300K. Vapours of ***X*** and ***Y*** react to form a product which is first observed at distance ***d*** cm from the plug soaked in ***X***. Take ***X*** and ***Y*** to have equal molecular diameter and assume ideal behaviour for the inert gas and the two vapours. ***[JEE-2014]***




**9*.** The value of d in cam (shown in the figure), as estimated from Graham's law, is

(A) 8 (B) 12 (C) 16 (D) 20

**10*.** The experiment value of ***d*** is found to be smaller than the estimate obtained using Graham's law. This is due to

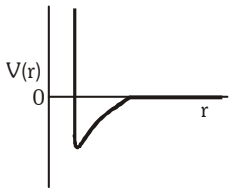
(A) larger mean free path for ***X*** as compared to that of ***Y***.

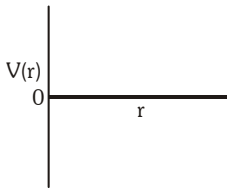
(B) larger mena free path for ***Y*** as compared to that of ***X***.

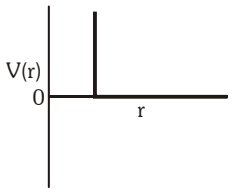
(C) increased collision frequency of ***Y*** with the inert gas as compared to that of ***X*** with the inert gas.

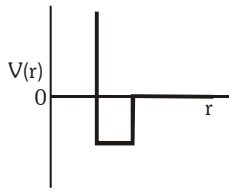
(D) increased collision frequency of ***X*** with the inert gas as compared to that of ***Y*** with the inert gas.

**11*.** One mole of a monoatomic real gas satisfies the equation p(V – b) = RT where b is a constant. The relationship of interatomic potential V(r) and interatomic distance r for the gas is given by ***[JEE-2015]***

(A)



(B)



(C)



(D)


**12*.** The diffusion coefficient of an ideal gas is proportional to its mean free path and mean speed. The absolute temperature of an ideal gas is increased 4 times and its pressure is increased 2 times. As a result, the diffusion coefficient of this gas increases x times. The value of x is ***[JEE-2016]***

**13.** A closed tank has two compartments A and B, both filled with oxygen (assumed to be ideal gas). The partition separating the two compartments is fixed and is a perfect heat insulator (Figure 1). If the old partition is replaced by a new partition which can slide and conduct heat but does NOT allow the gas to leak across (Figure 2), the volume (in $m^3$) of the compartment A after the system attains equilibrium is____. ***[JEE 2018]***

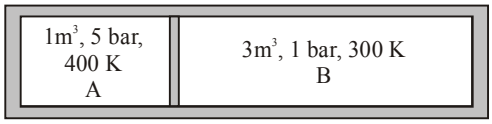



Figure 1

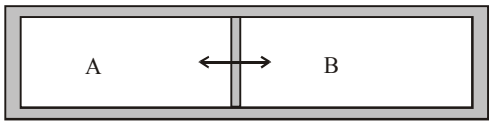



Figure 2

**14.** Which of the following statement(s) is (are) correct regarding the root mean square speed ($U_{rms}$) and average translational kinetic energy ($\varepsilon_{av}$) of a molecule in a gas at equilibrium? ***[JEE 2019]***

(A) $U_{rms}$ is doubled when its temperature is increased four times

(B) $\varepsilon_{av}$ at a given temperature does not depend on its molecular mass

(C) $U_{rms}$ is inversely proportional to the square root of its molecular mass

(D) $\varepsilon_{av}$ is doubled when its temperature is increased four times

# ANSWERS

## EXERCISE-1

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | B | A | A | C | C | C | B | A | A | D | B | B | B | D | C |
| Que. | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | | | | |
| Ans. | A | B | B | A | A | B | B | B | A | C | C | | | | |

## EXERCISE-2

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | BC | BD | AB | ABCD | BD | AC | AD | AB | AD | ACD |
| Que. | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | | |
| Ans. | ABC | BC | BC | ABC | BC | ABC | CD | BC | | |

- ***Match the Column***

**19*.** (A) - (w), (B) - (u), (C) - (v), (D) - (p), (E) - (x), (F) - (y), (G) - (r), (H) - (q), (I) - (s), (J) - (t)

**20.** (A) - (s), (B) - (r), (C) - (q), (D) - (p)

## EXERCISE-3

**1.** P = 0.062 atm, T = 75 k

**2.** 9.08 cm

**3.** $3.8 \times 10^3$ kPa

**4*.** 16.07 g, 12 $dm^3$

**5.** 66.74 atm

**6.** $P_{total} = 27.54 \times 10^5 N/m^2$, $P_{final} = 19.66 \times 10^5 N/m^2$

**7*.** 2.19 atm

**8.** 228

**9.** 50.8 cm

**10*.** 16 min

**11.** M = 46.6

**12*.** (a) 0.32 Torr/sec (b) 0.29 Torr/sec

**13.** Yes

**14*.** 32.14 g/mol, 460.28 m/s

**15.** 236.29°C

**16.** $U_{RMS}$ = 493 m/s, $U_{mp}$ = 403 m/s, $U_{av}$ = 454.4 m/s

## EXERCISE-4

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | A | B | A | D | C | C | D | C | C | B | D | C | D | D | D |
| Que. | 16 | 17 | 18 | 19 | 20 | 21 | 22 | | | | | | | | |
| Ans. | D | D | A | A | C | C | D | | | | | | | | |

## EXERCISE-5

**1*.** (D)

**2*.** (A) p, s ; (B) r ; (C) p, q ;(D) r

**3.** (AC or ACD)

**4.** (B)

**5.** $M_Y$ = 4.

**6.** (B)

**7.** (C)

**8.** (4)

**9*.** (C)

**10*.** (D)

**11*.** (C)

**12*.** (4)

**13.** (2.22)

**14.** (A, B, C)

# Important Notes