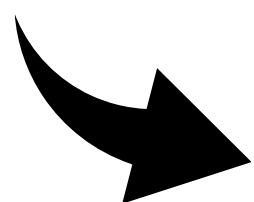


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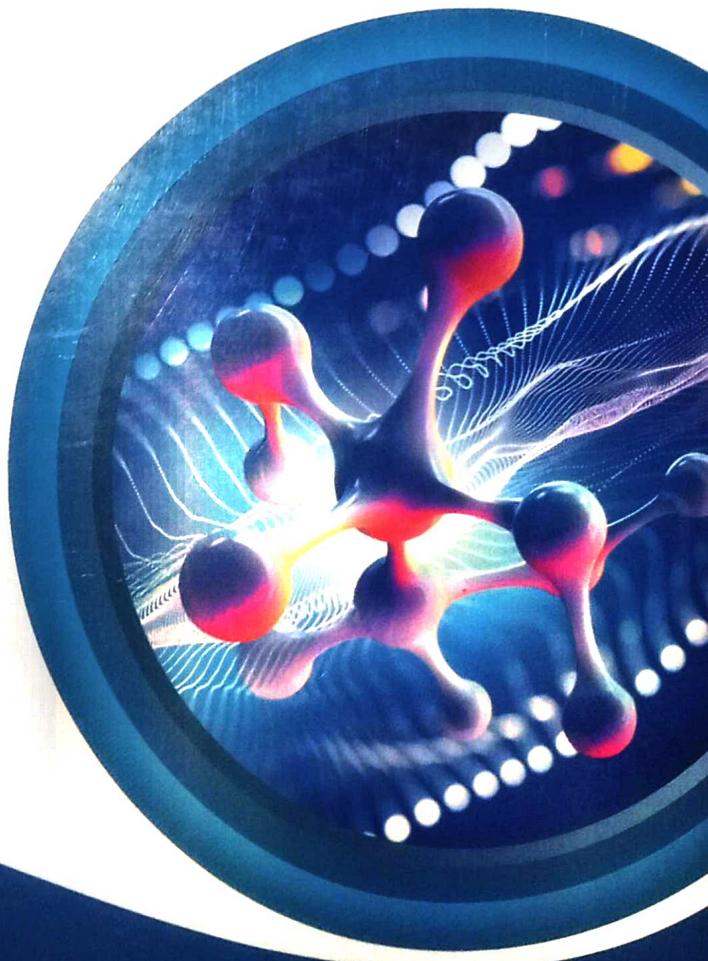
JEE MAIN & ADVANCED

CHEMISTRY

FULL COURSE STUDY MATERIAL

Class XI

- Some Basic Concepts of Chemistry
- Atomic Structure
- States of Matter



Module-1



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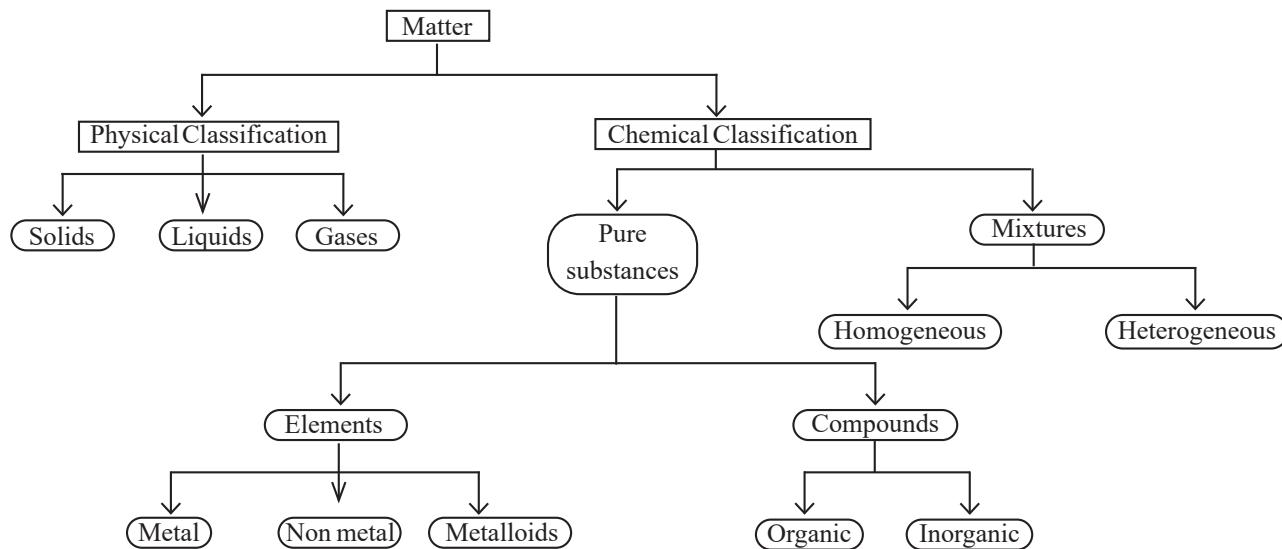
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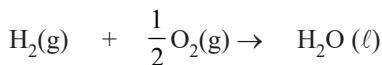
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Some Basic Concepts of Chemistry

CLASSIFICATION OF MATTER



Law of conservation of mass [Lavoisier]: In a chemical change total mass remains conserved i.e., mass before the reaction is always equal to mass after the reaction.



$$1 \text{ mole} \quad \frac{1}{2} \text{ mole} \quad 1 \text{ mole}$$

$$\text{Mass before the reaction} = 1 \times 2 + \frac{1}{2} \times 32 = 18 \text{ gm}$$

$$\text{Mass after the reaction} = 1 \times 18 = 18 \text{ gm}$$

Law of constant composition [Proust]: All chemical compounds are found to have constant composition irrespective of their method of preparation or sources.

e.g. In H_2O , hydrogen & oxygen combine in 2 : 1 molar ratio, this ratio remains constant whether it is tap water, river water or seawater or produced by any chemical reaction.

Law of Multiple Proportions [Dalton]: When one element combines with the other element to form two or more different compounds, the mass of one element, which combines with a constant mass of the other bear a simple ratio to one another.

e.g. Carbon is found to form two oxides which contain 42.9% & 27.3% of carbon respectively show that these figures shows the law of multiple proportion.

	First oxide	Second oxide
Carbon	42.9 %	27.3 %
Oxygen	57.1 %	72.7%

Given

In the first oxide, 57.1 parts by mass of oxygen combine with 42.9 parts of carbon.

1 part of oxygen will combine with $\frac{42.9}{57.1}$ part of carbon = 0.751

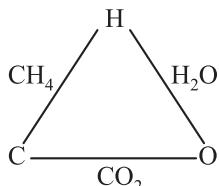
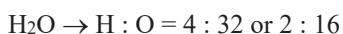
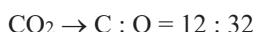
Similarly in 2nd oxide, 1 part of oxygen will combine with $\frac{27.3}{72.7}$ part of carbon = 0.376.

The ratio of carbon that combine with the same mass of oxygen = 0.751 : 0.376 = 2 : 1.

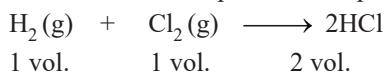
This is a simple whole no. ratio this means above data shows the law of multiple proportion.

Laws of Reciprocal Proportion: The ratio of the masses of two elements A and B which combine separately with a fixed mass of the third element C is either the same or some simple multiple of the ratio of the masses in which A and B combine directly with each other.

Like CH_4 , CO_2 and H_2O



Gay-Lussac's Law of Combining Volume: According to him, elements combine in a simple ratio of atoms, gases combine in a simple ratio of their volumes provided all measurements should be done at the same temperature and pressure.



Avogadro's hypothesis: Equal volume of all gases have equal number of molecules (not atoms) at same temperature and pressure condition.

N.T.P. (Normal Temperature and Pressure) at N.T.P. condition: Temperature = 0°C or 273 K, Pressure = 1 atm = 760 mm of Hg and volume of one mole of gas at NTP is found to be experimentally equal to 22.4 litres which is known as molar volume.

Note: Measuring the volume is equivalent to counting the number of molecules of the gas.



Train Your Brain

Example 1: A 15.9 g sample of sodium carbonate is added to a solution of acetic acid weighing 20.0 g. The two substances react, releasing carbon dioxide gas to the atmosphere. After reaction, the contents of the reaction vessel weigh 29.3 g. What is the mass of carbon dioxide given off during the reaction?

Sol. The total mass of reactants taken = $15.9 + 20.0 = 35.9$ gm. From the conservation of mass, the final mass of the contents of the vessel should also be 35.9 gm. But it is only 29.3 gm. The difference is due to the mass of released carbon dioxide gas.

Hence, the mass of carbon dioxide gas released
= $35.9 - 29.3 = 6.6$ gm

Example 2: The following are results of analysis of two samples of the same or two different compounds of phosphorus and chlorine. From these results, decide whether the two samples are from the same or different compounds. Also state the law, which will be obeyed by the given samples.

	Amount P	Amount Cl
Compound A	1.156 gm	3.971 gm
Compound B	1.542 gm	5.297 gm

Sol. The mass ratio of phosphorus and chlorine in compound

$$A, m_p : m_{\text{Cl}} = 1.156 : 3.971 = 0.2911 : 1.000$$

The mass ratio of phosphorus and chlorine in compound B, $m_p : m_{\text{Cl}} = 1.542 : 5.297 = 0.2911 : 1.000$

As the mass ratio is same, both the compounds are **same** and the samples obey the **law of definite proportion**.

Example 3: 2.5 ml of a gaseous hydrocarbon exactly requires 12.5 ml oxygen for complete combustion and produces 7.5 ml carbon dioxide and 10.0 ml water vapour. All the volumes are measured at the same pressure and temperature. Show that the data illustrates Gay Lussac's law of volume combination.

$$\begin{aligned} \text{Sol. } V_{\text{hydrocarbon}} : V_{\text{oxygen}} : V_{\text{carbon dioxide}} : V_{\text{water vapour}} &= 2.5 : \\ 12.5 : 7.5 : 10.0 \end{aligned}$$

$$= 1 : 5 : 3 : 4 \text{ (simple ratio)}$$

Hence, the data is according to the **law of volume combination**.



Concept Application

- A sample of pure carbon dioxide, irrespective of its source contains 27.27% carbon and 72.73% oxygen. The data support:
 - Law of constant composition.
 - Law of conservation of mass.
 - Law of reciprocal proportions.
 - Law of multiple proportions.
- The percentage of hydrogen in water and hydrogen peroxide is 11.1 and 5.9 respectively. These figures illustrate:
 - Law of multiple proportions.
 - Law of conservation of mass.
 - Law of constant proportions.
 - Law of combining volumes.
- 1.0 g of an oxide of A contained 0.5 g of A. 4.0 g of another oxide of A contained 1.6 g of A. The data indicate the law of:
 - Reciprocal proportions.
 - Constant proportions.
 - Conservation of energy.
 - Multiple proportions.

BASIC DEFINITIONS

Relative Atomic Mass: One of the most important concept come out from Dalton's atomic theory was that of relative atomic mass or relative atomic weight. This is done by expressing mass of one atom with respect to a fixed standard. Dalton used hydrogen as the

6. The atomic mass & molecular mass of hydrogen is:
 (a) 1amu & 2amu (b) 2 amu & 4 amu
 (c) 3amu & 6amu (d) 4 amu & 8 amu
7. One 'u' stands for the mass of:
 (a) An atom of carbon-12.
 (b) 1/12th of carbon-12.
 (c) 1/12th of hydrogen atom.
 (d) One atom of any of the elements.
8. Mass of 1 amu in g:
 (a) 1.66×10^{-24} (b) 1.66×10^{-24}
 (c) 1.008 (d) 9.1×10^{-28}

MOLE CONCEPT

Mole

Mole is a chemical counting SI unit and defined as follows:

A mole is the amount of a substance that contains as many entities (atoms, molecules or other particles) as there are atoms in exactly 0.012 kg (or 12 gm) of the carbon-12 isotope.

From mass spectrometer we found that there are 6.023×10^{23} atoms present in 12 gm of C-12 isotope.

The number of entities in 1 mol is so important that it is given a separate name and symbol known as Avogadro constant denoted by N_A .

i.e., on the whole we can say that 1 mole is the collection of 6.02×10^{23} entities. Here entities may represent atoms, ions, molecules or even pens, chair, paper etc also include in this but as this number (N_A) is very large therefore it is used only for very small things.

How Big is a Mole?

Amount of water in world's oceans (litres)	Age of earth (seconds)
	Population of earth
Avogadro's number	Distance from earth to sun (centimeters)
602,200,000,000,000,000,000,000	

Note: In modern practice gram-atom and gram-molecule are termed as mole.

METHODS OF CALCULATIONS OF MOLE

- (a) If no. of some species is given, then no. of moles = $\frac{\text{Given no.}}{N_A}$
- (b) If weight of a given species is given, then no. of moles = $\frac{\text{Given wt.}}{\text{Atomic wt.}} \text{ (for atoms),}$
 or $\frac{\text{Given wt.}}{\text{Molecular wt.}} \text{ (for molecules)}$

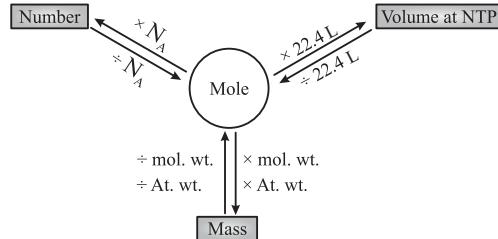
- (c) If volume of a gas is given along with its temperature (T) and pressure (P) use $n = \frac{PV}{RT}$
 where $R = 0.0821 \text{ lit-atm/mol-K}$ (when P is in atmosphere and V is in litre.)

1 mole of any gas at STP (0°C & 1 bar) occupies 22.7 litre.

1 mole of any gas at STP (0°C & 1 atm) occupies 22.4 litre.

Atom: Atom is smallest particle which can not be divided into its constituents.

Y-map: Interconversion of mole - volume, mass and number of particles:



Note: Measuring the volume is equivalent to counting the number of molecules of the gas.



Train Your Brain

Example 6: Total number of atoms of all elements present in 1 mole of ammonium dichromate is?

- (a) 14 (b) 19
 (c) 6×10^{23} (d) 114×10^{23}

Sol. (d) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 = 19 \times 6.02 \times 10^{23} = 114 \times 10^{23}$ atoms.

Example 7: How many atoms of oxygen are their in 16 g of oxygen?

Sol. Let x atoms of oxygen are present

$$\text{So, } 16 \times 1.66 \times 10^{-24} \times x = 16 \text{ g}$$

$$x = \frac{1}{1.66 \times 10^{-24}} = N_A$$

Example 8: Calculate the volume in litres of 20 g hydrogen gas at NTP.

Sol. No. of moles of hydrogen gas = $\frac{\text{Mass}}{\text{Molecular mass}}$
 $= \frac{20 \text{ gm}}{2 \text{ gm}} = 10 \text{ mol}$

Volume of hydrogen gas at NTP = $10 \times 22.4 \text{ L}$

Example 9: The number of atoms contained in 11.2 L of

SO_2 at N.T.P. are:

- (a) $3/2 \times 6.02 \times 10^{23}$ (b) $2 \times 6.02 \times 10^{23}$
 (c) 6.02×10^{23} (d) $4 \times 6.02 \times 10^{23}$

Sol. (a) 22.4 litre gas has = 1 mole

$$\begin{aligned} 1 \text{ litre gas has} &= \frac{1}{22.4} \times 11.2 = \frac{1}{2} \text{ mole} \\ &= \text{S} + 2\text{O} = 3 \\ &= \frac{3}{2} \times 6.02 \times 10^{23} \end{aligned}$$



Concept Application

9. The number of particles present in 1 mol of nitrogen atom are:
 (a) 6.022×10^{25} (b) 6.022×10^{24}
 (c) 6.022×10^{23} (d) 6.022×10^{22}
10. The mass of one molecule of water is approximately:
 (a) 3×10^{-23} g (b) 18 g
 (c) 1.5×10^{-23} g (d) 4.5×10^{-23} g
11. The molar mass of ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) is:
 (a) 152 gm (b) 278 gm
 (c) 137 gm (d) None of these

ELEMENTAL ANALYSIS

For n mole of a compound ($\text{C}_3\text{H}_7\text{O}_2$):

Moles of C = $3n$

Moles of H = $7n$

Moles of O = $2n$

Example: Find the wt. of water present in 1.61 g of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

$$\text{Sol. Moles of Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = \frac{\text{wt. in gram}}{\text{Molecular wt.}} = \frac{1.61}{322}$$

$$= 0.005 \text{ moles}$$

$$\text{Moles of water} = 10 \times \text{moles of Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$$

$$= 10 \times 0.005 = 0.05$$

$$\text{wt. of water} = 0.05 \times 18 = 0.9 \text{ gm}$$

PERCENTAGE FORMULAE COMPOSITION

% of element in compound

$$= \frac{\text{Atomic weight of element} \times \text{Number of atom} \times 100}{\text{Total molecular weight of compound}}$$

Here we are going to find out the percentage of each element in the compound by knowing the molecular formula of compound.

We know that according to law of definite proportions any sample of a pure compound always possess constant ratio with their combining elements.

Example: Every molecule of ammonia always has formula NH_3 irrespective of method of preparation or sources. i.e. 1 mole of ammonia always contains 1 mol of N and 3 mole of H. In other words 17 gm of NH_3 always contains 14 gm of N and 3 gm of H. Now find out % of each element in the compound.

Sol. Mass % of N in NH_3 =

$$\frac{\text{Mass of N in 1 mol NH}_3}{\text{Mass of 1 mol of NH}_3} \times 100 = \frac{14 \text{ gm}}{17} \times 100 = 82.35 \%$$

Mass % of H in NH_3 =

$$\frac{3 \times \text{Mass of H in 1 mol NH}_3}{\text{Mass of 1 mole of NH}_3} \times 1 = \frac{3}{17} \times 100 = 17.65 \%$$

DENSITY

- (a) Absolute density (b) Relative density

$$\text{Absolute density} = \frac{\text{Mass}}{\text{Volume}}$$

$$\text{Relative density} = \frac{\text{Density of substance}}{\text{Density of standard substance}}$$

$$\text{Specific gravity} = \frac{\text{Density of substance}}{\text{Density of H}_2\text{O at } 4^\circ\text{C}}$$

Vapour density: It is defined only for gas.

It is a density of gas with respect to H_2 gas at same temperature & pressure.

$$\text{V.D.} = \frac{d_{\text{gas}}}{d_{\text{H}_2}} = \frac{PM_{\text{gas}} / RT}{PM_{\text{H}_2} / RT} = \frac{M_{\text{gas}}}{M_{\text{H}_2}} = \frac{M}{2}$$

$$\text{V.D.} = \frac{M}{2}$$



Train Your Brain

Example 10: What is the V.D. of SO_2 with respect to CH_4 ?

$$\text{Sol. V.D.} = \frac{\text{M.W. of SO}_2}{\text{M.W. of CH}_4}$$

$$\text{V.D.} = \frac{64}{16} = 4$$

Example 11: 7.5 litre of the particular gas at S.T.P. weighs 16 gram. What is the V.D. of gas?

$$\text{Sol. Moles at S.T.P.} = \frac{7.5}{22.4} = \frac{16}{M}$$

$$M = 48 \text{ gram} \quad \text{V.D.} = \frac{48}{2} = 24.$$

Example 12: Find the density of $\text{CO}_2(\text{g})$ with respect to $\text{N}_2\text{O}(\text{g})$.

$$\text{Sol. R.D.} = \frac{\text{M.wt. of CO}_2}{\text{M.wt. of N}_2\text{O}} = \frac{44}{44} = 1$$

Example 13: Find the vapour density of N_2O_5 .

$$\text{Sol. V.D.} = \frac{\text{Mol.wt. of N}_2\text{O}_5}{2} = 54.$$



Concept Application

12. The vapour density of carbon dioxide is:

- (a) 44 (b) 32 (c) 22 (d) 12

13. The density of air is 0.001293 g/cm^3 at STP. Identify which of the following statement is correct?

- (a) Vapour density is 14.48.
 (b) Molecular weight is 28.96.
 (c) Vapour density is 0.001293 g/cm^3 .
 (d) Vapour density and molecular weight cannot be determined.

EMPIRICAL AND MOLECULAR FORMULA

We have just seen that knowing the molecular formula of the compound we can calculate percentage composition of the elements. Conversely if we know the percentage composition of the elements initially, we can calculate the relative number of atoms of each element in the molecules of the compound. This gives us the empirical formula of the compound. Further if the molecular mass is known then the molecular formula can easily be determined.

The empirical formula of a compound is a chemical formula showing the relative number of atoms in the simplest ratio. An empirical formula represents the simplest whole number ratio of various atoms present in a compound.

The molecular formula gives the actual number of atoms of each element in a molecule. The molecular formula shows the exact number of different types of atoms present in a molecule of a compound.

The molecular formula is an integral multiple of the empirical formula.

i.e. Molecular formula = Empirical formula \times n

$$\text{where } n = \frac{\text{Molecular Formula Mass}}{\text{Empirical Formula Mass}}$$



Train Your Brain

Example 14: Acetylene and benzene both have the empirical formula CH. The molecular masses of acetylene and benzene are 26 and 78 respectively. Deduce their molecular formulae.

Sol. \therefore Empirical Formula is CH

Step-1: The empirical formula of the compound is CH

$$\therefore \text{Empirical formula mass} = (1 \times 12) + 1 = 13.$$

$$\text{Molecular mass} = 26$$

Step-2: To calculate the value of 'n'

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{26}{13} = 2$$

Step-3: To calculate the molecular formula of the Compound.

Molecular formula = n \times (Empirical formula of the compound)

$$= 2 \times \text{CH} = \text{C}_2\text{H}_2$$

Thus the molecular formula is C₂H₂

Similarly for benzene

To calculate the value of 'n'

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{78}{13} = 6.$$

Thus the molecular formula is 6 \times CH = C₆H₆

Example 15: An organic substance containing carbon, hydrogen and oxygen gave the following percentage composition.

$$\text{C} = 40.684\% ; \text{H} = 5.085\% \text{ and O} = 54.228\%$$

The molecular weight of the compound is 118. Calculate the molecular formula of the compound.

Sol. Step-1: To calculate the empirical formula of the compound.

Element	Symbol	Percentage of element	At. mass of element	Relative no. of atoms =	Percentage At. mass	Simplest atomic ratio	Simplest whole no. atomic ratio
Carbon	C	40.687	12	$\frac{40.687}{12} = 3.390$	$\frac{3.390}{3.389} = 1$	3.390 3.389	2
Hydrogen	H	5.085	1	$\frac{5.085}{1} = 5.085$	$\frac{5.085}{3.389} = 1.5$	5.085 3.389	3
Oxygen	O	54.228	16	$\frac{54.228}{16} = 3.389$	$\frac{3.389}{3.389} = 1$	3.389 3.389	2

\therefore Empirical Formula is C₂H₃O₂

Step-2: To calculate the empirical formula mass.

The empirical formula mass of the compound is $12 \times 2 + 3 \times 1 + 16 \times 2 = 59$.

Step-3: To calculate the value of 'n'

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{118}{59} = 2$$

Step-4: To calculate the molecular formula of the salt.

Molecular formula = n \times (Empirical formula)

$$= 2 \times \text{C}_2\text{H}_3\text{O}_2 = \text{C}_4\text{H}_6\text{O}_4$$

Thus the molecular formula is C₄H₆O₄.

Example 16: Acetylene & butene have empirical formula CH & CH₂ respectively. The molecular masses of acetylene and butene are 26 & 56 respectively. Deduce their molecular formulae.

Sol. C₂H₂ & C₄H₈

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

$$\text{For Acetylene : } n = \frac{26}{13} = 2$$

\therefore Molecular formula = C₂H₂

$$\text{For Butene: } n = \frac{56}{14} = 4$$

\therefore Molecular formula = C₄H₈

Example 17: An oxide of nitrogen gave the following percentage composition by mass:

$$\text{N} = 25.94 \text{ and O} = 74.06$$

Calculate the empirical formula of the compound.

Sol. N₂O₅.

Element	%/Atomic mass	Simple ratio	Simple integer ratio
N	$\frac{25.94}{14} = 1.85$	1	2
O	$\frac{74.06}{16} = 4.63$	2.5	5

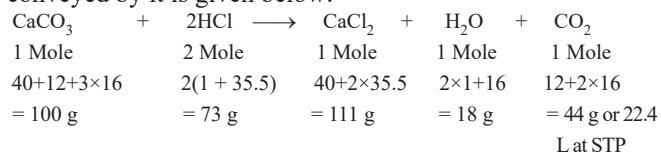
So empirical formula is N₂O₅.



Concept Application

Stoichiometry Based Concept (Problems Based on Chemical Reaction)

One of the most important aspects of a chemical equation is that when it is written in the balanced form, it gives quantitative relationships between the various reactants and products in terms of moles, masses, molecules and volumes. This is called stoichiometry (Greek word, meaning ‘to measure an element’). For example, a balanced chemical equation along with the quantitative information conveyed by it is given below:

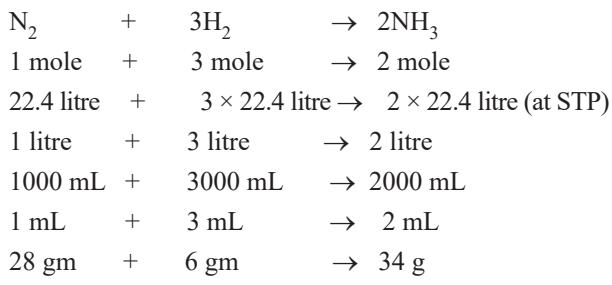


Thus,

- (i) 1 mole of calcium carbonate reacts with 2 moles of hydrochloric acid to give 1 mole of calcium chloride, 1 mole of water and 1 mole of carbon dioxide.

(ii) 100 g of calcium carbonate react with 73 g hydrochloric acid to give 111 g of calcium chloride, 18 g of water and 44 g (or 22.4 litres at STP) of carbon dioxide.

Stoichiometry:



(According to the law of conservation of mass).

Note: Gram can not be represented by stoichiometry.

The quantitative information conveyed by a chemical equation helps in a number of calculations. The problems involving these calculations may be classified into the following different types:

- (1) Mass - Mass Relationships i.e. mass of one of the reactants or products is given and the mass of some other reactant or product is to be calculated.
 - (2) Mass - Volume Relationships i.e. mass/volume of one of the reactants or products is given and the volume/mass of the other is to be calculated.
 - (3) Volume - Volume Relationships i.e. volume of one of the reactants or the products is given and the volume of the other is to be calculated.

The general method of calculations for all the problems of the above types consists of the following steps:

 - (i) Write down the balanced chemical equation.
 - (ii) Write the relative number of moles or the relative masses (gram atomic or molecular masses) of the reactants and the products below their formula.
 - (iii) In case of a gaseous substance, write down 22.4 litres at STP below the formula in place of 1 mole
 - (iv) Apply unitary method to make the required calculations.

Quite often one of the reactants is present in larger amount than the other as required according to the balanced equation. The amount of the product formed then depends upon the reactant which has reacted completely. This reactant is called the limiting reactant. The excess of the other is left unreacted.

The excess of the other is left unreacted.

Combustion reaction: For balancing the combustion reaction, first of all balance carbon atoms, then balance hydrogen atom, finally balance Oxygen atom.

For Example:

Combustion reaction of C₂H₆: C₂H₆ + O₂ → CO₂ + H₂O
 (skeleton equation)

Balance carbon atoms: $\text{C}_2\text{H}_6 + \text{O}_2 \rightarrow 2\text{CO}_2 + \text{H}_2\text{O}$

Now balance hydrogen atoms: $\text{C}_2\text{H}_6 + \text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$

Now balance oxygen atoms: $\text{C}_2\text{H}_6 + \frac{7}{2}\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$

Type (I) Involving Mass-Mass Relationship

Example: How much iron can be theoretically obtained in the reduction of 1 kg of Fe_2O_3 ?

Sol. Writing the balanced equation for the reaction.

$$n = \frac{\text{Weight}}{M_w} = \frac{1000}{160} \text{ mol}$$

The equation shows that 2 mol of iron are obtained from 1 mol of ferric oxide.

Hence, the obtained no. of moles of Fe = $\frac{2 \times 1000}{160} = 12.5$ mol

$$= \frac{\text{Weight}}{\text{Atomic weight}} = \frac{\text{Weight}}{56}$$

$$\text{Weight of iron obtained} = 12.5 \times 56 \text{ g} = 700 \text{ g}$$

Example: What amount of silver chloride is formed by the action of 5.850 g of sodium chloride on an excess of silver nitrate?

Sol. Writing the equation for the reaction



$$n = \frac{\text{Weight}}{M_w} = \frac{5.85}{58.5} = 0.1 \text{ mol}$$

1 mol of AgCl is obtained with 1 mol of NaCl.

Hence, the number of moles of AgCl obtained with 0.1 mol of NaCl = 0.1 mol

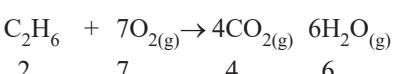
$$\therefore n = \frac{\text{Weight}}{M_w} \Rightarrow 0.1 \text{ mol} = \frac{\text{Weight}}{M_w} = \frac{\text{Weight}}{143.5}$$

$$\Rightarrow \text{weight} = 0.1 \times 143.5 \text{ g} = 14.35 \text{ g.}$$

Type (II) Mass - Volume Relationship

Example: At 100°C for complete combustion of 3g ethane the required volume of O₂ & produced volume of CO₂ at STP will be?

Sol.



$$n = \frac{\text{Weight}}{M_w} = \frac{3}{30} = \frac{1}{10} = 0.1 \text{ mole}$$

$$\therefore \text{Required moles of O}_2 = \frac{7}{2} \times 0.1 = 0.35 \text{ mol.}$$

$$\text{Volume of O}_2 \text{ at STP} = 0.35 \times 22.4 = 7.84 \text{ L.}$$

$$\text{And produced moles of CO}_2 = \frac{4}{2} \times 0.1 = 0.2 \text{ mol.}$$

$$\text{Volume of CO}_2 \text{ at STP} = 0.2 \times 22.4 = 4.48 \text{ L.}$$

Example: In the following reaction, if 10 g of H₂, react with N₂. What will be the volume of NH₃ at STP?



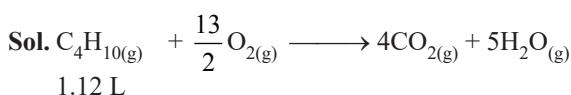
$$n = \frac{\text{Weight}}{M_w} = \frac{10}{2} = 5 \text{ mol.}$$

$$\text{Produced moles of NH}_3 = \frac{2}{3} \times 5 = \frac{10}{3}.$$

$$\text{Volume of NH}_3 \text{ at STP} = \frac{10}{3} \times 22.4 = 74.67 \text{ L}$$

Type (III) Volume-Volume Relationship

Example: At 100°C for complete combustion of 1.12 litre of butane (C₄H₁₀), the produced volume of H₂O_(g) & CO₂ at STP will be.

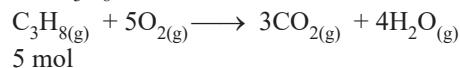


$$\text{Volume of H}_2\text{O}_{(\text{g})} \text{ at STP} = 5 \times 1.12 = 5.6 \text{ L.}$$

$$\text{Volume of CO}_{2(\text{g})} \text{ at STP} = 4 \times 1.12 = 4.48 \text{ L.}$$

Example: At 25°C for complete combustion of 5 mol propane (C₃H₈). The required volume of O₂ at STP will be?

Sol. For C₃H₈, the combustion reaction is



$$\text{Required moles of O}_2 = 5 \times 5 = 25 \text{ mol} = \frac{V}{22.4}.$$

$$\text{Volume of O}_2 \text{ gas at STP (V)} = 25 \times 22.4 = 560 \text{ L.}$$

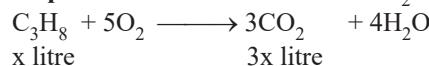
Example: 3 litre of mixture of propane (C₃H₈) & butane (C₄H₁₀) on complete combustion gives 10 litre CO₂. Find the composition of mixture.

Sol. Let the volume of propane in the mixture = x litre,

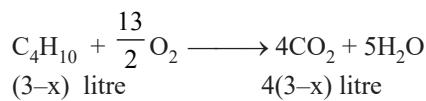
$$\therefore \text{The volume of butane in the mixture} = (3 - x) \text{ litre}$$

Now let us calculate the volume of CO₂ evolved with the help of chemical equation.

Step-I: Calculation of volume of CO₂ from x litre of propane.



Step-II: Calculation of volume of CO₂ from (3 - x) litre of butane. The combustion equation for butane is:



Step-III: Calculation of composition of the mixture.

Total volume of CO₂ formed in the step (I) and step (II) = [3x + 4(3 - x)] litre

But the volume of CO₂ actually formed = 10 litre

$$3x + 4(3 - x) = 10$$

$$\text{or } 3x + 12 - 4x = 10 \quad \text{or } x = 2 \text{ litre}$$

$$\therefore \text{Volume of propane} = x \text{ litre} = 2 \text{ litre}$$

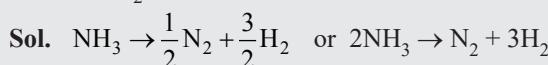
$$\therefore \text{Volume of butane} = (3 - x) \text{ litre} = (3 - 2) = 1 \text{ litre}$$



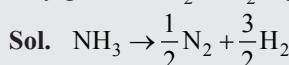
Train Your Brain

Example 18: Write a balanced chemical equation for following reaction:

When ammonia (NH₃) decompose into nitrogen (N₂) gas & hydrogen (H₂) gas.



Example 19: When 170 g NH₃ (M = 17) decomposes, how many grams of N₂ & H₂ is produced?



$$\frac{\text{moles of NH}_3}{1} = \frac{\text{moles of N}_2}{1/2} = \frac{\text{moles of H}_2}{3/2}$$

$$\text{So, moles of N}_2 = \frac{1}{2} \times \frac{170}{17} = 5$$

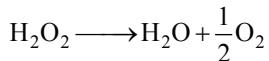
$$\text{So, wt. of N}_2 = 5 \times 28 = 140 \text{ g}$$

$$\text{Similarly moles of H}_2 = \frac{3}{2} \times \frac{170}{17} = 15$$

$$\text{So, wt. of H}_2 = 15 \times 2 = 30 \text{ g.}$$

Volume Strength of H₂O,

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 decomposition gives 20L of O_2 gas at STP. Decomposition of H_2O_2 is given as:



$$1 \text{ mole} = 34\text{g} \quad \frac{1}{2} \times 22.4\text{L O}_2 \text{ at STP} = 11.2 \text{ L O}_2 \text{ at STP}$$

$$\text{Molarity of H}_2\text{O}_2 (\text{M}) = \frac{\text{Volume strength of H}_2\text{O}_2}{11.2}$$

Strength (in g/L): Denoted by S

Strength = Molarity × Mol. wt = Molarity × 34

Quantitative Analysis

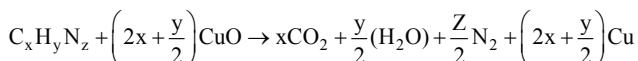
Estimation of Nitrogen

(a) Dumas method

(b) Kjeldahl's method

Dumas Method

- ❖ In this method nitrogen present in the organic compound is converted into N₂ (molecular nitrogen).
 - ❖ A weighed amount of organic compound is heated with cupric oxide in an atmosphere of carbon dioxide.
 - ❖ Carbon and hydrogen present in the compound are oxidised to CO₂ and H₂O, while N₂ is set free.
 - ❖ Some oxides of nitrogen formed are reduced to free nitrogen by passing over heated copper gauze.



- ❖ Oxides of nitrogen + Cu \rightarrow N₂ + CuO.
 - ❖ The mixture of gases produced is collected over caustic potash solution (KOH solution) which absorbs CO₂.
 - ❖ Nitrogen is collected in the upper part of nitro meter.

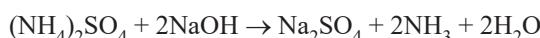
$$\% \text{N} = \frac{28}{22400} \times \frac{\text{Volume of nitrogen in ml at STP}}{\text{Weight of organic compound}} \times 100$$

Kjeldahl's Method

- In this method nitrogen present in the organic compound is converted into ammonia. (NH_3)
 - A known mass of organic compound containing nitrogen is heated with concentrated sulphuric acid in presence of K_2SO_4 and CuSO_4 then nitrogen present in the compound is converted into ammonium sulphate.
 - $\text{Organic compound} + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4$



- The resulting solution is distilled with excess of sodium hydroxide.



- Ammonia evolved is absorbed in a known but excess volume of standard HCl or H_2SO_4 solution. The acid left unreacted is estimated by titration against standard solution of sodium hydroxide.

%Nitrogen

$$= \frac{14}{1000} \times \frac{V \times N}{\text{wt. of organic compound}} \times 100$$

$$\%N = \frac{1.4 \times V \times N}{\text{Wt. of organic compound}}$$

Where V = Volume of acid in ml neutralised by ammonia
N = Normality of acid.

- This method is simpler and more convenient.
- It is mainly used to find percentage of nitrogen present in food stuffs, soils, fertilizers and various agricultural products.
- This method is not applicable to compounds containing nitro ($-NO_2$), Nitroso (NO), azo group ($-N=N-$), azoxy compounds ($-N=\overset{O}{N}-$) and nitrogen present in the ring (pyridin



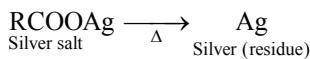
quinoline). Because nitrogen present in these compounds is not quantitatively converted into ammonium sulphate.

- K_2SO_4 increases boiling point of H_2SO_4 and $CuSO_4$ acts as catalyst.

Chemical Methods Used to Find Molecular Mass

Silver Salt Method for Acids:

Organic acid form insoluble silver salts, which on heating undergoes decomposition to leave a residue of metallic silver.



$$\frac{\text{Equivalent wt. of silver salt}}{\text{Equivalent wt. of silver}} = \frac{\text{Mass of silver salt}}{\text{Mass of silver}}$$

$$\frac{E+108-1}{108} = \frac{\text{Mass of silver salt}}{\text{Mass of silver}}$$

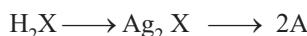
$$E = \left[\frac{\text{Mass of silver salt}}{\text{Mass of silver}} \times 108 \right] - 107$$

Molecular weight of acid = Equivalent weight of acid (E) \times basicity

Example: 0.41g of the silver salt of a dibasic organic acid left a residue to 0.216g of silver on ignition.

Calculate the molecular mass of the acid.

Sol. Mass of of the silver salt taken (W) = 0.41 g , Mass of Ag formed = 0.216g



$$w = 0.41 \text{ g} \quad x = 0.216 \text{ g}$$

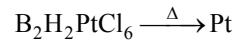
$$\text{Now molar mass acid} = n \left(\frac{108W}{x} - 107 \right) \text{gmol}^{-1}$$

$$= 2 \left(\frac{108 \times 0.41}{0.216} - 107 \right) \text{gmol}^{-1} = 196 \text{gmol}^{-1}$$

Molar mass = 196 g/mol

Platinic Chloride Method for Bases

- Organic bases combines with chloroplatinic acid (H_2PtCl_6) to insoluble platinichloride, which on ignition gives metallic platinum.
- If 'B' is mono acidic base then formula of salt will be $B_2H_2PtCl_6$.



$$\frac{\text{Molecular mass of platinum salt}}{\text{Atomic mass of platinum}} = \frac{\text{Mass of platinum salt}}{\text{Mass of platinum}}$$

If E in equivalent weight of base then:

$$\frac{2E+410}{195} = \frac{\text{Mass of platinum salt}}{\text{Mass of platinum}}$$

$$E = \frac{1}{2} \left[\frac{\text{Mass of platinum salt}}{\text{Mass of platinum}} \times 195 - 410 \right]$$

Molecular mass of base = Equivalent mass of base \times acidity

Example: 0.30 gm chloroplatinate salt of a diacidic organic base exactly produce 0.09 gm platinum, on strong ignition. The molecular mass of organic base is (Pt = 195):

Sol. Molar mass of base is

$$= \frac{n}{2} \left(\frac{w \times 195}{x} - 410 \right)$$

$$= \frac{2}{2} \left(\frac{0.3 \times 195}{0.09} - 410 \right) = 240 \text{ gm / mol}$$

Determination of Molecular Mass by Victor Meyer's Method

- A known mass of the volatile substance is vapourised in victor meyer's method.
- The vapours obtained displaces an equal volume of air into graduated tube.

The resonance of these indicators responsible for the colour change.

Most common example of indicator are listed below:

Indicator	Notation	pH range	Colour change
Phenolphthalein	HPh	8.2-10	Colourless to pink
Methyl orange	MeOH	4-6	Orange to yellow
Alizarin Yellow	DHQ	10-12	Yellow to red



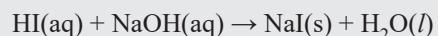
Train Your Brain

Example 39: What will be the pH of the equivalence point of the reaction when 60mL of 0.25M HI is titrated with 0.5M KOH solution?

Sol. Both HI and KOH are strong acid and strong base respectively. Thus strong acid and strong base neutralize completely at equivalence point and solution becomes neutral, the pH must be 7.

Example 40: It takes 90mL of a 0.5M NaOH solution to neutralize 220mL of an HI solution. What will be the concentration of the HI solution?

Sol. The valance chemical reaction between HI and NaOH is as follow:



Molarity equation:

$$M_A V_A (n_f)_A = M_B V_B (n_f)_B.$$

M_A and V_A are the molarity and volume of an acid.

M_B and V_B are the molarity and volume of base.

$$\text{Hence, } M_A = \frac{M_B V_B (n_f)_B}{V_A (n_f)_A} = \frac{0.5M \times 90\text{mL} \times 1}{220\text{mL} \times 1} = 0.20M$$

The concentration of the HI solution is 0.20M.



Concept Application

Short Notes

Some Useful Conversion Factors

$$1 \text{ \AA} = 10^{-10} \text{ m}, 1 \text{ nm} = 10^{-9} \text{ m}$$

$$1 \text{ pm} = 10^{-12} \text{ m}$$

$$1 \text{ litre} = 10^{-3} \text{ m}^3 = 1 \text{ dm}^3$$

$$1 \text{ atm} = 760 \text{ mm or torr}$$

$$= 101325 \text{ Pa or } \text{Nm}^{-2}$$

$$1 \text{ bar} = 10^5 \text{ Nm}^{-2} = 10^5 \text{ Pa}$$

$$1 \text{ calorie} = 4.184 \text{ J}$$

$$1 \text{ electron volt(eV)} = 1.6022 \times 10^{-19} \text{ J}$$

$$(1 \text{ J} = 10^7 \text{ ergs})$$

$$(1 \text{ cal} > 1 \text{ J} > 1 \text{ erg} > 1 \text{ eV})$$

Atomic Mass or Molecular Mass

Mass of one atom or molecule in a.m.u.

$$\text{C} \rightarrow 12 \text{ amu}$$

$$\text{NH}_3 \rightarrow 17 \text{ amu}$$

Actual Mass

Mass of one atom or molecule in grams:

$$\text{C} \rightarrow 12 \times 1.6 \times 10^{-24} \text{ g}$$

$$\text{CH}_4 \rightarrow 16 \times 1.6 \times 10^{-24} \text{ g}$$

Relative Atomic Mass or Relative Molecular Mass

Mass of one atom or molecule w.r.t. $1/12^{\text{th}}$ of ^{12}C atom:

$$\text{C} \rightarrow 12$$

$$\text{CH}_4 \rightarrow 16$$

It is unitless.

Gram Atomic Mass or Gram Molecular Mass

Mass of one mole of atom or molecule:

$$\text{C} \rightarrow 12 \text{ g}$$

$$\text{CO}_2 \rightarrow 44 \text{ g}$$

It is also called molar mass.

Definition of Mole

One mole is a collection of that many entities as there are number of atoms exactly in 12 gm of C-12 isotope.

The number of atoms present in exactly 12 gm of C-12 isotope is called Avogadro's number [$N_A = 6.022 \times 10^{23}$]

$$\begin{aligned} 1\text{u} &= 1\text{amu} = (1/12)^{\text{th}} \text{ of mass of 1 atom of } \text{C}^{12} = \frac{1\text{g}}{N_A} \\ &= 1.66 \times 10^{-24} \text{ g} \end{aligned}$$

For Elements

$$\diamond 1 \text{ g atom} = 1 \text{ mole of atoms} = N_A \text{ atoms}$$

$$\diamond \text{g atomic mass (GAM)} = \text{mass of } N_A \text{ atoms in g}$$

$$\diamond \text{Mole of atoms} = \frac{\text{Mass (g)}}{\text{GAM or Molar mass}}$$

For Molecule

$$\diamond 1 \text{ g molecule} = 1 \text{ mole of molecule} = N_A \text{ molecule}$$

$$\diamond \text{g molecular mass (GMM)} = \text{mass of } N_A \text{ molecule in g.}$$

$$\diamond \text{Mole of molecule} = \frac{\text{Mass (g)}}{\text{GMM or Molar mass}}$$

1 Mole of Substance

$$\diamond \text{Contains } 6.022 \times 10^{23} \text{ particles.}$$

\diamond Weighs as much as molecular mass/ atomic mass/ionic mass in grams.

\diamond If it is a gas, one mole occupies a volume of 22.4 L at 1 atm & 273 K or 22.7 L at STP.

For Ionic Compounds

$$\diamond 1 \text{ g formula unit} = 1 \text{ mole of formula unit} = N_A \text{ formula unit.}$$

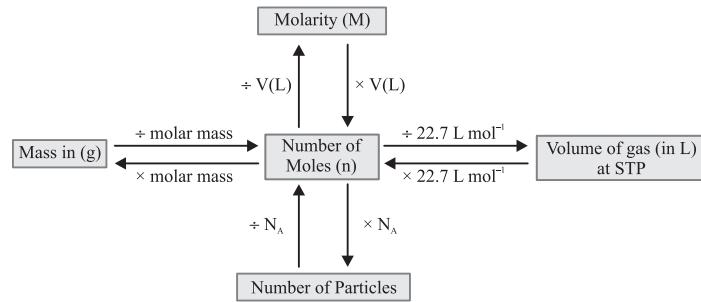
$$\diamond \text{g formula mass (GFM)} = \text{mass of } N_A \text{ formula unit in g.}$$

$$\diamond \text{Mole of formula unit} = \frac{\text{Mass (g)}}{\text{GMM or Molar mass}}$$

Vapour density

Ratio of density of vapour to the density of hydrogen at similar pressure and temperature.

$$\text{Vapour density} = \frac{\text{Molar mass}}{2}$$



Stoichiometry Based Concept



- ❖ a,b,c,d, represents the ratios of moles, volumes [for gaseous] molecules in which the reactants react or products formed.
- ❖ a,b,c,d does not represent the ratio of masses.
- ❖ The stoichiometric amount of components may be related as:

$$\frac{\text{Moles of A reacted}}{a} = \frac{\text{Moles of B reacted}}{b} = \frac{\text{Moles of C reacted}}{c} = \frac{\text{Moles of D reacted}}{d}$$

Concept of Limiting Reagent

If data of more than one reactant is given then first convert all the data into moles then divide the moles of reactants with their respective stoichiometric coefficient. The reactant having minimum ratio will be L.R. then find the moles of product formed or excess reagent left by comparing it with L.R. through stoichiometric concept.

Percentage Purity

The percentage of a specified compound or element in an impure sample may be given as:

$$\% \text{ purity} = \frac{\text{Actual mass of compound}}{\text{Total mass of sample}} \times 100$$

If impurity is unknown, it is always considered as inert (unreactive) material.

Empirical and Molecular Formula

- ❖ **Empirical formula:** Formula depicting constituent atoms in their simplest ratio.
 - ❖ **Molecular formula:** Formula depicting actual number of atoms in one molecule of the compound.
 - ❖ The molecular formula is generally an integral multiple of the empirical formula.
- i.e. molecular formula = empirical formula $\times n$
- where $n = \frac{\text{molecular formula mass}}{\text{empirical formula mass}}$

Concentration Terms

Concentration Type	Mathematical Formula	Concept
Percentage by mass	$\% \left(\frac{w}{W} \right) = \frac{\text{Mass of solute} \times 100}{\text{Mass of solution}}$	Mass of solute (in gm) present in 100 gm of solution.
Volume percentage	$\% \left(\frac{v}{V} \right) = \frac{\text{Volume of solute} \times 100}{\text{Volume of solution}}$	Volume of solute (in cm ³) present in 100 cm ³ of solution.
Mass-volume percentage	$\% \left(\frac{w}{v} \right) = \frac{\text{Mass of solute} \times 100}{\text{Volume of solution}}$	Mass of solute (in gm) present in 100 cm ³ of solution.
Parts per million	$\text{ppm} = \frac{\text{Mass of solute} \times 10^6}{\text{Mass of solution}}$	Parts by mass of solute per million parts by mass of the solution.
Mole fraction	$X_A = \frac{\text{Mole of A}}{\text{Mole of A} + \text{Mole of B} + \text{Mole of C} + \dots}$ $X_B = \frac{\text{Mole of B}}{\text{Mole of A} + \text{Mole of B} + \text{Mole of C} + \dots}$	Ratio of number of moles of one component to the total number of moles.
Molarity	$M = \frac{\text{Mole of solute}}{\text{Volume of solution (in L)}}$	Moles of solute in one liter of solution.
Molality	$m = \frac{\text{Mole of solute}}{\text{Mass of solvent (Kg)}}$	Moles of solute in one kg of solvent.

Mixing of Solutions

It is based on law of conservation of moles.

(i) Two solutions having same solute:

$$\text{Final molarity} = \frac{\text{Total moles}}{\text{Total volume}} = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$$

$$\text{(ii) Dilution Effect: Final molarity, } M_2 = \frac{M_1 V_1}{V_1 + V_2}$$



Solved Examples

1. Find the relative atomic mass, atomic mass of the following elements.

- (i) Na (ii) F (iii) H (iv) Ca (v) Ag

Sol. (i) 23, 23 amu (ii) 19, 19 amu

(iii) 1, 1.008 amu, (iv) 40, 40 amu,

(v) 108, 108 amu.

2. A sample of (C_2H_6) ethane has the same mass as 10^7 molecules of methane. How many C_2H_6 molecules does the sample contain?

$$\text{Sol. Moles of } CH_4 = \frac{10^7}{N_A}$$

$$\text{Mass of } CH_4 = \frac{10^7}{N_A} \times 16 = \text{mass of } C_2H_6$$

$$\text{So Moles of } C_2H_6 = \frac{10^7 \times 16}{N_A \times 30}$$

$$\text{So no. of molecules of } C_2H_6 = \frac{10^7 \times 16}{N_A \times 30} \times N_A = 5.34 \times 10^6.$$

3. From 160 g of SO_2 (g) sample, 1.2046×10^{24} molecules of SO_2 are removed then find out the volume of left over SO_2 (g) at NTP.

$$\text{Sol. Given moles} = \frac{160}{64} = 2.5.$$

$$\text{Removed moles} = \frac{1.2046 \times 10^{24}}{6.023 \times 10^{23}} = 2.$$

So left moles = 0.5.

Volume left at STP = $0.5 \times 22.4 = 11.2$ L.

4. 14 g of Nitrogen gas and 22 g of CO_2 gas are mixed together. Find the volume of gaseous mixture at NTP.

$$\text{Sol. Moles of } N_2 = \frac{14}{28} = 0.5.$$

$$\text{Moles of } CO_2 = \frac{22}{44} = 0.5.$$

So total moles = $0.5 + 0.5 = 1$.

So vol. at STP = $1 \times 22.4 = 22.4$ L.

5. Show that in the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, mass is conserved.



moles before reaction	1	3	0
-----------------------	---	---	---

moles after reaction	0	0	2
----------------------	---	---	---

Mass before reaction = mass of 1 mole $N_2(g)$ + mass of 3 mole $H_2(g)$

$$= 14 \times 2 + 3 \times 2 = 34 \text{ g}$$

Mass after reaction = mass of 2 mole NH_3

$$= 2 \times 17 = 34 \text{ g.}$$

6. Calculate the mass in gm of $2N_A$ molecules of CO_2 :

- (a) 22 gm (b) 44 gm
 (c) 88 gm (d) None of these

Sol. (c)

$\because N_A$ molecules of CO_2 has molecular mass = 44.

$\therefore 2N_A$ molecules of CO_2 has molecular mass = $44 \times 2 = 88$ gm.

7. How many carbon atoms are present in 0.35 mol of $C_6H_{12}O_6$?

- (a) 6.023×10^{23} carbon atoms.
 (b) 1.26×10^{23} carbon atoms.
 (c) 1.26×10^{24} carbon atoms.
 (d) 6.023×10^{24} carbon atoms.

Sol. (c)

$\because 1 \text{ mol of } C_6H_{12}O_6 \text{ has } 6 N_A \text{ atoms of C}$

$\therefore 0.35 \text{ mol of } C_6H_{12}O_6 \text{ has } 6 \times 0.35 N_A \text{ atoms of C}$
 $= 2.1 N_A \text{ atoms} = 2.1 \times 6.023 \times 10^{23} = 1.26 \times 10^{24}$ carbon atoms.

8. How many molecules are in 5.23 gm of glucose ($C_6H_{12}O_6$)?

- (a) 1.65×10^{22} (b) 1.75×10^{22}
 (c) 1.75×10^{21} (d) None of these

Sol. (b)

$\because 180 \text{ gm glucose has } = N_A \text{ molecules}$

$$\therefore 5.23 \text{ gm glucose has} = \frac{5.23 \times 6.023 \times 10^{23}}{180}$$

$$= 1.75 \times 10^{22} \text{ molecules}$$

9. What is the weight of 3.01×10^{23} molecules of ammonia?

- (a) 17 gm (b) 8.5 gm
 (c) 34 gm (d) None of these

Sol. (b)

$\because 6.023 \times 10^{23}$ molecules of NH_3 has weight = 17 gm

$\therefore 3.01 \times 10^{23}$ molecules of NH_3 has weight

$$= \frac{17 \times 3.01 \times 10^{23}}{6.023 \times 10^{23}} = 8.50 \text{ gm}$$

10. How many molecules are present in one ml of water vapours at NTP?

- (a) 1.69×10^{19} (b) 2.69×10^{-19}
 (c) 1.69×10^{-19} (d) 2.69×10^{19}

Sol. (d)

$\because 22.4 \text{ litre water vapour at NTP has } 6.023 \times 10^{23} \text{ molecules.}$

$\therefore 1 \times 10^{-3} \text{ litre water vapours at NTP has}$

$$\frac{6.023 \times 10^{23}}{22.4} \times 10^{-3} = 2.69 \times 10^{19}$$

11. How many years it would take to spend Avogadro's number of rupees at the rate of 1 million rupees in one second?

(a) 19.098×10^{19} years

(b) 19.098 years

(c) 19.098×10^9 years

(d) None of these

Sol. (c)

$\because 10^6$ rupees are spent in 1 sec.

$\therefore 6.023 \times 10^{23}$ rupees are spent in

$$\frac{1 \times 6.023 \times 10^{23}}{10^6} \text{ sec}$$

$$\text{or } \frac{1 \times 6.023 \times 10^{23}}{10^6 \times 60 \times 60 \times 24 \times 365} \text{ years} = 19.098 \times 10^9 \text{ year}$$

12. An atom of an element weighs 6.644×10^{-23} g. Calculate g atoms of element in 40 kg:

(a) 10 gm atom (b) 100 gm atom

(c) 1000 gm atom (d) 10^4 gm atom

Sol. (c)

$$\begin{aligned} \because \text{Weight of 1 atom of element} \\ &= 6.644 \times 10^{-23} \text{ gm} \end{aligned}$$

$$\therefore \text{Weight of 'N' atoms of element}$$

$$= 6.644 \times 10^{-23} \times 6.023 \times 10^{23} = 40 \text{ gm}$$

$\therefore 40 \text{ gm of element has } 1 \text{ gm atom.}$

$$\therefore 40 \times 10^3 \text{ gm of element has } \frac{40 \times 10^3}{40} \text{ or} \\ = 10^3 \text{ gm atom.}$$

13. The density of O_2 at NTP is 1.429 g / litre. Calculate the standard molar volume of gas:

(a) 22.4 lit. (b) 11.2 lit

(c) 33.6 lit (d) 5.6 lit.

Sol. (a)

$\because 1.429 \text{ gm of } O_2 \text{ gas occupies volume} = 1 \text{ litre.}$

$$\therefore 32 \text{ gm of } O_2 \text{ gas occupies} = \frac{32}{1.429}, \\ = 22.4 \text{ litre/mol.}$$

14. Which of the following will weigh maximum amount?

(a) 40 g iron

(b) 1.2 g atom of N

(c) 1×10^{23} atoms of carbon

(d) 1.12 litre of O_2 at NTP

Sol. (a)

(a) Mass of iron = 40 g

(b) Mass of 1.2 g atom of N = $14 \times 1.2 = 16.8$ gm

$$(c) \text{Mass of } 1 \times 10^{23} \text{ atoms of C} = \frac{12 \times 1 \times 10^{23}}{6.023 \times 10^{23}} = 1.99 \text{ gm.}$$

$$(d) \text{Mass of 1.12 litre of } O_2 \text{ at NTP} = \frac{32 \times 1.2}{22.4} = 1.6 \text{ g}$$

15. Calculate the weight of lime (CaO) obtained by heating 200 kg of 95% pure lime stone (CaCO₃).

(a) 104.4 kg

(b) 105.4 kg

(c) 212.8 kg

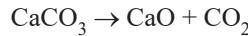
(d) 106.4 kg

Sol. (d)

$$\begin{aligned} \because 100 \text{ kg impure sample has pure} \\ \text{CaCO}_3 = 95 \text{ kg} \end{aligned}$$

$\therefore 200 \text{ kg impure sample has pure CaCO}_3$

$$= \frac{95 \times 200}{100} = 190 \text{ kg.}$$



$$\therefore 100 \text{ kg CaCO}_3 \text{ gives CaO} = 56 \text{ kg.}$$

$$\therefore 190 \text{ kg CaCO}_3 \text{ gives CaO} = \frac{56 \times 190}{100} = 106.4 \text{ kg.}$$

16. Calculate the weight of one atom of Ag. (At. wt. of Ag = 108)

(a) 17.93×10^{-23} gm (b) 16.93×10^{-23} gm

(c) 17.93×10^{23} gm (d) 36×10^{-23} gm

Sol. (a)

$\because N_A$ atoms of Ag weighs 108 gm

$$\begin{aligned} \therefore 1 \text{ atom of Ag weighs} &= \frac{108}{N_A} \\ &= \frac{108}{6.023 \times 10^{23}} = 17.93 \times 10^{-23} \text{ gm} \end{aligned}$$

17. In 5g atom of Ag (at. wt. = 108), calculate the no. of atoms of Ag ($N = N_A$).

(a) 1 N (b) 3N

(c) 5 N (d) 7 N

Sol. (c)

$\because 1 \text{ gm atom of Ag has atoms} = N$

$\therefore 5 \text{ gm atom of Ag has atoms} = 5N.$

18. Calculate the number of atoms of each element present in 122.5 g of KClO₃.

$$\text{Sol. No. of moles of KClO}_3 = \frac{122.5}{122.5} = 1.$$

(mol. wt. of KClO₃ = 122.5)

From the formula KClO₃, we know that 1 mole of KClO₃ contains 1 mole of K atoms, 1 mole of Cl atoms and 3 moles of O atoms.

$$\left. \begin{aligned} \therefore \text{No. of atoms of K} &= 1 \times 6.022 \times 10^{23} \\ \text{No. of atoms of Cl} &= 1 \times 6.022 \times 10^{23} \\ \text{No. of atoms of O} &= 3 \times 6.022 \times 10^{23} \end{aligned} \right\}$$

19. The vapour density of a mixture consisting of NO₂ and N₂O₄ is 38.3 at 26.7°C. Calculate the number of moles of NO₂ in 100 g of the mixture.

Sol. Wt. of NO₂ = x g.

$$\text{Obs. mol. wt. (wt./mole)} = \frac{\text{wt. in g}}{\text{Total moles}}$$

$$\left[\frac{100}{\left(\frac{x}{46} + \frac{100-x}{92} \right)} = 2 \times 38.3. \right] (0.437 \text{ mole})$$

20. Calculate the following for 49 gm of H_2SO_4 :

- (a) Moles (b) Molecules
(c) Total H atoms (d) Total O atoms
(e) Total electrons

Sol. Molecular wt. of H_2SO_4 = 98

$$(a) \text{Moles} = \frac{\text{wt. in gm}}{\text{molecular wt.}} = \frac{49}{98} = \frac{1}{2} \text{ mole}$$

(b) Since 1 mole = 6.023×10^{23} molecules.

$$\frac{1}{2} \text{ mole} = 6.023 \times 10^{23} \times \frac{1}{2} \text{ molecules} = 3.011 \times 10^{23} \text{ molecules.}$$

(c) 1 molecule of H_2SO_4 Contains 2 H atom, so

$$3.011 \times 10^{23} \text{ of } \text{H}_2\text{SO}_4 \text{ contain } 2 \times 3.011 \times 10^{23} \text{ atoms} = 6.022 \times 10^{23} \text{ atoms}$$

(d) 1 molecules of H_2SO_4 contains 4 Oxygen atoms.

$$\therefore 3.011 \times 10^{23} \text{ molecular of } \text{H}_2\text{SO}_4 \text{ contains} = 4 \times 3.011 \times 10^{23} = 12.044 \times 10^{23}$$

(e) 1 molecule of H_2SO_4 contains 2H atoms + 1 S atom + 4 O atom this means 1 molecule of H_2SO_4 Contains $(2 + 16 + 4 \times 8) e^-$

$$\text{So } 3.011 \times 10^{23} \text{ molecules have } 3.011 \times 10^{23} \times 50 \text{ electrons} = 1.5055 \times 10^{25} e^-$$

21. Calculate the total ions & charge present in 4.2 gm of N^-_3 .

$$\text{Sol. Mole} = \frac{\text{wt.in gm}}{\text{Ionic wt.}} = \frac{4.2}{14} = 0.3$$

$$\text{Total no. of ions} = 0.3 \times N_A \text{ ions.}$$

$$\text{Total charge} = 0.3 N_A \times 3 \times 1.6 \times 10^{-19} \\ = 0.3 \times 6.023 \times 10^{23} \times 3 \times 1.6 \times 10^{-19} = 8.67 \times 10^4 C$$

22. Find the total number of iron atom present in 224 amu iron.

Sol. Since 56 amu = 1 atom

$$\therefore 224 \text{ amu} = \frac{1}{56} \times 224 = 4 \text{ atom.}$$



Exercise-1 (Topicwise)

CALCULATION OF MOLE NO. OF ENTITY, LAW OF CHEMICAL COMBINATION, MOLAR VOLUME OF IDEAL GASES AT STP, AVERAGE MOLAR MASS

- A sample of pure carbon dioxide, irrespective of its source contains 27.27% carbon and 72.73% oxygen. The data support:
 (a) Law of constant composition.
 (b) Law of conservation of mass.
 (c) Law of reciprocal proportions.
 (d) Law of multiple proportions.
- The law of definite proportions is not applicable to nitrogen oxide because:
 (a) Nitrogen atomic weight is not constant.
 (b) Nitrogen molecular weight is variable.
 (c) Nitrogen equivalent weight is variable.
 (d) Oxygen atomic weight is variable.
- 1 amu is equal to:
 (a) $\frac{1}{12}$ of C-12 (b) $\frac{1}{14}$ of O-16
 (c) 1 g of H₂ (d) 1.66×10^{-23} kg
- In chemical scale, the relative mass of the isotopic mixture of oxygen atoms (O¹⁶, O¹⁷, O¹⁸) is assumed to be equal to:
 (a) 16.002 (b) 16.00
 (c) 17.00 (d) 11.00
- 1 mol of CH₄ contains:
 (a) 6.02×10^{23} atoms of H
 (b) 4 g-atom of Hydrogen
 (c) 1.81×10^{23} molecules of CH₄
 (d) 3.0 g of carbon
- 7.5 grams of a gas occupy 5.8 litres of volume at STP, the gas is:
 (a) NO (b) N₂O
 (c) CO (d) CO₂
- The number of atoms in 4.25 g of NH₃ is approximately:
 (a) 1×10^{23} (b) 2×10^{23}
 (c) 4×10^{23} (d) 6×10^{23}
- One litre of a gas at STP weights 1.16 g. The possible gas is:
 (a) C₂H₂ (b) CO
 (c) O₂ (d) CH₄
- The mass of a molecule of water is:
 (a) 3×10^{-26} kg (b) 3×10^{-25} kg
 (c) 1.5×10^{-26} kg (d) 2.5×10^{-26} kg

- If N_A is Avogadro's number, then number of valence electrons in 4.2 g of nitride ions (N³⁻) is:
 (a) 2.4 N_A (b) 4.2 N_A
 (c) 1.6 N_A (d) 3.2 N_A
- The number of molecules at NTP in 1 ml of an ideal gas will be:
 (a) 6×10^{23} (b) 2.69×10^{19}
 (c) 2.69×10^{23} (d) None of these
- Volume of a gas at STP is 1.12×10^{-7} cc. The number of molecules in it are:
 (a) 3.01×10^{20} (b) 3.01×10^{12}
 (c) 3.01×10^{23} (d) 3.01×10^{24}
- 4.4 g of an unknown gas occupies 2.24 L of volume at standard temperature and pressure. The gas may be:
 (a) Carbon dioxide (b) Carbon monoxide
 (c) Oxygen (d) Sulphur dioxide
- The number of oxygen atoms in 4.4 g of CO₂ is approx.:
 (a) 1.2×10^{23} (b) 6×10^{22}
 (c) 6×10^{23} (d) 12×10^{23}
- The total number of protons in 10 g of calcium carbonate is: (N_A = 6.023×10^{23})
 (a) 1.5057×10^{24} (b) 2.0478×10^{24}
 (c) 3.0115×10^{24} (d) 4.0956×10^{24}
- Number of molecules in 100 ml each of O₂, NH₃ and CO₂ at STP are:
 (a) In the order: CO₂ < O₂ < NH₃
 (b) In the order: NH₃ < O₂ < CO₂
 (c) The same in all
 (d) In the order: NH₃ < CO₂ < O₂
- The number of water molecules in 1 litre of water is:
 (a) 18 (b) 18×1000
 (c) N_A (d) $55.55 N_A$
- 2 g of oxygen contains number of atoms equal to that in:
 (a) 0.5 g of hydrogen (b) 4 g of sulphur
 (c) 7 g of nitrogen (d) 2.3 g of sodium

EMPIRICAL FORMULA, % COMPOSITION OF A GIVEN COMPOUND BY MASS, % BY MOLE, MINIMUM MOLECULAR MASS DETERMINATION.

- Caffeine has a molecular weight of 194. If it contains 28.9% by mass of nitrogen, number of atoms of nitrogen in one molecule of caffeine is:
 (a) 4 (b) 6
 (c) 2 (d) 3

STOICHIOMETRY, EQUATION BASED CALCULATIONS

30. 12 g of Mg (at. mass 24) will react completely with acid to give:

 - One mole of H_2
 - 1/2 mole of H_2
 - 2/3 mole of O_2
 - Both 1/2 mol of H_2 and 1/2 mol of O_2

31. 100 g $CaCO_3$ reacts with 1 litre 1 N HCl. On completion of reaction, how much weight of CO_2 will be obtained?

 - 5.5 g
 - 11 g
 - 22 g
 - 33 g

32. What weight of HNO_3 is needed to convert 5 g of iodine into iodic acid according to the reaction,

$$I_2 + HNO_3 \rightarrow HIO_3 + NO_2 + H_2O$$
 - 12.4 g
 - 24.8 g
 - 0.248 g
 - 49.6 g

33. How much Cl_2 at STP is liberated when 1 mole $KMnO_4$ reacts with HCl?

 - 11.2 L
 - 22.4 L
 - 44.8 L
 - 56 L

34. NX is produced by the following step of reactions:

$$M + X_2 \rightarrow MX_2, 3MX_2 + X_2 \rightarrow M_3X_8, M_3X_8 + N_2CO_3 \rightarrow NX + CO_2 + M_3O_4$$

How much M (metal) is consumed to produce 206 g of NX.
(Take at wt. of M = 56, N = 23, X = 80)

 - 42 g
 - 56 g
 - $\frac{14}{3}$
 - $\frac{7}{4}$

35. 27 g of Al will react completely with how many grams of oxygen?

 - 8 g
 - 16 g
 - 32 g
 - 24 g

36. If 0.50 mole of $BaCl_2$ is mixed with 0.20 mol of Na_3PO_4 , the maximum number of moles of $Ba_3(PO_4)_2$ that can be formed is:

 - 0.70
 - 0.50
 - 0.20
 - 0.10

37. How many moles of potassium chlorate need to be heated to produce 11.2 litre oxygen at N.T.P.:

 - $\frac{1}{2}$ mol
 - $\frac{1}{3}$ mol
 - $\frac{1}{4}$ mol
 - $\frac{2}{3}$ mol

38. 0.5 mole of H_2SO_4 is mixed with 0.2 mole of $Ca(OH)_2$. The maximum number of moles of $CaSO_4$ formed is:

 - 0.2
 - 0.5

CONCENTRATION TERM



Exercise-2 (Learning Plus)

46. Equal weight of 'X' (At. wt. = 36) and 'Y' (At. wt. = 24) are reacted to form the compound X_2Y_3 . Then

 - X is the limiting reagent
 - Y is the limiting reagent
 - No reactant is left over and mass of X_2Y_3 formed is double the mass of 'X' taken
 - None of these

47. A person adds 1.71 gram of sugar ($C_{12}H_{22}O_{11}$) in order to sweeten his tea. The number of carbon atoms added are (mol. mass of sugar = 342)

 - 3.6×10^{22}
 - 7.2×10^{21}
 - 0.05×10^{20}
 - 6.6×10^{22}

48. A compound contains 38.8 % C, 16.0 % H and 45.2 % N. The formula of the compound would be

 - CH_3NH_2
 - CH_3CN
 - C_2H_5CN
 - $CH_2(NH)_2$

49. When 100 g of ethylene polymerises entirely to polyethene, the weight of polyethene formed as per the equation $n(C_2H_4) \longrightarrow (-CH_2-CH_2-)_n$ is:

 - $(n/2)g$
 - 100g
 - $(100/n)g$
 - $100ng$

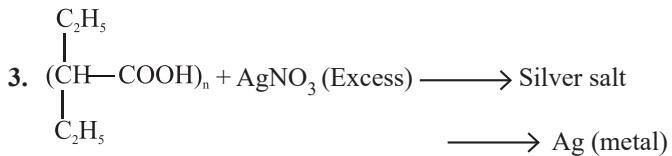
50. What is the molarity of H_2SO_4 solution that has a density of 1.84 g/cc and contains 98% by mass of H_2SO_4 ? (Given atomic mass of S = 32)

 - 4.18 M
 - 8.14 M
 - 18.4 M
 - 18 M

Exercise-3 (JEE Advanced Level)

MULTIPLE CORRECT TYPE QUESTIONS

1. Which is/are correct statements about 1.7 g of NH_3 ?
 - (a) It contain 0.3 mol H – atoms.
 - (b) It contain 2.408×10^{23} atoms.
 - (c) Mass % of hydrogen is 17.65%.
 - (d) It contains 0.3 mol N-atoms.
 2. If 27 g of carbon is mixed with 88 g of oxygen and is allowed to burn to produce CO_2 , then:
 - (a) Oxygen is the limiting reagent.
 - (b) Volume of CO_2 gas produced at NTP is 50.4 L.
 - (c) C and O combine in mass ratio of 3.8.
 - (d) Volume of unreacted O_2 at STP is 11.2 L.



If 0.5 mole of silver salt is taken and weight of residue obtained is 216 g. ($\text{Ag} = 108 \text{ g/mol}$), then which of the following is correct?

- (a) n = 4
 - (b) n = 2
 - (c) M.wt. of silver salt is 718 g/mol
 - (d) M.wt. of silver salt is 388 g/mol

4. For the following reaction;

$$\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$$

Identify the compositions which will produce same amount of NH_3 .

 - (a) 140 g N_2 & 35 g H_2
 - (b) 18 g H_2 & 52 g N_2
 - (c) Total 20 moles of mixture having N_2 & H_2 present in stoichiometric ratio (No limiting reagent).
 - (d) 136 gm of mixture having mass fraction of $\text{H}_2 = \frac{6}{34}$.

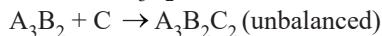
5. For the following reaction : $\text{Na}_2\text{CO}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{CO}_2 + \text{H}_2\text{O}$

106.0 g of Na_2CO_3 reacts with 109.5 g of HCl .
 Which of the following is/are correct?

 - (a) The HCl is in excess amount.
 - (b) 117.0 g of NaCl is formed.
 - (c) The volume of CO_2 produced at NTP is 22.4 L.
 - (d) None of these

6. A sample of a mixture of CaCl_2 and NaCl weighing 4.44 g was treated to precipitate all the Ca as CaCO_3 , which was then heated and quantitatively converted to 1.12 g of CaO . (At . wt. Ca = 40, Na = 23, Cl = 35.5)

 - (a) Mixture contains 50% NaCl
 - (b) Mixture contains 60% CaCl_2
 - (c) Mass of CaCl_2 is 2.22 g
 - (d) Mass of CaCl_2 is 1.11 g



Above two reactions are carried out by taking 3 moles each of A and B and one mole of C. Then, which option is/are correct?

- (a) 1 mole of $A_3B_2C_2$ is formed.
- (b) 1/2 mole of $A_3B_2C_2$ is formed.
- (c) 1/2 mole of A_3B_2 is formed.
- (d) 1/2 mole of A_3B_2 is left finally.

8. 21.2 g sample of impure Na_2CO_3 is dissolved and reacted with a solution of $CaCl_2$, the weight of precipitate of $CaCO_3$ is 10.0 g. Which of the following statements is/are correct?

- (a) The % purity of Na_2CO_3 is 50%.
- (b) The percentage purity of Na_2CO_3 is 60%.
- (c) $n_{Na_2CO_3} = n_{CaCO_3} = 0.1$ mol.
- (d) The number of moles of $NaCl$ formed is 0.1 mol.

9. A mixture of C_3H_8 and O_2 having total volume of 100 ml in an eudiometry tube is sparked & it is observed that a contraction of 45 mL is observed. What can be the composition of the reacting mixture?

- (a) 15 mL C_3H_8 & 85 mL O_2
- (b) 25 mL C_3H_8 & 75 mL O_2
- (c) 45 mL C_3H_8 & 55 mL O_2
- (d) 55 mL C_3H_8 & 45 mL O_2

10. The incorrect statement(s) regarding 2 M $MgCl_2$ aqueous solution is/are: ($d_{\text{solution}} = 1.09$ gm/ml)

- (a) Molality of Cl^- is 4.44 m.
- (b) Mole fraction of $MgCl_2$ is exactly 0.035.
- (c) The conc. of $MgCl_2$ is 19% w/v.
- (d) The conc. of $MgCl_2$ is 19×10^4 ppm.

11. Solution containing 23 g $HCOOH$ is/are:

- (a) 46 g of 70% $\left(\frac{w}{v}\right)$ $HCOOH$ ($d_{\text{solution}} = 1.40$ g/mL)
- (b) 50 g of 10 M $HCOOH$ ($d_{\text{solution}} = 1$ g/mL)
- (c) 50 g of 25% $\left(\frac{w}{v}\right)$ $HCOOH$
- (d) 46 g of 5 M $HCOOH$ ($d_{\text{solution}} = 1$ g/mL)

12. Which of the following solution contains same molar concentration?

- (a) 166 g KI per liter solution
- (b) 33.0 g $(NH_4)_2SO_4$ in 200 mL solution
- (c) 25.0 g $CuSO_4 \cdot 5H_2O$ in 100 mL solution
- (d) 27.0 mg Al^{3+} per mL solution

13. If 100 ml of 1M H_2SO_4 solution is mixed with 100 ml of 9.8%(w/w) H_2SO_4 solution ($d = 1$ g/mL), then:

- (a) Concentration of solution remains same.
- (b) Volume of solution become 200 mL.
- (c) Mass of H_2SO_4 in the solution is 98 g.
- (d) Mass of H_2SO_4 in the solution is 19.6 g.

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 14 to 16): According to the Avogadro's law, equal number of moles of gases occupy the same volume at identical condition of temperature and pressure. Even if we have a mixture of non-reacting gases, then Avogadro's law is still obeyed by assuming mixture as a new gas.

Now let us assume air to consist of 80% by volume of nitrogen (N_2) and 20% by volume of oxygen (O_2). If air is taken at STP, then its 1 mol would occupy 22.4 L. 1 mol of air would contain 0.8 mol of N_2 and 0.2 mol of O_2 , hence the mole fractions of N_2 and O_2 are given by $X_{N_2} = 0.8$ and $X_{O_2} = 0.2$.

14. Volume occupied by air at NTP containing exactly 11.2 g of nitrogen, is:

- (a) 22.4 L
- (b) 8.96 L
- (c) 11.2 L
- (d) 2.24 L

15. If air is treated as a solution of O_2 and N_2 , then % w/w of oxygen is:

- (a) $\frac{10}{9}$
- (b) $\frac{200}{9}$
- (c) $\frac{700}{9}$
- (d) $\frac{350}{9}$

16. Density of air at NTP is:

- (a) 1 g/L
- (b) $\frac{9}{7}$ g/L
- (c) $\frac{2}{7}$ g/L
- (d) Can't be determined

Comprehension (Q. 17 to 19): A chemist decided to determine the molecular formula of an unknown compound. He collects following informations:

I. Compound contain 2 : 1 'H' to 'O' atoms (number of atoms).

II. Compound has 40% C by mass.

III. Approximate molecular mass of the compound is 178 g.

IV. Compound contains C, H and O only.

17. What is the % by mass of oxygen in the compound?

- (a) 53.33%
- (b) 88.88%
- (c) 33.33%
- (d) None of these

18. What is the empirical formula of the compound?

- (a) CH_3O
- (b) CH_2O
- (c) C_2H_2O
- (d) CH_3O_2

19. Which of the following could be molecular formula of compound?

- (a) $C_6H_6O_6$
- (b) $C_6H_{12}O_6$
- (c) $C_6H_{14}O_{12}$
- (d) $C_6H_{14}O_6$

MATCH THE COLUMN TYPE QUESTIONS

20. One type of artificial diamond (commonly called YAG for yttrium aluminium garnet) can be represented by the formula $\text{Y}_3\text{Al}_5\text{O}_{12}$. [Y = 89, Al = 27]

Column-I		Column-II	
Element		Weight percentage	
A.	Y	p.	22.73%
B.	Al	q.	32.32%
C.	O	r.	44.95%

- (a) A → r; B → p; C → q
 (b) A → q; B → p; C → r
 (c) A → r; B → q; C → p
 (d) A → p; B → r; C → q

21.

Column-I		Column-II	
A.	100 mL of 0.2 M AlCl_3 solution + 400 ml of 0.1 M HCl solution	p.	Total concentration of cation(s) = 0.12 M
B.	50 mL of 0.4 M KCl + 50 ml H_2O	q.	$[\text{SO}_4^{2-}] = 0.06 \text{ M}$
C.	30 mL of 0.2 M K_2SO_4 + 70 ml H_2O	r.	$[\text{SO}_4^{2-}] = 2.5 \text{ M}$
D.	200 mL 24.5% (w/v) H_2SO_4	s.	$[\text{Cl}^-] = 0.2 \text{ M}$

- (a) A → r,s; B → s; C → p,q; D → r
 (b) A → p,s; B → s; C → p,q; D → r
 (c) A → p,s; B → s; C → s,q; D → r
 (d) A → p,s; B → p,s; C → p,q; D → r

22.

Column-I		Column-II	
A.	A gaseous organic compound containing C = 52.17%, H = 13.04% & O = 34.78% (by weight) having molar mass 46 g/mol.	p.	One mole of compound contains $4N_A$ atoms of hydrogen.
B.	0.3 g of an organic compound containing C, H and O on combustion yields 0.44 g of CO_2 and 0.18 g of H_2O , with two O	q.	The empirical formula of the compound is same as its molecular formula.

C.	A hydrocarbon containing C = 42.857% and H = 57.143% (by mole) containing 3C atoms.	r.	Combustion products of one mole of compound contains larger number of moles of CO_2 than that of H_2O .
D.	A hydrocarbon containing 10.5 g carbon per gram of hydrogen having vapour density 46.	s.	CO_2 gas produced by the combustion of 0.25 mole of compound occupies a volume of 11.2 L at NTP.

- (a) A → p,s; B → p,s; C → p,q,r; D → q,r
 (b) A → q,s; B → q,s; C → p,q,r; D → q,r
 (c) A → q,s; B → p,s; C → r,s; D → q,r
 (d) A → q,s; B → p,s; C → p,q,r; D → q,r

NUMERICAL TYPE QUESTIONS

23. Find the oxidation state of osmium (Os) in OsO_4 .
24. Find the oxidation number of nitrogen in $(\text{NH}_4)_2\text{SO}_4$.
25. Molarity of H_2SO_4 is 18 M. Its density is 1.8 g/cm³, calculate its molality.
26. Find the percentage of oxygen in NaOH.
27. Calculate the mass of NaOH that is required to neutralise 1500 cm³ of 0.1 N HCl (Atomic mass: Na = 23).
28. One mole of potassium chlorate (KClO_3) is thermally decomposed and excess of aluminium is burnt in the gaseous product. How many mol of aluminium oxide (Al_2O_3) are formed?
29. 100 g CaCO_3 reacts with 1 litre 1 N HCl. On completion of reaction, how much weight of CO_2 will be obtained?
30. 2 M of 100 ml Na_2SO_4 is mixed with 3 M of 100 ml NaCl solution and 1 M of 200 ml CaCl_2 solution. Then, the ratio of the concentration of cation and anion, is ____.
31. What is the quantity of water that should be added to 16 g. methanol to make the mole fraction of methanol as 0.25.



Exercise-4 (Past Year Questions)

JEE MAIN

1. 1 gram of a carbonate (M_2CO_3) on treatment with excess HCl produces 0.01186 mole of CO_2 , the molar mass of M_2CO_3 in g mol⁻¹ is: (2017)

(a) 1186 (b) 84.3
(c) 1186 (d) 11.86

2. The most abundant elements by mass in the body of a healthy human adult are:
Oxygen (61.4%) : Carbon (22.9%), Hydrogen (10.0%), and Nitrogen (2.6%). The weight which a 75 kg person would gain if all 1H atoms are replaced by 2H atoms, is: (2017)

(a) 15 kg (b) 37.5 kg
(c) 7.5 kg (d) 10 kg

3. The ratio of mass percent of C and H of an organic compound ($C_XH_YO_Z$) is 6 : 1. If one molecule of the above compound ($C_XH_YO_Z$) contains half as much oxygen as required to burn one molecule of compound C_XH_Y completely to CO_2 and H_2O . The empirical formula of compound $C_XH_YO_Z$ is: (2018)

(a) C_2H_4O (b) $C_3H_4O_2$
(c) $C_2H_4O_3$ (d) $C_3H_6O_3$

4. A 10 mg effervescent tablet containing sodium bicarbonate and oxalic acid releases 0.25 ml of CO_2 at $T = 298.15\text{ K}$ and $p = 1\text{ bar}$. If molar volume of CO_2 is 25.0 L under such condition, what is the percentage of sodium bicarbonate in each tablet? (2019)
[Molar mass of $NaHCO_3$ = 84 g mol⁻¹]

(a) 0.84 (b) 33.6
(c) 16.8 (d) 8.4

5. Water filled in two glasses A and B have BOD values of 10 and 20 respectively. The correct statement regarding them is: (2019)

(a) B is more polluted than A.
(b) A is suitable for drinking, whereas B is not.
(c) Both A and B are suitable for drinking.
(d) A is more polluted than B.

6. For the following reaction, the mass of water produced from 445 g of $C_{57}H_{110}O_6$ is: (2019)

$$2C_{57}H_{110}O_6(s) + 163 O_2(g) \rightarrow 114 CO_2(g) + 110 H_2O(l)$$

(a) 490 g (b) 445 g
(c) 495 g (d) 4 g

7. 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: (2019)

(c) 20 g (d) 80 g

8. A solution of sodium sulphate contains 92 g of Na^+ ions per kilogram of water. The molality of Na^+ ions in that solution in mol kg⁻¹ is: (2019)

(a) 12 (b) 4
(c) 8 (d) 16

9. The hardness of water sample (in terms of equivalents of $CaCO_3$) containing 10^{-3} M $CaSO_4$ is: (molar mass of $CaSO_4$ = 136 g mol⁻¹) (2019)

(a) 10 ppm (b) 50 ppm
(c) 90 ppm (d) 100 ppm

10. The amount of sugar ($C_{12}H_{22}O_{11}$) required to prepare 2 L of its 0.1 M aqueous solution is: (2019)

(a) 136.8 g (b) 17.1 g
(c) 68.4g (d) 34.2 g

11. 8 g of NaOH is dissolved in 18 g of H_2O . Mole fraction of NaOH in solution and molality (in mol kg⁻¹) of the solution respectively, are: (2019)

(a) 0.2, 22.20 (b) 0.2, 11.11
(c) 0.167, 11.11 (d) 0.167, 22.20

12. The volume strength of 1 M H_2O_2 is (Molar mass of H_2O_2 = 34 g mol⁻¹) (2019)

(a) 5.6 (b) 16.8
(c) 11.35 (d) 22.4

13. 100 mL of a water sample contains 0.81 g of calcium bicarbonate and 0.73 g of magnesium bicarbonate. The hardness of this water sample expressed in terms of equivalents of $CaCO_3$ is: (molar mass of calcium bicarbonate is 162 g mol⁻¹ and magnesium bicarbonate is 146 g mol⁻¹) (2019)

(a) 1,000 ppm (b) 10,000 ppm
(c) 100 ppm (d) 5,000 ppm

14. For a reaction,
 $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$; identify dihydrogen (H_2) as a limiting reagent in the following reaction mixtures. (2019)

(a) 14 g of N_2 + 4 g of H_2
(b) 28 g of N_2 + 6 g of H_2
(c) 56 g of N_2 + 10 g of H_2
(d) 35 g of N_2 + 8 g of H_2

- 15.** The percentage composition of carbon by mole in methane is: (2019)
- (a) 80% (b) 25%
(c) 75% (d) 20%
- 16.** The maximum prescribed concentration of copper in drinking water is: (2019)
- (a) 5 ppm (b) 0.5 ppm
(c) 0.05 ppm (d) 3 ppm
- 17.** The percentage strength of 11.2 volumes solution of H_2O_2 is : [Given that molar mass of H = 1 g mol⁻¹ and O = 16 g mol⁻¹] (2019)
- (a) 13.6% (b) 3.4%
(c) 34% (d) 1.7%
- 18.** 25 g of an unknown hydrocarbon upon burning produces 88 g of CO_2 and 9 g of H_2O . This unknown hydrocarbon contains. (2019)
- (a) 20 g of carbon and 5 g of hydrogen.
(b) 24 g of carbon and 1 g of hydrogen.
(c) 18 g of carbon and 7 g of hydrogen.
(d) 22 g of carbon and 3 g of hydrogen.
- 19.** What would be the molality of 20% (mass/mass) aqueous solution of KI? (2019)
(molar mass of KI = 166 g mol⁻¹)
- (a) 1.08 (b) 1.48
(c) 1.51 (d) 1.35
- 20.** 5 moles of AB_2 weigh 125×10^{-3} kg and 10 moles of A_2B_2 weigh 300×10^{-3} kg. The molar mass of $\text{A}_{(\text{M}_\text{A})}$ and molar mass of $\text{B}_{(\text{M}_\text{B})}$ in kg mol⁻¹ are: (2019)
- (a) $\text{M}_\text{A} = 50 \times 10^{-3}$ and $\text{M}_\text{B} = 25 \times 10^{-3}$
(b) $\text{M}_\text{A} = 25 \times 10^{-3}$ and $\text{M}_\text{B} = 50 \times 10^{-3}$
(c) $\text{M}_\text{A} = 5 \times 10^{-3}$ and $\text{M}_\text{B} = 10 \times 10^{-3}$
(d) $\text{M}_\text{A} = 10 \times 10^{-3}$ and $\text{M}_\text{B} = 5 \times 10^{-3}$
- 21.** The mole fraction of a solvent in aqueous solution of a solute is 0.8. The molality (in mol kg⁻¹) of the aqueous solution is: (2019)
- (a) 13.88×10^{-1} (b) 13.88×10^{-2}
(c) 13.88 (d) 13.88×10^{-3}
- 22.** At 300 K and 1 atmospheric pressure, 10 mL of a hydrocarbon required 55 mL of O_2 for complete combustion and 40 mL of CO_2 is formed. The formula of the hydrocarbon is: (2019)
- (a) C_4H_8 (b) $\text{C}_4\text{H}_7\text{Cl}$
(c) C_4H_{10} (d) C_4H_6
- 23.** The minimum amount of $\text{O}_2(\text{g})$ consumed per gram of reactant is for the reaction: (2019)
(Given atomic mass: Fe = 56, O = 16, Mg = 24, P = 31, C = 12, H = 1)
- (a) $\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{l})$
(b) $\text{P}_4(\text{s}) + 5 \text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{s})$
(c) $4 \text{Fe}(\text{s}) + 3 \text{O}_2(\text{g}) \rightarrow 2\text{Fe}_2\text{O}_3(\text{s})$
(d) $2 \text{Mg}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2 \text{MgO}(\text{s})$
- 24.** Amongst the following statements, that which was not proposed by Dalton was: (2020)
- (a) When gases combine or reproduced in a chemical reaction, they do so in a simple ratio by volume provided all gases are at the same T & P.
(b) Matter consists of indivisible atoms.
(c) Chemical reactions involve reorganization of atoms. These are neither created nor destroyed in a chemical reaction.
(d) All the atoms of a given element have identical properties including identical mass. Atoms of different elements differ in mass.
- 25.** The volume (in mL) of 0.125 M AgNO_3 required to quantitatively precipitate chloride ions in 0.3 g of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is _____. (2020)
 $\text{M}_{[\text{Co}(\text{NH}_3)_6]\text{Cl}_3} = 267.46 \text{ g/mol}$
 $\text{M}_{\text{AgNO}_3} = 169.87 \text{ g/mol}$
- 26.** NaClO_3 is used, even in space crafts, to produce O_2 . The daily consumption of pure O_2 by a person is 492 L at 1 atm, 300 K. How much amount of NaClO_3 , in grams, is required to produce O_2 for the daily consumption of a person at 1 atm, 300 K? _____. (2020)
 $\text{NaClO}_3(\text{s}) + \text{Fe}(\text{s}) \rightarrow \text{O}_2(\text{g}) + \text{NaCl}(\text{s}) + \text{FeO}(\text{s})$
 $R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$
- 27.** The hardness of a water sample containing 10⁻³ M MgSO_4 expressed as CaCO_3 equivalents (in ppm) is _____. (molar mass of MgSO_4 is 120.37 g/mol) (2020)
- 28.** 6.023×10^{22} molecules are present in 10 g of a substance 'x'. The molarity of a solution containing 5 g of substance 'x' in 2 L solution is ____ $\times 10^{-3}$. (2020)
- 29.** The strengths of 5.6 volumes hydrogen peroxide (of density 1 g/mL) in terms of mass percentage and molarity (M), respectively, are (2020)
(Take molar mass of hydrogen peroxide as 34 g/mol)
- (a) 1.7 and 0.5 (b) 0.85 and 0.5
(c) 1.7 and 0.25 (d) 0.85 and 0.25
- 30.** The mole fraction of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in an aqueous binary solution is 0.1. The mass percentage of water in it, to the nearest integer, is _____. (2020)
- 31.** The volume strength of 8.9 M H_2O_2 solution calculated at 273 K and 1 atm is _____. (2020)
($R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$)
(Rounded off to the nearest integer)

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50. The ammonia prepared by treating ammonium sulphate with calcium hydroxide is completely used by $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ to form a stable coordination compound. Assume that both the reactions are 100% complete. If 1584 g of ammonium sulphate and 952 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ are used in the preparation, the combined weight (in grams) of gypsum and the nickel-ammonia coordination compound thus produced is _____. (Atomic weights in g mol⁻¹: H = 1, N = 14, O = 16, S = 32, Cl = 35.5, Ca = 40, Ni = 59)

(2018)

51. The mole fraction of urea in an aqueous urea solution containing 900 g of water is 0.05. If the density of the solution is 1.2 g cm⁻³, the molarity of urea solution is _____. (2019)
(Given data: Molar masses of urea and water are 60 g mol⁻¹ and 18 g mol, respectively)

52. Aluminium reacts with sulfuric acid to form aluminium sulfate and hydrogen. What is the volume of hydrogen gas in liters (L) produced at 300 K and 1.0 atm pressure, when 5.4 g of aluminium and 50.0 mL of 5.0 M sulfuric acid are combined for the reaction?

(Use molar mass of aluminium as 27.0 g mol⁻¹, R = 0.082 atm L mol⁻¹ K⁻¹) (2020)

53. To check the principle of multiple proportions, a series of pure binary compounds (P_mQ_n) were analyzed and their composition is tabulated below. The correct option(s) is(are) (2022)

Compound	Weight % of P	Weight % of Q
1	50	50
2	44.4	55.6
3	40	60

- (a) If empirical formula of compound 3 is P_3Q_4 , then the empirical formula of compound 2 is P_2A_5^- .
- (b) If empirical formula of compound 3 is P_2Q_5 and atomic weight of element P is 20, then the atomic weight of Q is 45.
- (c) If empirical formula of compound 2 is PQ, then the empirical formula of the compound 1 is P_5Q_4 .
- (d) If atomic weight of P and Q are 70 and 35, respectively, then the empirical formula of compound 1 is P_2Q .

ANSWER KEY

CONCEPT APPLICATION

- | | | | | | | | | | |
|---------|---------|-----------|---------|---------|---------|---------|---------|---------|---------|
| 1. (a) | 2. (a) | 3. (d) | 4. (a) | 5. (a) | 6. (a) | 7. (b) | 8. (b) | 9. (c) | 10. (a) |
| 11. (b) | 12. (c) | 13. (a,b) | 14. (a) | 15. (b) | 16. (b) | 17. (c) | 18. (c) | 19. (b) | 20. (c) |
| 21. (d) | 22. (a) | 23. (b) | 24. (a) | 25. (c) | 26. (d) | 27. (d) | 28. (b) | 29. (a) | 30. (c) |
| 31. (b) | 32. (a) | 33. (d) | 34. (b) | 35. (b) | | | | | |

EXERCISE-1 (TOPICWISE)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (a) | 2. (c) | 3. (a) | 4. (b) | 5. (b) | 6. (a) | 7. (d) | 8. (a) | 9. (a) | 10. (a) |
| 11. (b) | 12. (b) | 13. (a) | 14. (a) | 15. (c) | 16. (c) | 17. (d) | 18. (b) | 19. (a) | 20. (a) |
| 21. (d) | 22. (c) | 23. (b) | 24. (b) | 25. (c) | 26. (c) | 27. (c) | 28. (d) | 29. (c) | 30. (b) |
| 31. (c) | 32. (a) | 33. (d) | 34. (a) | 35. (d) | 36. (d) | 37. (b) | 38. (a) | 39. (d) | 40. (c) |
| 41. (c) | 42. (b) | 43. (c) | 44. (c) | 45. (a) | 46. (c) | 47. (a) | 48. (a) | 49. (c) | 50. (a) |
| 51. (a) | | | | | | | | | |

EXERCISE-2 (LEARNING PLUS)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c) | 2. (a) | 3. (c) | 4. (a) | 5. (c) | 6. (b) | 7. (a) | 8. (a) | 9. (a) | 10. (d) |
| 11. (c) | 12. (a) | 13. (a) | 14. (b) | 15. (a) | 16. (b) | 17. (b) | 18. (a) | 19. (a) | 20. (a) |
| 21. (a) | 22. (a) | 23. (d) | 24. (b) | 25. (c) | 26. (b) | 27. (b) | 28. (a) | 29. (c) | 30. (b) |
| 31. (c) | 32. (a) | 33. (b) | 34. (d) | 35. (d) | 36. (b) | 37. (b) | 38. (c) | 39. (b) | 40. (c) |
| 41. (a) | 42. (c) | 43. (a) | 44. (c) | 45. (c) | 46. (c) | 47. (a) | 48. (a) | 49. (b) | 50. (c) |
| 51. (a) | | | | | | | | | |

EXERCISE-3 (JEE ADVANCED LEVEL)

- | | | | | | | | | | |
|------------|-------------|-------------|----------|------------|----------|----------|----------|-----------|-----------|
| 1. (a,b,c) | 2. (b,c,d) | 3. (a,c) | 4. (a,c) | 5. (a,b,c) | 6. (a,c) | 7. (b,d) | 8. (a,c) | 9. (a,b) | 10. (b,d) |
| 11. (a,b) | 12. (a,c,d) | 13. (a,b,d) | 14. (c) | 15. (b) | 16. (b) | 17. (a) | 18. (b) | 19. (b) | 20. (a) |
| 21. (b) | 22. (d) | 23. [+8] | 24. [-3] | 25. [500] | 26. [40] | 27. [6g] | 28. [1] | 29. [22g] | 30. [1] |
| 31. [27g] | | | | | | | | | |

EXERCISE-4 (PAST YEAR QUESTIONS)

JEE Main

- | | | | | | | | | | |
|-------------|----------|-------------------------|-----------|----------------------|----------|--------------------------|------------------------|----------|---------|
| 1. (b) | 2. (c) | 3. (c) | 4. (d) | 5. (a) | 6. (c) | 7. (a) | 8. (b) | 9. (d) | 10. (c) |
| 11. (c) | 12. (c) | 13. (b) | 14. (c) | 15. (d) | 16. (d) | 17. (b) | 18. (b) | 19. (c) | 20. (c) |
| 21. (c) | 22. (d) | 23. (c) | 24. (a) | 25. [26.80 to 27.00] | | 26. [2120.00 to 2140.00] | 27. [100.00 to 100.00] | | |
| 28. [25.00] | 29. (a) | 30. [47] | 31. [100] | 32. [3400] | 33. [18] | 34. (c) | 35. (b) | 36. [64] | 37. [2] |
| 38. [13] | 39. [20] | 40. [2592 g and 2376 g] | 41. [46] | 42. [24] | 43. [54] | | | | |

JEE Advanced

- | | | | | | | | | |
|-----------|---------|------------|---------|---------|---------|-------------|--------------------|------------|
| 44. [5] | 45. (c) | 46. (8 mL) | 47. [8] | 48. [9] | 49. [6] | 50. [29.92] | 51. [2.98 or 2.99] | 52. [6.15] |
| 53. (b,c) | | | | | | | | |

CHAPTER

2

Atomic Structure

DALTON'S ATOMIC THEORY

Dalton proposed the atomic theory on the basis of the law of conservation of mass and law of definite proportions. He also proposed the law of multiple proportion as a logical consequence of this theory. The salient features of this theory are:

- (a) Each element is composed by extremely small particles called atoms.
- (b) Atoms of a particular element are all like but differ with the atoms of other elements.
- (c) Atom of each element is an ultimate particle, and has a characteristic mass but is structureless.
- (d) Atom is indestructible i.e. it can neither be created nor destroyed by simple chemical reactions.
- (e) Atom of an element takes part in chemical reaction to form molecule.
- (f) In a given compound, the relative number and kind of atom are same.
- (g) Atoms of different elements combine in fixed ratio of small whole numbers to form compound atoms (now called molecules).

Merits and Demerits of Dalton's Theory

(i) Merits:

- (a) Dalton's theory explains the law of conservation of mass and some other laws of chemical combination.
- (b) Atoms of elements take part in chemical reaction is true till today.

(ii) Demerits:

- (a) There is no mention of atomic weights of elements.
- (b) He could not explain that why do atoms of same element combined with each other.
- (c) The law of definite proportion fails if different isotopes are used.

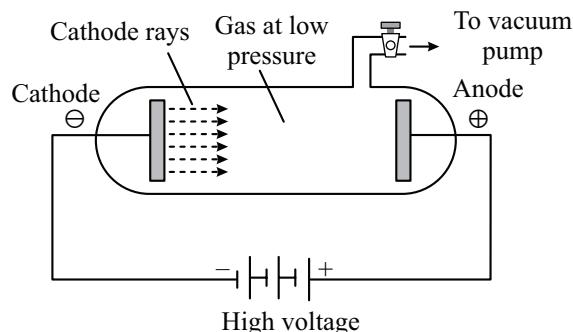
FUNDAMENTAL PARTICLES

(a) Properties of Electron:

- (a) Electron was discovered by Sir J.J. Thomson.
- (b) The charge on the electron is -1.6×10^{-19} coulomb (Millikan)

- (c) The molar mass of electron is 5.48×10^{-4} gm/mole.
- (d) The value of e/m has been found to be -1.7588×10^{11} C/kg.
- (e) The first precise measurement of the charge on the electron was made by Robert A. Millikan in 1909 by oil drop experiment. Its value was found to be -1.6022×10^{-19} coulomb.
- (f) The mass of electron can be calculated from the value of e/m and the value of which is 9.1096×10^{-31} Kg.

Cathode Rays



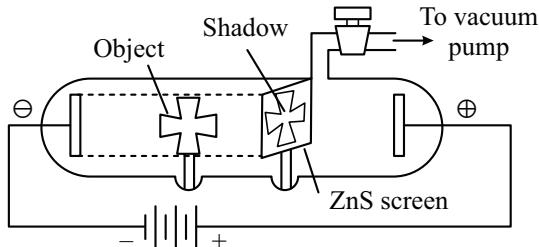
- (a) The electron was discovered as a result of the studies of the passage of electricity through gases at extremely low pressures known as discharge tube experiments.

- (b) When a high voltage of the order of 10,000 volts or more was impressed across the electrodes, some sort of invisible rays moved from the negative electrode to the positive electrodes these rays are called as cathode rays.

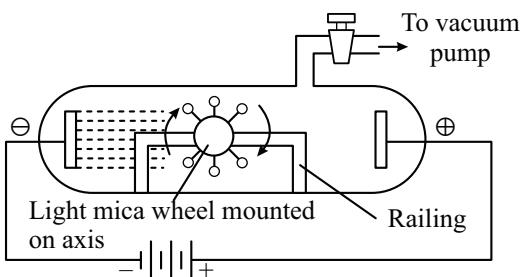
- (c) Cathode rays have the following properties.

- (i) Path of travelling is straight from the cathode with a very high velocity.

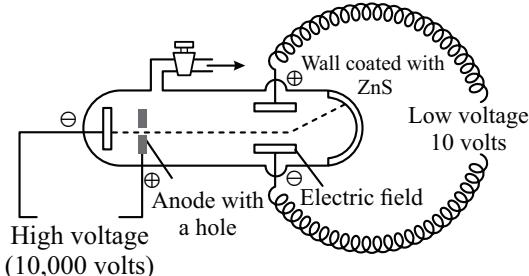
As it produces shadow of an object placed in its path.



- (ii) Cathode rays produce mechanical effects. If a small pedal wheel is placed between the electrodes, it rotates. This indicates that the cathode rays consist of material part rays possess heating effect.



- (iii) When electric and magnetic fields are applied to the cathode rays in the discharge tube, the rays are deflected thus establishing that they consist of charged particles.



- (iv) Cathode rays produce X-rays when they strike against hard metals like tungsten, copper etc.
 (v) When the cathode rays are allowed to strike a thin metal foil, it gets heated up. Thus the cathode rays possess heating effect.
 (vi) They produce a green glow when strike the glass wall beyond the anode. Light is emitted when they strike the zinc sulphide screen.
 (vii) They produce a green glow when strike the glass wall beyond the anode. Light is emitted when they strike the zinc sulphide screen.
 (viii) Cathode rays penetrate through thin sheets of aluminium and other metals.
 (ix) They affect the photographic plates.
 (x) The ratio of charge to mass i.e. charge/mass is same for all the cathode rays irrespective of the gas used in the tube.

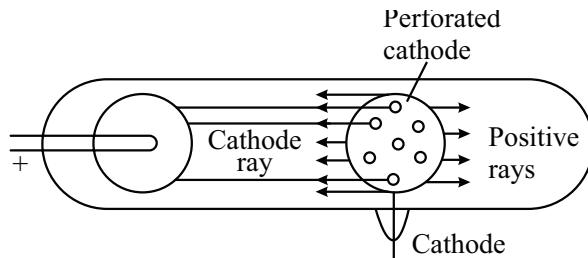
(b) Properties of Proton

- Proton was discovered by Goldstein.
- Proton carries a charge of $+1.602 \times 10^{-19}$ coulomb, i.e., one unit positive charge.
- Mass of proton is 1.672×10^{-27} kg or 1.0072 amu.
- A proton is defined as a sub-atomic particle which has a mass nearly 1 amu and a charge of +1 unit.

Positive Rays-Discovery of Proton

- The existence of positively charged particles in an atom was shown by E. Goldstein in 1886.
- He repeated the same discharge tube experiments by using a perforated cathode.

- (c) It was observed that when a high potential difference was applied between the electrodes, not only cathode rays were produced but also a new type of rays were produced simultaneously from anode moving towards cathode and passed through the holes or canal of the cathode. These termed as canal ray or cathode ray.



- (d) Characteristics of Anode Rays are as follows.

- These rays travel in straight lines and cast shadow of the object placed in their path.
- The anode rays are deflected by the magnetic and electric fields like cathode rays but direction is different that mean these rays are positively charged.
- These rays have kinetic energy and produces heating effect also.
- The e/m ratio of for these rays is smaller than that of electrons.
- Unlike cathode rays, their e/m value is dependent upon the nature of the gas taken in the tube.
- These rays produce flashes of light on ZnS screen.
- These rays can pass through thin metal foils.
- They are capable to produce ionisation in gases.
- They can produce physical and chemical changes.

(c) Properties of Neutron

- This was discovered 20 years after the structure of atom was elucidated by Rutherford.
- It has been found that for all atoms except hydrogen atomic mass is more than the atomic number. Thus Rutherford (1920) suggested that in an atom, there must be present at least a third type of fundamental particle.
- It should be electrically neutral and posses mass nearly equal to that of proton. He proposed its name as neutron.
- Chadwick (1932), bombarded beryllium with a stream of α -particles and observed electrically and magnetically neutral radiations.
- There were neutral particles which was called neutron. Nuclear reaction is as follows:



- A neutron is a subatomic particle which has a mass 1.675×10^{-24} g, approximately 1 amu, or nearly equal to the mass of proton on hydrogen atom and carrying no electrical charge.



Train Your Brain

Example 1: Which has highest e/m ratio:

- (a) He^{2+} (b) H^+
 (c) He^{1+} (d) H

Sol. (b) Mass of H^+ is minimum

Example 2: Arrange the following particles in increasing order of values of e/m ratio: Electron (e), proton (p), neutron (n) and α -particle (α):

- (a) n, p, e, a (b) n, a, p, e
 (c) n, p, a, e (d) e, p, n, a

Sol. (b)

	Electron	Proton	Neutron	α -particle
e	1 unit	1 unit	zero	2 units
m	$1/1837$ unit	1 unit	1 unit	4-units
e/m	1837	1	zero	$1/2$

Example 3: Mass of neutron is times the mass of electron:

- (a) 1840 (b) 1480
 (c) 2000 (d) None of these

Sol. (a) Mass of neutron = 1.675×10^{-27} kg, mass of electron = 9.108×10^{-31} kg.

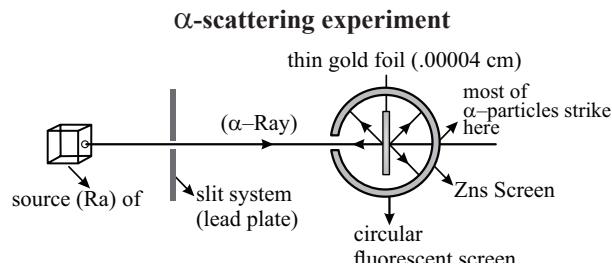
This model of atom is known as "Plum-Pudding model" or "Raisin Pudding Model" or "Water Melon Model".

Drawbacks: An important drawback of this model is that the mass of the atoms is considered to be evenly spread over that atom.

It is a static model. It does not reflect the movement of electron.

It couldn't explain the stability of an atom.

RUTHERFORD'S SCATTERING EXPERIMENT

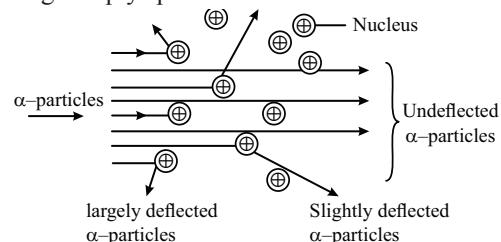


Rutherford Observed that

- (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 (about one in 20,000) did not pass through the foil at all but suffered large deflections (more than 90°) or even came back in the direction from which they have come i.e. a deflection of 180°.

Following conclusions were drawn from the above observations:

- (1) 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.



- (2) Since few of the α -particles were deflected from their original paths 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.

When 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.

A very few of the α -particles suffered strong deflections or 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.

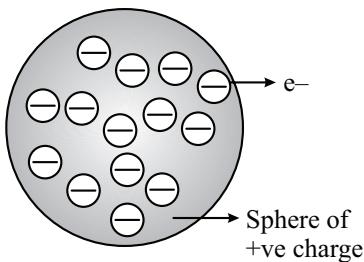


Concept Application

1. The mass of cathode ray particle is:
 (a) Same for different gases
 (b) Different for different gases
 (c) Minimum for H_2 gas
 (d) Different for same gases
2. The ratio of the "e/m" (specific charge) values of a electron and an α -particle is -
 (a) 2 : 1 (b) 1 : 1
 (c) 1 : 2 (d) None of these

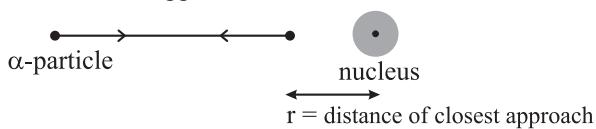
THOMSON'S MODEL OF ATOM (1904)

Thomson was the first to propose a detailed model of the atom. Thomson proposed that an atom consists of a uniform sphere of positive charge in which the electrons are distributed more or less uniformly.



DISTANCE OF CLOSEST APPROACH

Rutherford estimated the size of nucleus by calculating the distance of closest approach.



The initial kinetic energy of α -particle must be equal to potential energy at distance of closest approach.

$$K.E. = \frac{1}{4\pi\epsilon_0} \cdot \frac{q_1 q_2}{r} = \frac{1}{4\pi\epsilon_0} \cdot \frac{(2e)(Ze)}{r}$$

$$r = \frac{2Ze^2}{(4\pi\epsilon_0)(K.E.)}$$

where Z = atomic number of element used in foil.

- (iv) Almost all mass of the atom is densely concentrated in extremely small region (nucleus).
- (v) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits. Electrons and the nucleus are held together by electrostatic forces of attraction.



Train Your Brain

Example 4: An α -particles of kinetic energy of 10 MeV is projected towards gold nucleus. Calculate the distance of closet approach. (Atomic number of gold = 79, 1 eV = 1.6×10^{-19} J)

$$\text{Sol. } K.E. = \frac{1}{4\pi\epsilon_0} \cdot \frac{q_1 q_2}{r}$$

$$\text{or } 10 \times 10^6 \times 1.6 \times 10^{-19} = 9 \times 10^9 \times \frac{(2 \times 1.6 \times 10^{-19}) \times (79 \times 1.6 \times 10^{-19})}{r}$$

$$\frac{9 \times 10^9 \times 2 \times 1.6 \times 10^{-19} \times 79}{10 \times 10^6} = 2.88 \times 10^{-16} \text{ m}$$

Example 5: An α -particles is projected towards the following nucleus with same kinetic energy in different experimenter the distance of closet approach is maximum for

- (a) Na ($Z = 11$)
- (b) Ca ($Z = 20$)
- (c) Ag ($Z = 47$)
- (d) Au ($Z = 79$)

$$\text{Sol. (a) } K.E. = \frac{kq_1q_2}{r}$$

$q_1 = \alpha$ -particle

$q_1 = \text{charge on given element}$

$$\text{therefor } r = \frac{Kq_1q_2}{K.E.}$$

if $K.E. = \text{constant}$ & $q_1 = 2e^-$

then $r \propto q_2$ total charge on other element.

Example 6: An α -particle, a proton, a deuteron and a neutron are projected towards the same nucleus with the same kinetic energy in different experimenter. The distance of closet approach is minimum for

- (a) a
- (b) P
- (c) d
- (d) n

$$\text{Sol. (d) } K.E. = \frac{kq_1q_2}{r}$$

$$\text{or } r = \frac{kq_1q_2}{K.E.}$$

$K.E. = \text{constant}$

$q_1 = \text{charge on bombarded particle}$

q_2 (constant) = charge on target particle
lower the charge on projected particle, minimum will be closest approach.

Example 7: An α -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

$$= 7.7 \times 10^6 \times 1.6 \times 10^{-19} \text{ J}$$

$$K.E. = \frac{kq_1q_2}{r} \text{ or } r_0 = \frac{Kq_1q_2}{K.E.}$$

$$r_0 = \frac{9 \times 10^9 \times 2 \times (1.6 \times 10^{-19})^2 \times 79}{7.7 \times 10^6 \times 1.6 \times 10^{-19}} \text{ m}$$

$$r_0 = 2.95 \times 10^{-14} \text{ m or } r_0 \approx 3.0 \times 10^{-14} \text{ m.}$$

From the above example it is clear that nuclear dimension cannot be greater than 3×10^{-14} m.

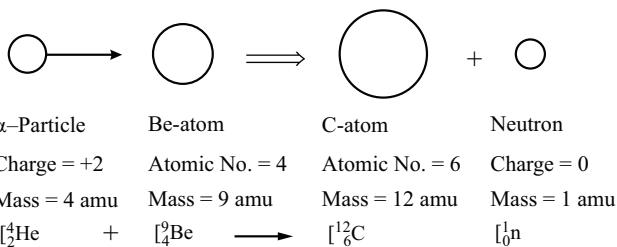


Concept Application

3. The approximate radius of a H-atom is 0.05 nm, and that of proton is 1.5×10^{-15} m. Assuming both the hydrogen atom and the proton to be spherical, calculate fraction of the space in an atom of hydrogen that is occupied by the nucleus.
4. Rutherford's alpha particle scattering experiment eventually led to the conclusion that
 - (a) mass and energy are related
 - (b) electrons occupy space around the nucleus
 - (c) neutrons are buried deep in the nucleus
 - (d) the point of impact with matter can be precisely determined

NEUTRON

In 1932, Chadwick bombarded beryllium with a stream of α -particles. He observed that penetrating radiations were produced which were not affected by electric & magnetic fields. These radiations consists of neutral particles, which were called **neutrons**. The nuclear reaction can be shown as.



Thus a neutron is a sub atomic particle which has a mass 1.675×10^{-24} g approximately 1amu, or nearly equal to the mass of proton or hydrogen atom and carrying no electrical charge.

The specific charge (e/m value) of a **neutron** is zero.

APPLICATIONS OF RUTHERFORD MODEL

On the basis of scattering experiments, Rutherford proposed model of the atom, which is known as nuclear atomic model. According to this model-

$$\frac{D_A}{D_N} = \frac{\text{Diameter of the atom}}{\text{Diameter of the nucleus}} = \frac{10^{-8}}{10^{-13}} = 10^5,$$

$$R \propto A^{1/3} \Rightarrow R = R_0 A^{1/3} \text{ cm}$$

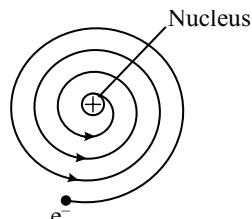
Where $R_0 = 1.33 \times 10^{-13}$ (a constant) and A = mass number (p + n) and R = radius of the nucleus.

$$R = 1.33 \times 10^{-13} A^{1/3} \text{ cm}$$

$$\frac{\text{volume of the atom}}{\text{volume of the nucleus}} = \frac{(10^{-8})^3}{(10^{-13})^3} = 10^{15}$$

Drawbacks of Rutherford Model

- (1) This theory could **not** explain stability of atom. According to Maxwell, electron loses its energy continuously in the form of electromagnetic radiations. As a result of this, the e⁻ should lose 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.



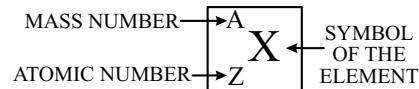
- (2) If the electrons loss energy continuously, the observed spectrum should be continuous but the actual observed spectrum consists of well defined lines of definite frequencies. Hence, the loss of energy by electron is **not** continuous in an atom.

ATOMIC NUMBER (Z) AND MASS NUMBER (A)

Atomic number (Z) of an element

- = Total number of protons present in the nucleus.
- = Total number of electrons present in the neutral atom.

- ❖ Since the electrons have negligible mass, the entire mass of the atom is mainly due to protons and neutrons only. Since these particles are present in the nucleus, therefore they are collectively called **nucleons**.
- ❖ As each of these particles has one unit mass on the atomic mass scale, therefore the sum of the number of protons and neutrons will be nearly equal to the mass of the atom.
Mass number of an element = No. of protons (Z) + No. of neutrons (n).
- ❖ The mass number of an element is nearly equal to the atomic mass of that element.
- ❖ The atomic number (Z) and mass number (A) of an element 'X' are usually represented along with the symbol of the element as



- (i) Isotopes:** Such atoms of the same element having same atomic number but different mass numbers are called isotopes.

${}_1^1\text{H}$, ${}_1^2\text{D}$ and ${}_1^3\text{T}$ and named as protium, deuterium (D) and tritium (T) respectively. Ordinary hydrogen is protium.

- (ii) Isobars:** Such atoms of different elements which have same mass numbers (and of course different atomic numbers) are called isobars.

e.g. ${}_{18}^{40}\text{Ar}$, ${}_{19}^{40}\text{K}$, ${}_{20}^{40}\text{Ca}$.

- (iii) Isotones:** Such atoms of different elements which contain the same number of neutrons are called isotones.

e.g. ${}_{6}^{14}\text{C}$, ${}_{7}^{15}\text{N}$, ${}_{8}^{16}\text{O}$.

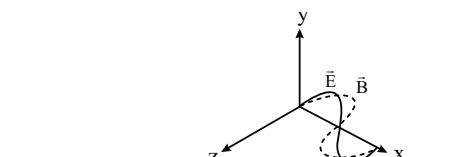
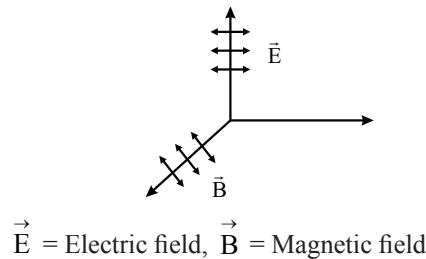
- (iv) Isoelectronic:** The species (atoms or ions) containing the same number of electrons are called isoelectronic.

For example, O²⁻, F⁻, Na⁺, Mg²⁺, Al³⁺, Ne all contain 10 electrons each and hence they are isoelectronic.

WAVES AND IT'S CHARACTERISTICS

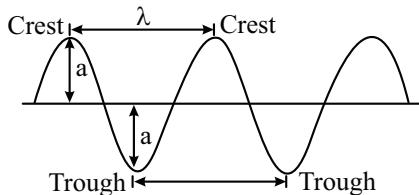
Electromagnetic Wave Radiation

The oscillating electrical/magnetic field are electromagnetic radiations. Experimentally, the direction of oscillations of electrical and magnetic field are perpendicular to each other.



Direction of wave propagation.

Some important characteristics of a wave:



- (i) **Wavelength** of a wave is defined as the distance between any two consecutive crests or troughs. It is represented by λ (Lambda) and is expressed in Å or m or cm or nm (nanometer) or pm (picometer).

$$1 \text{ Å} = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$$

$$1 \text{ nm} = 10^{-9} \text{ m}, 1 \text{ pm} = 10^{-12} \text{ m}$$

- (ii) **Frequency** of a wave is defined as the number of waves passing through a point in one second. It is represented by v (nu) and is expressed in Hertz (Hz) or cycles/sec or simply sec^{-1} or s^{-1} .

$$1 \text{ Hz} = 1 \text{ cycle/sec}$$

- (iii) **Velocity** of a wave is defined as the linear distance travelled by the wave in one second. It is represented by v and is expressed in cm/sec or m/sec (ms^{-1}).

- (iv) **Amplitude** of a wave is the height of the crest or the depth of the trough. It is represented by 'a' and is expressed in the units of length.

- (v) **Wave number** is defined as the number of waves present in 1 cm length. Evidently, it will be equal to the reciprocal of the wavelength. It is represented by \bar{v} (read as nu bar).

$$\bar{v} = \frac{1}{\lambda}$$

If λ (Lambda) is expressed in cm, \bar{v} will have the units cm^{-1} .

Relationship between velocity, wavelength and frequency of

a wave. As frequency is the number of waves passing through a point per second and λ is the length of each wave, hence their product will give the velocity of the wave.

Order of wavelength in Electromagnetic spectrum:

Cosmic rays < γ -rays < X-rays < Ultraviolet rays < Visible < Infrared < Micro waves < Radio waves.

NATURE OF LIGHT

- ❖ **Maxwell electromagnetic wave theory (wave nature of light):** An accelerated electrically charged particle produces and transmits electrical and magnetic field. These are transmitted in the form of waves known as electromagnetic waves or electromagnetic radiations.

He stated that light also possess electrical and magnetic field and it is also known as electromagnetic radiations.

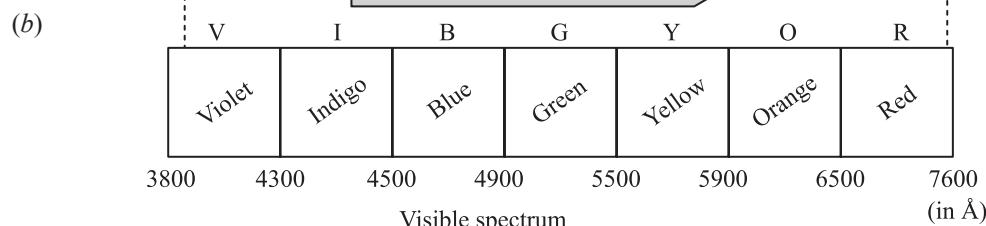
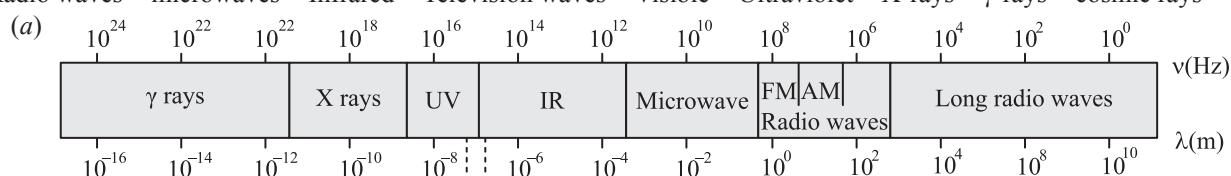
- ❖ **Characteristics of Electromagnetic Radiations:**

- (i) In these electromagnetic radiation electrical and magnetic field oscillates perpendicular to each other and it also propagates perpendicular to both field.
- (ii) All these electromagnetic radiation do not require any medium and can travel in vacuum.
- (iii) Velocity of all electromagnetic radiation is $3 \times 10^8 \text{ m/s}$ in vacuum.
- (iv) Energy of an electromagnetic wave is directly proportional to intensity and it is independent of frequency.
- (v) They also show diffraction and interference and therefore, Maxwell concluded light to be wave nature. But Maxwell theory couldn't explain the results of photoelectric effect and black body radiations.

ELECTRO MAGNETIC SPECTRUM

The arrangement of various types of electromagnetic radiations in the order of their increasing or decreasing wavelength or frequencies is known as electromagnetic spectrum. The wavelength decreases in the following order.

Radio waves > microwaves > Infrared > Television waves > Visible > Ultraviolet > X-rays > γ -rays > cosmic rays



Wavelength λ (Å)

(a) The spectrum of electromagnetic radiation.

(b) Visible spectrum.

The visible region is only a small part of the entire spectrum.

PLANCK'S QUANTUM THEORY

Particle nature of light: He stated that a body radiates energy in the form of discontinuous energy packets or bundles. Each bundle of energy is known as quantum and quantum of light is known as photons.

Energy of each quantum is directly proportional to frequency of radiation.

$$E \propto v \\ E = hv \quad h = 6.62 \times 10^{-34} \text{ J-s} \\ \downarrow \\ \text{Planck's constant}$$

Total energy absorbed or emitted by a body will be whole no. integral multiple of energy of quantum.

$$E = \frac{nhc}{\lambda}$$

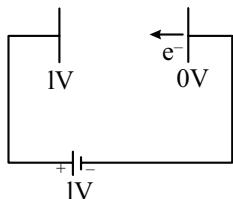
One electron volt (e.v.): Energy gained by an electron when it is accelerated from rest through a potential difference of 1 volt.

Note: Positive charge always moves from high potential to low potential and -ve charge always moves from low potential to high potential if set free.

If a charge 'q' is accelerated through a potential difference of 'V' volt then its kinetic energy will be increased by $q \times V$.

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ C} \times 1 \text{ volt}$$

$$\therefore 1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$



Train Your Brain

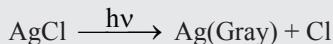
Example 8: Calculate the no. of photons emitted by 60 watt bulb in 10 hrs. When light of wavelength 6000 Å is emitted by it.

$$\text{Sol. } P = \frac{E}{t} = \frac{nhv}{t} \text{ or } P = \frac{nhc}{\lambda t} \text{ or } n = \frac{P \times \lambda \times t}{h \times c}$$

$$\text{or } n = \frac{60 \times 6000 \times 10^{-10} \times 10 \times 60 \times 60}{6.626 \times 10^{-34} \times 3 \times 10^8}$$

$$\text{or } n = 6.52 \times 10^{24}$$

Example 9: Certain sun glasses having small of AgCl incorporated in the lenses, on exposure to light of appropriate wavelength turns to gray colour to reduce the glare following the reactions:



If the heat of reaction for the decomposition of AgCl is 248 kJ mol⁻¹, what maximum wavelength is needed to induce the desired process?

Sol. Energy needed to change = $248 \times 10^3 \text{ J/mol}$

If photon is used for this purpose, then according to Einstein law one molecule absorbs one photon.
Therefore,

$$\therefore N_A \cdot \frac{hc}{\lambda} = 248 \times 10^3 \\ \lambda = \frac{6.626 \times 10^{-34} \times 3.0 \times 10^8 \times 6.023 \times 10^{23}}{248 \times 10^3} \\ = 4.83 \times 10^{-7} \text{ m}$$

Example 10: A bulb is rated as 110 watt. If it emits 25% of absorbed energy as red light ($\lambda = 6626 \text{ \AA}$), how many photons are emitted out by the bulb per second?

$$\text{Sol. } P \times \eta = \frac{n \times h \times c}{\lambda \times t}$$

$$\text{or } 110 \times \frac{25}{100} = n \times \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{6626 \times 10^{-10}}$$

$$\text{or } n = 9.2 \times 10^{19}$$

Example 11: Wavelength of micro wave radiation is 0.08 m. How many moles of photons is needed to increase the temperature of 400 gm water from 25° to 45°C, assuming 25% efficiency?

Specific heat capacity = 4.2 J/K.gm

$$\text{Sol. } \left(\frac{nhc}{\lambda} \right) \times \frac{25}{100} = ms\Delta t$$

$$n \times \frac{6.626510^{-34} \times 3 \times 10^8}{0.08} \times \frac{25}{100} = 400 \times 4.2 \times 20$$

$$\therefore \text{Number of moles of photon} = \frac{n}{N_A}$$

$$\text{or Number of moles of photon} = \frac{540.86 \times 10^{26}}{6.023 \times 10^{23}} \\ = 9.0 \times 10^{14} \text{ mol.}$$

Example 12: A dye absorbs the radiation of 4000 Å and fluoresces the radiation of 5000 Å. If only 40% of the absorbed energy is emitted out, calculate the ratio of number of quanta emitted out and the number of quanta absorbed.

$$E_a \times \frac{40}{100} = E_e$$

$$n_a \times \frac{hc}{4000 \text{ \AA}} \times \frac{40}{100} = n_e \times \frac{hc}{5000 \text{ \AA}}$$

$$\frac{n_e}{n_a} = \frac{40}{100} \times \frac{5000}{4000} \times \frac{1}{2}$$

$$\frac{n_e}{n_a} = \frac{1}{4}$$



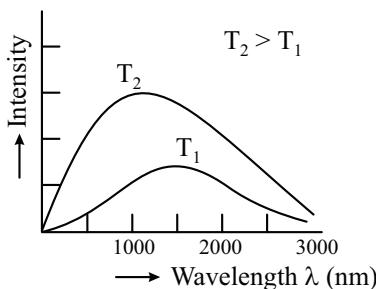
Concept Application

APPLICATION OF PLANCK'S QUANTUM THEORY

Black Body Radiation:

When solids are heated they emit radiation over a wide range of wavelengths.

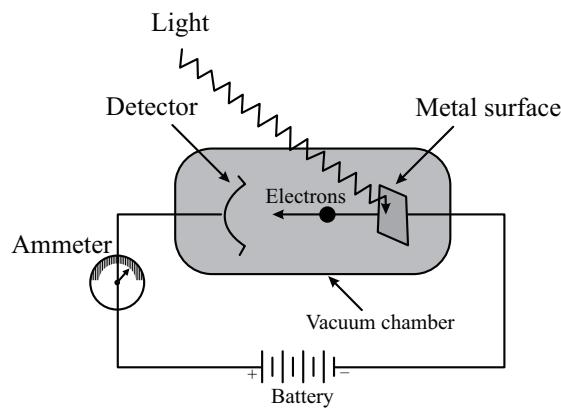
The ideal body, which emits and absorbs all frequencies, is called a black body and the radiation emitted by such a body is called black body radiation. The exact frequency distribution of the emitted radiation (i.e., intensity versus frequency curve of the radiation) from a black body depends only on its temperature.



The above experimental results cannot be explained satisfactorily on the basis of the wave theory of light. Planck suggested that atoms and molecules could emit (or absorb) energy only in discrete quantities.

Photoelectric Effect:

When certain metals (for example Potassium, Rubidium, Caesium etc.) were exposed to a beam of light electrons were ejected as shown in Fig.



The phenomenon is called **Photoelectric effect**. The results observed in this experiment were:

- ❖ The electrons are ejected from the metal surface as soon as the beam of light strikes the surface, i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface.
 - ❖ The number of electrons ejected is proportional to the intensity or brightness of light.

TERMS USED IN PHOTO ELECTRIC EFFECT

- 1. Work function (w):** It is the minimum amount of energy required to cause a photo emission from the metal surface. It is also known as threshold energy or Binding energy. Work function depends upon ionisation energy and therefore w is minimum for alkali metals).
 - 2. Threshold frequency (v_0):** The minimum value of frequency that can cause photo emissions. If $v < v_0$, then there is no photo emission.

$$w = hv_0 \Rightarrow w = \frac{hc}{\lambda_0}$$

3. **Threshold wavelength:** (λ_0) The maximum value of wavelength that can cause photo emission.
If $\lambda > \lambda_0$, then photo emission is not possible.
 4. **Intensity (I):** Energy falling on metal surface of unit area of unit time.

$$I = \frac{E}{At} = \frac{n\hbar v}{At}$$

- 5. Photo intensity (I_p):** It is number of photons falling per unit area per unit time.

$$I_p = \frac{n}{At}$$

Relation between I and I_p :

$$I = I_p h\nu$$

Photo intensity is independent of frequency while intensity depends on frequency.

Power: Total energy radiated per unit time.

$$P = \frac{E}{t} = \frac{n\hbar\nu}{t}$$

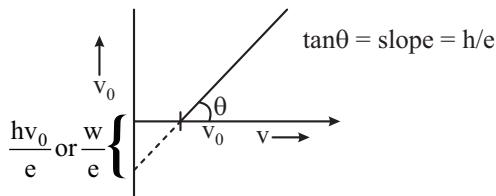
SATURATION CURRENT & STOPPING POTENTIAL

It is the minimum potential required to stop the fastest moving electrons completely or it is the minimum potential at which photo current becomes zero.

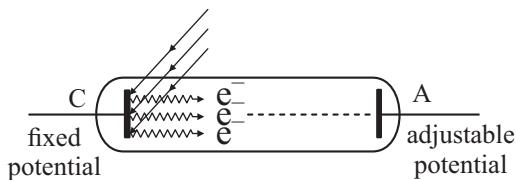
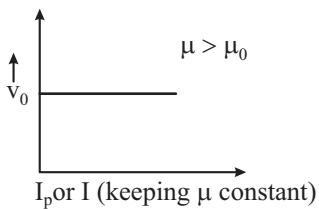
$$eV_0 = h\nu - w$$

$$eV_0 = h\nu - hv_0$$

$$\Rightarrow V_0 = \frac{h\nu}{e} - \frac{hv_0}{e}$$



It can be commented that stopping potential increase with increase in frequency. However if photo intensity is changed there is no effect on stopping potential.



Case-I: $V_C = V_A$

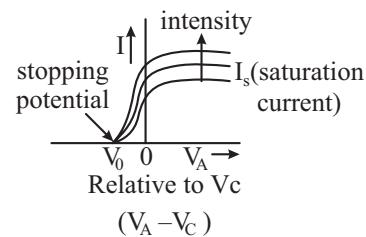
Some of the ejected electrons reach at electrode A resulting photocurrent.

Case-II: $V_C < V_A$

As electrode (A) is at high potential it attracts the electron & even a slower electron will reach at electrode A. It will result in increase in photocurrent. Further increase in the potential difference, a situation may result when the slowest photocurrent electron reaches at electrode. It results maximum called saturation current. Further increase in potential will not increase photocurrent.

Case-III: $V_C > V_A$

As electrode (A) is at low potential. It will repel electron resulting decrease in photocurrent. Further decrease in potential at electrode (A) may result a situation when the fastest electron just fails to reach at (A) and the photocurrent drops to zero. The potential of (A) relative to C to just stop photocurrent is called stopping potential.

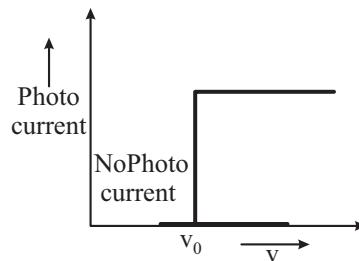


On increasing the intensity of light the stopping potential does not change because the maximum K.E. of photoelectron does not change. But the photocurrent increases, because the number of photon falling on the surface increases.

EFFECT OF VARIATION OF FREQUENCY

(a) Effect of Photo Emission: $I = I_p h\nu$

If frequency of subjected photon increases (intensity increases keeping photo intensity constant) then there is no change in no. of ejected photo electrons as well as no change in photo current.



(b) Effect on kinetic Energy: Average K.E. as well as K.E. max increases with increases in frequency.

$$h\nu - W = KE_{\max}$$

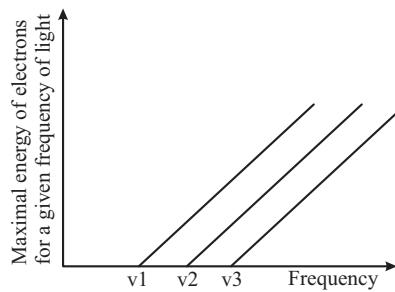
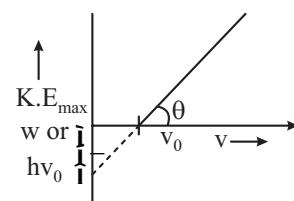
$$KE_{\max} = h\nu - hv_0$$

$$y = mx + c$$

$$KE_{\max} = h\nu - \frac{hc}{\lambda_0}$$

$$KE_{\max} = h\nu - w$$

$$\tan \theta = \text{slope} = h$$



- 10.** A laser producing monochromatic lights of different wavelength is used to eject electron from the sheet of gold having threshold frequency $6.15 \times 10^{14} \text{ s}^{-1}$ which of the following incident radiation will be suitable for the ejection of electrons:
- 1.5 moles of photons having frequency $3.05 \times 10^{14} \text{ s}^{-1}$
 - 0.5 moles of photon of frequency $12.3 \times 10^{12} \text{ s}^{-1}$
 - One photon with frequency $5.16 \times 10^{15} \text{ s}^{-1}$
 - All of the above
- 11.** The number of photoelectrons emitted depends upon:
- The intensity of the incident radiation
 - The frequency of the incident radiation
 - The product of intensity and frequency of incident radiation
 - None of these

BOHR'S MODEL

It was the first model based on Planck's quantum theory and the model explained stability of atom and line spectrum of hydrogen.

Postulates of Bohr's Model

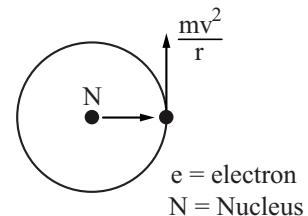
- An atom consist of centrally located small, dense, positively charged nucleus and electrons are revolving around the nucleus in circular paths known as circular orbits and coulombic force of attraction between nucleus and electron is balanced by centrifugal force of the revolving electron.
 - Out of the infinite circular orbits only those circular orbits are possible in which angular momentum of electron is integral multiple of $h/2\pi$ i.e. angular momentum of an electron can have fixed values like $\frac{nh}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}$ etc. i.e., angular momentum of electron is quantised.
- $$mv = \frac{nh}{2\pi}$$
- m and v are mass and velocities of electron respectively and r is radius of orbit and n is integer which is later related with orbit number and shell number and h is Plank's constant.
- The energy of these circular orbits have fixed values and hence electron in an atom can have only certain values of energy. It is characteristic of an orbit and it cannot have any orbit value of its own. And therefore energy of an electron is also quantised.
 - As long as electrons remains in these fixed orbits, it doesn't lose energy i.e. energy of an electron is stationary (not changing with time) and therefore these orbits are known as allowed energy levels or stationary states and this explains the stability of atom.
 - The energy levels are designated as K, L, M, N and numbered as 1, 2, 3, 4 etc from nucleus outwards and as the distance of the shells or energy level from the nucleus increases the energy of the energy level also increases i.e., $E_N > E_M > E_L > E_K$

- (vi) The emission or absorption of energy in the form of radiations can only occur when an electron jump from one stationary orbit to other.

$$\Delta E = E_{\text{higher}} - E_{\text{lower}}$$

$\Delta E = hv$ where hv is the energy of absorbed photon or emitted photon which corresponds to the difference in energy levels. Energy is absorbed when electron jumps from lower energy level (normal state) to higher energy level (excited, unstable state) and energy is emitted when electrons jumps from higher energy level to lower energy level.

- ❖ Bohr's model is applicable for one electron species only, like H, He^+ , Li^{+2} , Be^{+3} etc.
- ❖ Derivation of Radius of different orbits in one electron species (using Bohr's model):



$$mv = \frac{nh}{2\pi} \quad \dots(i)$$

$$q_1 = e, q_2 = Ze$$

$$\frac{mv^2}{r} = \frac{kq_1 q_2}{r^2} = \frac{kze^2}{r^2} \quad \dots(ii)$$

$$\Rightarrow \frac{mn^2h^2}{4\pi^2m^2r^2 \cdot r} = \frac{kZe^2}{r^2}$$

$$\Rightarrow r = \frac{mn^2h^2}{4\pi^2m^2kZe^2} \Rightarrow r = \frac{n^2h^2}{4\pi^2mkZe^2}$$

$$\Rightarrow \frac{h^2}{4\pi^2mke^2} \times \frac{n^2}{Z}$$

$$= \frac{(6.625 \times 10^{-34})^2}{4\pi^2 \times 9.1 \times 10^{-31} \times 9 \times 10^9 \times (1.6 \times 10^{-19})^2} \times \frac{n^2}{Z}$$

$$r = 0.529 \times \frac{n^2}{Z} \text{ Å} \Rightarrow r \propto \frac{n^2}{Z}$$

For a particular atom $r \propto n^2$

Radius of 1st orbit of H atom

$$r = 0.529 \text{ Å}$$

Example 14: Calculate ratio of radius of 2nd orbit of H atom to 3rd orbit of Li^{+2} ion:

$$\text{Sol.} = \frac{\text{Radius of 2}^{\text{nd}} \text{ orbit of H atom}}{\text{Radius of 3}^{\text{rd}} \text{ orbit of Li}^{+2} \text{ atom}}$$

$$= \frac{n^2}{Z} \times \frac{Z_1}{n_1^2} = \frac{4}{3}$$

Derivation of Velocity of Electron in Bohr's Orbit

$$v = \frac{nh}{2\pi mr}, \text{ putting value of } r.$$

$$v = \frac{nh \times 4\pi^2 mkZ e^2}{2\pi mn^2 h^2}$$

$$v = \frac{2\pi k Z e^2}{h n} = \frac{2\pi k e^2}{h} \times \frac{Z}{n}$$

$$v = 2.18 \times 10^6 \frac{Z}{n} \text{ m/s}$$

$$v \propto \frac{Z}{n}$$

Derivation of Total Energy of Electron/System

T.E. of system = K.E. of e^- + P.E. of system (nucleus and e^-)

$$\text{kinetic energy of electron} = \frac{1}{2} mv^2 = \frac{1}{2} \frac{kze^2}{r}$$

$$PE = -\frac{kze^2}{r}$$

$$T.E. = \frac{-KZe^2}{2r} \quad \left[r = \frac{n^2 h^2}{4\pi^2 m^2 k z e^2} \right]$$

$$T.E. = -13.6 \times \frac{Z^2}{n^2} \text{ eV/atom} \quad \dots(i)$$

$$T.E. = -2.18 \times 10^{-18} \frac{Z^2}{n^2} \text{ J/atom}$$

As shell no. or distance increases, the value of T.E. and P.E. increases (however magnitude decreases) and becomes maximum at infinity i.e., zero.

Negative sign indicates that electron is under the influence of attractive forces of nucleus.

$$K.E. = -\frac{P.E.}{2}$$

$$T.E. = \frac{P.E.}{2}$$

$$T.E. = -K.E.$$

Calculation of Energy of Energy Level in H atom

(i) When $n = 1$ (ground level)

$$K.E. = 13.6 \text{ eV (atom)}$$

$$P.E. = -27.2 \text{ eV / atom}$$

$$T.E. = -13.6 \text{ eV/atom}$$

(ii) When $n = 2/2^{\text{nd}}$ energy level / 1st excited state

$$K.E. = \frac{13.6}{4} \text{ eV/atom} = 3.4 \text{ eV/atom}$$

$$P.E. = -6.8 \text{ eV/atom}$$

$$T.E. = -3.4 \text{ eV/atom}$$

$$E_2 - E_1 = -3.4 + 13.6 \text{ eV/atom} = 10.2 \text{ eV/atom}$$

(iii) When $n = 3/3^{\text{rd}}$ energy level/2nd excited state.

$$K.E. = \frac{13.6}{9} \text{ eV/atom} = 1.51 \text{ eV/atom}$$

$$P.E. = -3.02 \text{ eV/atom}$$

$$\text{T.E.} = -1.51 \text{ eV/atom}$$

$$E_3 - E_2 = -1.51 \text{ eV/atom} + 3.4 \text{ eV/atom}$$

$$= 1.89 \text{ eV atom.}$$

(iv) When $n = 4/3^{\text{rd}}$ excited state

$$K.E. = \frac{13.6}{4^2} \Rightarrow \frac{13.6}{16 \times 10} = 0.85 \text{ eV/atom}$$

$$P.E. = -1.70 \text{ eV/atom}$$

$$T.E. = -0.85 \text{ eV/atom}$$

$$E_4 - E_3 = 0.66$$

As distance increases (n increases) energy of the energy level increases but energy difference between consecutive energy level keeps on decreasing i.e., maximum energy difference between 2 to 1 (consecutive).

Conclusion from Equation of Energy

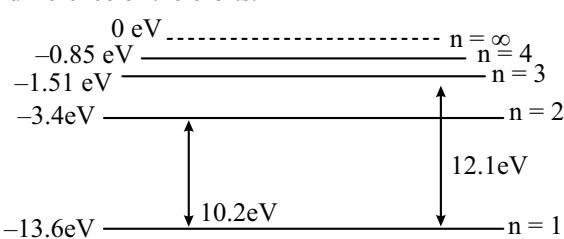
- (a) The negative sign of energy indicates that there is attraction between the negatively charged electron and positively charged nucleus.
- (b) All the quantities on R.H.S. in the energy equation are constant for an element having atomic number Z except 'n' which is an integer such as 1,2,3, etc. i.e. the energy of an electron is constant as long as the value of 'n' is kept constant.
- (c) The energy of an electron is inversely proportional to the square of 'n' with negative sign.

Failures/Limitations of Bohr's theory

- (a) He could not explain the line spectra of atoms containing more than one electron.
- (b) He also could not explain the presence of multiple spectral lines.
- (c) He was unable to explain the splitting of spectral lines in magnetic field (Zeeman effect) and in electric field (Stark effect).
- (d) No conclusion was given for the principle of quantisation of angular momentum.
- (e) He was unable to explain the de-Broglie's concept of dual nature of matter.
- (f) He could not explain Heisenberg's uncertainty principle.

ENERGY LEVEL DIAGRAM

- (i) Orbit of lowest energy is placed at the bottom, and all other orbits are placed above this.
- (ii) The gap between two orbits is proportional to the energy difference of the orbits.



Definition Valid for Single Electron System

- (i) **Ground state:** Lowest energy state of any atom or ion is called ground state of the atom, it is $n = 1$.
 Ground state energy of H-atom = -13.6 eV
 Ground state energy of He^+ Ion = -54.4 eV
- (ii) **Excited State:** States of atom other than the ground state are called excited states:
 $n = 2$ First excited state
 $n = 3$ Second excited state
 $n = 4$ Third excited state
 $n = (n + 1)$ n^{th} excited state
- (iii) **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
- (iv) **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
- (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 .
- (vi) **Excitation Potential:** Potential difference through which an electron must be accelerated from rest to higher energy level. So that its kinetic energy become equal to excitation energy of any state is called excitation potential of that state.
 Excitation potential of third state = excitation potential of second excited state = second excitation potential = 12.09 V .
- (vii) **Binding Energy 'or' Separation 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.



Train Your Brain

Example 16: A single electron system has ionization energy $11180 \text{ kJ mol}^{-1}$. Find the number of protons in the nucleus of the system.

$$\text{Sol. I.E.} = \frac{Z^2}{n^2} \times 21.69 \times 10^{-19} \text{ J/atom}$$

$$\frac{11180 \times 10^3}{6.023 \times 10^{23}} = \frac{Z^2}{1^2} \times 21.69 \times 10^{-19}$$

$$\text{or } Z = 3$$

Example 17: What are the frequency and wavelength of a photon emitted during a transition from $n = 5$ state to the $n = 2$ state in the hydrogen atom?

Sol. Since $n_i = 5$ and $n_f = 2$, this transition gives rise to a spectral line in the visible region of the Balmer series.

$$\Delta E = 2.18 \times 10^{-18} \text{ J} \left[\frac{1}{5^2} - \frac{1}{2^2} \right] = -4.58 \times 10^{-19} \text{ J}$$

It is an emission energy

The frequency of the photon (taking energy in terms of magnitude) is given by

$$v = \frac{\Delta E}{h} = \frac{4.58 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ Js}} = 6.91 \times 10^{14} \text{ Hz and}$$

$$c = v\lambda \text{ or } \lambda = \frac{3 \times 10^8}{6.91 \times 10^{14}} \text{ or } \lambda = 434 \text{ nm}$$

Example 18: The ionization energy of He^+ is $19.6 \times 10^{-18} \text{ J atom}^{-1}$. The energy of the first stationary state of Li^{+2} will be

- (a) $21.2 \times 10^{-18} \text{ J/atom}$ (b) $44.10 \times 10^{-18} \text{ J/atom}$
 (c) $63.2 \times 10^{-18} \text{ J/atom}$ (d) $84.2 \times 10^{-18} \text{ J/atom}$

$$\begin{aligned} \text{Sol. (b)} \quad E_1 \text{ for } \text{Li}^{+2} &= E_1 \text{ for H} \times Z^2_{\text{Li}} = E_1 \text{ for H} \times 9 \\ E_1 \text{ for } \text{He}^+ &= E_1 \text{ for H} \times Z^2_{\text{He}} = E_1 \text{ for H} \times 4 \\ \text{or } E_1 \text{ for } \text{Li}^{+2} &= \frac{9}{4} E_1 \text{ for He}^+ \\ &= 19.6 \times 10^{-18} \times \frac{9}{4} \\ &= 44.10 \times 10^{-18} \text{ J/atom} \end{aligned}$$



Concept Application

12. Consider Bohr's theory for hydrogen atom. The magnitude of angular momentum, orbit radius and velocity of the electron in n^{th} energy state in a hydrogen atom are l , r & v respectively. Find out the value of ' x ', if product of v , r and l (vr/l) is directly proportional to n^x .

- (a) ($x = 1$) (b) ($x = 2$)
 (c) ($x = 3$) (d) ($x = 4$)

13. A single electron ion has nuclear charge $+Ze$ where Z is atomic number and e is electronic charge. It requires 16.52 eV to excite the electron from the second Bohr orbit to third Bohr orbit. Then atomic number, kinetic energy of electron in first Bohr orbit respectively:

- (a) $Z = 3$, K.E. = 122.4 eV
 (b) $Z = 3$, K.E. = 122.2 eV
 (c) $Z = 2$, K.E. = 122.4 eV
 (d) $Z = 3$, K.E. = 121.4 eV

14. Correct order of radius of the Ist orbit of H, He^+ , Li^{2+} , Be^{3+} is:

- $\text{H} > \text{He}^+ > \text{Li}^{2+} > \text{Be}^{3+}$
- $\text{Be}^{3+} > \text{Li}^{2+} > \text{He}^+ > \text{H}$
- $\text{He}^+ > \text{Be}^{3+} > \text{Li}^{2+} > \text{H}$
- $\text{He}^+ > \text{H} > \text{Li}^{2+} > \text{Be}^{3+}$

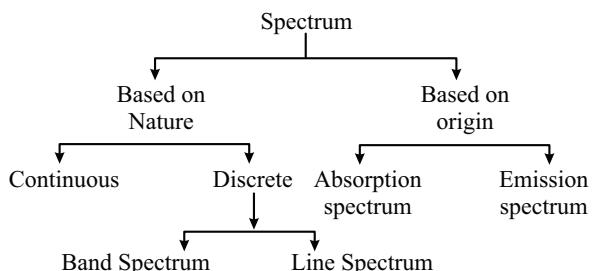
15. Match the following

A. Energy of ground state of He^+	(i) + 6.04 eV
B. Potential energy of I orbit of H-atom	(ii) -27.2 eV
C. Kinetic energy of II excited state of He^+	(iii) 54.4 V
D. Ionisation potential of He^+	(iv) -54.4 eV

- A – (i), B – (ii), C – (iii), D – (iv)
- A – (iv), B – (iii), C – (ii), D – (i)
- A – (iv), B – (ii), C – (i), D – (iii)
- A – (ii), B – (iii), C – (i), D – (iv)

SPECTRUM

Study of Emission and Absorption Spectra: An instrument used to separate the radiation of different wavelengths (or frequencies) is called spectroscope or a spectrograph. Photograph (or the pattern) of the emergent radiation recorded on the film is called a spectrogram or simply a spectrum of the given radiation. The branch or science dealing with the study of spectra is called **spectroscopy**.

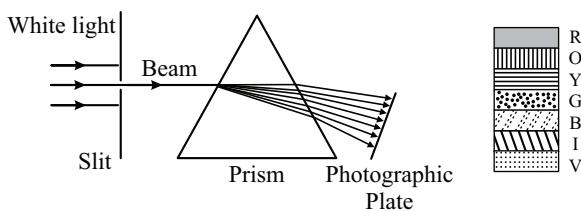


(a) **Emission spectra:** When the radiation emitted from some source e.g. from the sun or by passing electric discharge through a gas at low pressure or by heating some substance to high temperature etc, is passed directly through the prism and then received on the photographic plate, the spectrum obtained is called ‘Emission spectrum’.

Depending upon the source of radiation, the emission spectra are mainly of two type:

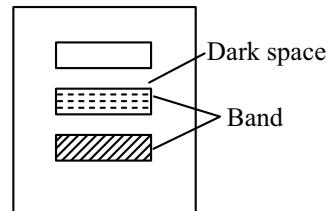
Continuous spectra: When white light from any source such as sun, a bulb or any hot glowing body is analysed by passing through a prism it is observed that it splits

up into seven different wide band of colours from violet to red. These colours are so continuous that each of them merges into the next. Hence the spectrum is called continuous spectrum.



Discrete spectra : It is of two type:

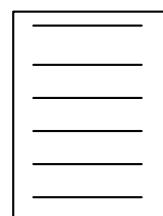
- (i) **Band spectrum**



Band spectrum contains colourful continuous bands separated by some dark space.

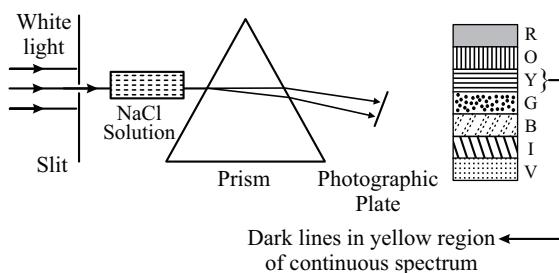
Generally molecular spectrum are band spectrum.

- (ii) **Line Spectrum:**

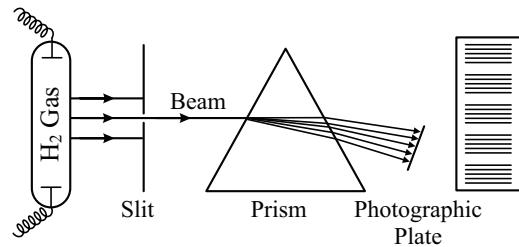


This is the ordered arrangement of lines of particular wavelength separated by dark space e.g. hydrogen spectrum. Line spectrum can be obtained from atoms.

(b) **Absorption spectra:** When white light from any source is first passed through the solution or vapours of a chemical substance and then analysed by the spectroscope, it is observed that some dark lines are obtained in the continuous spectrum. These dark lines are supposed to result from the fact that when white light (containing radiations of many wavelengths) is passed through the chemical substance, radiations of certain wavelengths are absorbed, depending upon the nature of the element.



Emission Spectrum of Hydrogen



When hydrogen gas at low pressure is taken in the discharge tube and the light emitted on passing electric discharge is examined with a spectroscope, the spectrum obtained is called the emission spectrum of hydrogen.

Hydrogen Spectrum (Before Bohr's Model)

The spectrum of H atom is observed as discontinuous line spectra. The line spectra of different in 3 regions UV, visible and IR. The different lines observed H spectrum were classified into different series and named after their discoverers.

Rydberg gave an empirical formula to calculate wavelength, which is applicable to all series.

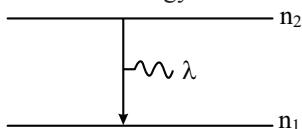
$$\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$R_H = 109677 \text{ cm}^{-1}$ Rydberg's constant.

n_1 and n_2 are integers.

Explanation of Hydrogen Spectrum using Bohr's Model

When electron in an excited atom comes back from higher energy level (n_2) to lower energy level (n_1) then it emits a photon, having energy equal to difference in energy levels.



$$hv = \Delta E = E_{n_2} - E_{n_1}$$

$$hv = \frac{-2\pi^2 mk^2 e^4 z^2}{n_2^2 h^2} - \left(-\frac{2\pi^2 mk^2 e^4 z^2}{n_1^2 h^2} \right)$$

$$hv = \frac{2\pi m k^2 e^4 z^2}{h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\frac{1}{\lambda} = \frac{2\pi m k^2 e^4 z^2}{h^3 C} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

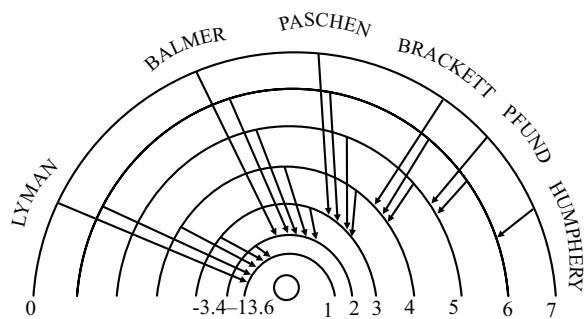
$$\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

The theoretical value is very close to observed value.

∴ Bohr's model provides theoretical explanation of H-spectrum. Wavelength or wave no. of any line of any one electron species can be calculated as:

$$\frac{1}{\lambda} = R_H Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right], \quad \frac{hc}{\lambda} = \Delta E$$

Different Series in Hydrogen Spectrum



Series	Discovered by	Regions	n_2	n_1
Lyman	Lyman	U.V. region	$n_2 = 2, 3, 4, \dots$	$n_1 = 1$
Balmer	Balmer	Visible region	$n_2 = 3, 4, 5, \dots$	$n_1 = 2$
Paschen	Paschen	Infra red (I.R.)	$n_2 = 4, 5, 6, \dots$	$n_1 = 3$
Brackett	Brackett	I.R. region	$n_2 = 5, 6, 7, \dots$	$n_1 = 4$
Pfund	Pfund	I.R. region	$n_2 = 6, 7, 8, \dots$	$n_1 = 5$
Humphrey	Humphrey	Far I.R. region	$n_2 = 7, 8, 9, \dots$	$n_1 = 6$

Key Points

First line / Starting line / Initial line (λ_{\max} and v_{\min})

Last line / Limiting line / Series limit (λ_{\min} and v_{\max})

First line of any series = α line

Second line of any series = β line

Third line of any series = γ line

Total no. of emission lines between n_2 & n_1

$$\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$$

For transition from any orbit 'n' to $n = 1$, total no. of emission lines = $\frac{n(n-1)}{2}$

NO. OF PHOTONS EMITTED BY A SAMPLE OF H-ATOM

If an electron is in any higher state n and makes a transition to ground state, then total no. of different photons emitted is equal

$$\text{to } \frac{n \times (n-1)}{2}.$$

If an electron is in any higher state $n = n_2$ and makes a transition to another excited state $n = n_1$, then total no. of different photons emitted is equal to $\frac{\Delta n(\Delta n + 1)}{2}$, where $\Delta n = n_2 - n_1$.

Note : In case of single isolated atom if electron makes transition from n^{th} state to the ground state then max. number of spectral lines observed = $(n - 1)$.

SPECTRA LINES OF HYDROGEN ATOM

Lyman Series

- ❖ It is first spectral series of H.
- ❖ It was found out in ultraviolet region in 1898 by Lyman.
- ❖ It's value of $n_1 = 1$ and $n_2 = 2,3,4$ where ' n_1 ' is ground state and ' n_2 ' is called excited state of electron present in a H - atom.
- ❖ $\frac{1}{\lambda} = R_H \left[\frac{1}{l^2} - \frac{1}{n_2^2} \right]$ where $n_2 > 1$ always.
- ❖ The wavelength of marginal line = $\frac{n_1^2}{R_H}$ for all series. So for Lyman series $\lambda = \frac{1}{R_H}$.
- ❖ Ist line of lyman series = $2 \rightarrow 1$
- ❖ IInd line of lyman series = $3 \rightarrow 1$
- ❖ Last line of lyman series = $\infty \rightarrow 1$
- ❖ First line of any spectral series is the longest (λ_{max}) line.
- ❖ Last line of any spectral series is the shortest (λ_{min}) line.

Series limit: It is the last line of any spectral series.

Wave no of Ist line of Lyman series

$$\begin{aligned} \frac{1}{\lambda} &= \bar{v} = R \times l^2 \left(\frac{1}{l^2} - \frac{1}{2^2} \right) \\ \bar{v} &= R \times l^2 \left(\frac{4-1}{4} \right) \\ \bar{v} &= \frac{R \times 3}{4} = \frac{3R}{4} \\ \therefore \left[\lambda \right] &= \frac{4}{3R} \end{aligned}$$

Wave no of last line of Lyman series

$$\bar{v} = R \times l^2 \left(\frac{1}{l^2} - \frac{1}{\infty^2} \right) \quad \bar{v} = R$$

Balmer Series

- ❖ It is the second series of H-spectrum.
- ❖ It was found out in 1892 in visible region by Balmer.
- ❖ It's value of $n_1 = 2$ and $n_2 = 3,4,5,\dots$
- ❖ The wavelength of marginal line of Balmer series = $\frac{n_1^2}{R_H}$
- ❖ $= \frac{2^2}{R_H} = \frac{4}{R_H}$
- ❖ $\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n_2^2} \right)$ where $n_2 > 2$ always.

1st line of balmer series = $3 \rightarrow 2$

last line of balmer series = $\infty \rightarrow 2$

$$(\bar{v}) 1^{st} \text{ line} = R \times 1 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = \frac{5R}{36}$$

$$(\bar{v}) \text{ last line} = R \left(\frac{1}{2^2} - \frac{1}{\infty^2} \right) = \frac{R}{4}$$

Paschen Series

- (a) It is the third series of H - spectrum.
 - (b) It was found out in infrared region by Paschen.
 - (c) It's value of $n_1 = 3$ and $n_2 = 4,5,6 \dots$
 - (d) The wavelength of marginal line of Paschen series
- $$\frac{n_1^2}{R_H} = \frac{3^2}{R_H} = \frac{9}{R_H}.$$
- (e) $\frac{1}{\lambda} = R_H \left[\frac{1}{3^2} - \frac{1}{n_2^2} \right]$ where $n_2 > 3$ always.

Brackett Series

- (a) It is fourth series of H - spectrum.
 - (b) It was found out in infrared region by Brackett.
 - (c) It's value of $n_1 = 4$ and $n_2 = 5,6,7 \dots$
 - (d) The wavelength of marginal line of brackett series
- $$= \frac{n_1^2}{R_H} = \frac{4^2}{R_H} = \frac{16}{R_H}$$
- (e) $\frac{1}{\lambda} = R_H \left[\frac{1}{4^2} - \frac{1}{n_2^2} \right]$ where $n_2 > 4$ always.

Pfund Series

- (a) It is fifth series of H- spectrum.
 - (b) It was found out in infrared region by Pfund.
 - (c) It's value of $n_1 = 5$ and $n_2 = 6,7,8 \dots$ where n_1 is ground state and n_2 is excited state.
 - (d) The wavelength of marginal line of Pfund series
- $$= \frac{n_1^2}{R_H} = \frac{5^2}{R_H} = \frac{25}{R_H}$$
- (e) $\frac{1}{\lambda} = R_H \left[\frac{1}{5^2} - \frac{1}{n_2^2} \right]$ where $n_2 > 5$ always.

Humphry Series

- (a) It is the sixth series of H - spectrum.
 - (b) It was found out in infrared region by Humphry.
 - (c) It's value of $n_1 = 6$ and $n_2 = 7, 8, 9 \dots$
 - (d) The wavelength of marginal line of Humphry series
- $$= \frac{n_1^2}{R_H} = \frac{6^2}{R_H} = \frac{36}{R_H}$$
- (e) $\frac{1}{\lambda} = R_H \left[\frac{1}{6^2} - \frac{1}{n_2^2} \right]$ where $n_2 > 6$.

21. An α -particle is accelerated through a potential difference of V volts from rest. The de-Broglie's wavelength associated with it is:

$$(a) \sqrt{\frac{150}{V}} \text{ \AA} \quad (b) \frac{0.286}{\sqrt{V}} \text{ \AA}$$

$$(c) \frac{0.101}{\sqrt{V}} \text{ \AA} \quad (d) \frac{0.983}{\sqrt{V}} \text{ \AA}$$

22. What possibly can be the ratio of the de Broglie wavelengths for two electrons each having zero initial energy and accelerated through 50 volts and 200 volts?

$$(a) 3 : 10 \quad (b) 10 : 3$$

$$(c) 1 : 2 \quad (d) 2 : 1$$

HEISENBERG'S UNCERTAINTY PRINCIPLE

The exact position and momentum of a fast moving particle cannot be calculated precisely at the same moment of time. If Δx is the error in the measurement of position of the particle and if Δp is the error in the measurement of momentum of the particle, then:

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \cdot (m\Delta v) \geq \frac{h}{4\pi}$$

where, Δx = uncertainty in position

Δp = uncertainty in momentum

h = Plank's constant

m = mass of the particle

Δv = uncertainty in velocity

If the position of a particle is measured precisely, i.e. $\Delta x \rightarrow 0$ then $\Delta p \rightarrow \infty$.

If the momentum of the particle is measured precisely. i.e. $\Delta p \rightarrow 0$ then $\Delta x \rightarrow \infty$.

This is because of a principle of optics that if a light of wavelength ' λ ' is used to locate the position of a particle then minimum error in the position measurement will be $\pm \lambda$ amount.

i.e. $\Delta x = \pm \lambda$

If $\Delta x \rightarrow 0$; $\lambda \rightarrow 0$

$$\text{But, } p = \frac{h}{\lambda} \Rightarrow p \rightarrow \infty$$

So, to make $\Delta x \rightarrow 0$, $\lambda \rightarrow 0$ a photon of very high energy is used to locate it.

∴ When this photon will collide with the electron then momentum of electron will get changed by a large amount.

$$\Delta p \cdot \Delta x \geq \frac{h}{4\pi} \quad (\text{Multiplied \& divided by } \Delta t)$$

$$\frac{\Delta p}{\Delta t} \Delta t \cdot \Delta x \geq \frac{h}{4\pi}$$

$$\left(\frac{\Delta p}{\Delta t} = \text{rate of change in momentum} = F \right)$$

$$F \cdot \Delta x \cdot \Delta t \geq \frac{h}{4\pi}$$

$$\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

ΔE → uncertainty in energy

Δt → uncertainty in time

- In terms of uncertainty in energy ΔE , and uncertainty in time Δt , this principle is written as,

$$\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

- Heisenberg replaced the concept of definite orbits by the concept of probability.



Train Your Brain

Example 28: A golf ball has a mass of 40 g, and a speed of 45 m/s. If the speed can be measured within accuracy of 2%, calculate the uncertainty in the position.

Sol. The uncertainty in the speed is 2%,

$$\text{i.e., } 45 \times \frac{2}{100} = 0.9 \text{ m s}^{-1}. \text{ Using the equation}$$

$$\Delta x = \frac{h}{4\pi m \Delta v} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 40 \times 10^{-3} (0.9 \text{ m s}^{-1})}$$

$$= 1.46 \times 10^{-33} \text{ m}$$

This is nearly $\sim 10^{18}$ times smaller than the diameter of a typical atomic nucleus. As mentioned earlier for large particles, the uncertainty principle sets no meaningful limit to the precision of measurements.

Example 29: The uncertainty in measuring speed of a particle is zero. Uncertainty in measuring its position will be

$$(a) \text{ Zero} \quad (b) \frac{h}{4\pi}$$

$$(c) \frac{h}{4\pi m} \quad (d) \text{ Infinite}$$

$$\text{Sol. } \Delta x \cdot \Delta p = \frac{h}{4\pi}$$

$$\text{or } \Delta x \times m \Delta v = \frac{h}{4\pi}$$

$$\text{or } \Delta x = \frac{h}{4\pi \times m \times \Delta v}$$

or $\Delta x = \infty$ as $\Delta v = 0$

Example 30: The mass of a particle is 10^{-10} g and its diameter is 10^{-4} cm. If its speed is 10^{-6} cm/s with 0.0001% uncertainty in measurement, the minimum uncertainty in its position is

$$(a) 5.28 \times 10^{-8} \text{ m} \quad (b) 5.28 \times 10^{-7} \text{ m}$$

$$(c) 5.28 \times 10^{-6} \text{ m} \quad (d) 5.28 \times 10^{-9} \text{ m}$$

Sol. $m = 10^{-10}$ g or $m = 10^{-13}$ kg

$$\Delta v = 10^{-6} \times 10^{-2} \times 0.0001 \times 10^{-2} \text{ m/s} = 10^{-14} \text{ m/s}$$

According to Heisenberg's Uncertainty Principle

$$\Delta x \times m \Delta v = \frac{h}{4\pi} \quad \text{or}$$

$$\Delta x = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 10^{-13} \times 10^{-14}} \text{ m} \quad \text{or} \quad \Delta x = 5.28 \times 10^{-8} \text{ m}$$



Concept Application

23. The uncertainty in the momentum of an electron is $1.0 \times 10^{-5} \text{ kg ms}^{-1}$. The uncertainty in its position will be: ($\hbar = 6.626 \times 10^{-34} \text{ Js}$)
 (a) $1.05 \times 10^{-28} \text{ m}$ (b) $1.05 \times 10^{-26} \text{ m}$
 (c) $5.27 \times 10^{-30} \text{ m}$ (d) $5.25 \times 10^{-28} \text{ m}$
24. If uncertainty in position and momentum of a particle is numerically equal, then the minimum uncertainty in speed of the particle is
 (a) $\sqrt{\frac{\hbar}{2\pi}}$ (b) $\frac{1}{2m}\sqrt{\frac{\hbar}{\pi}}$
 (c) $\sqrt{\frac{\hbar}{\pi}}$ (d) $\frac{1}{m}\sqrt{\frac{\hbar}{\pi}}$
25. Uncertainty in the position of an electron (mass = $9.1 \times 10^{-31} \text{ kg}$) moving with a velocity 300 m/s , accurate up to 0.001% , will be ($\hbar = 6.3 \times 10^{-34} \text{ Js}$)
 (a) $5.76 \times 10^{-2} \text{ m}$ (b) $1.92 \times 10^{-2} \text{ m}$
 (c) $3.84 \times 10^{-2} \text{ m}$ (d) $19.2 \times 10^{-2} \text{ m}$

QUANTUM NUMBER

As we know to search a particular person in this world 4 things are needed:

1. Country to which the person belongs.
2. The city in that country where the person is residing.
3. The area in that city.
4. House number.

Similarly to locate the position of an electron in the atom 4 identification number are required and these identification number are called as quantum number.

1. Principal quantum number (n) → Shell (Orbit)
2. Azimuthal quantum number (l) → Sub shell
3. Magnetic quantum number (m) → Orbital
4. Spin quantum number (s) → Spin of e^-

1. Principal quantum number: Given by Bohr's.

It represents the name, size and energy of the shell to which e^- belongs.

The value of n lies between 1 to ∞ .

i.e $n = 1, 2, 3, 4, \dots, \infty$ corresponding name of shells are K, L, M, N, O, ...

Greater the value of n , greater is the distance from the nucleus.

$$r = 0.529 \times \frac{n^2}{z} \text{ Å}$$

$$r_1 < r_2 < r_3 < r_4 < r_5 \dots$$

Greater the value of n , greater is the energy of shell.

$$E = -13.6 \times \frac{z^2}{n^2} \text{ eV/atom}$$

$$E_1 < E_2 < E_3 < E_4 \dots$$

The angular momentum of a revolving electron is $mv r = \frac{n\hbar}{2\pi}$

Where n = Principal quantum number.

The number of electrons in a particular shell is equal to $2n^2$

2. Azimuthal quantum number / Angular quantum number/ Secondary quantum number /Subsidiary quantum number: Represented by ' l ' (Given by Sommerfeld).

It represents the shape of the subshell and orbital and orbital angular momentum.

Value of l between 0 to $(n-1)$.

i.e. $l = 0, 1, 2, \dots, (n-1)$.

$l = 0$ (s Subshell)

$l = 1$ (p Subshell)

$l = 2$ (d Subshell)

$l = 3$ (f Subshell)

If $n = 1$ then $l = 0 \Rightarrow 1s$ i.e. in $n=1$ shell, only one subshell 's' is present.

If $n = 2$ then $l = 0, 1 \Rightarrow 2s, 2p$ i.e. in $n=2$ shell, two subshell 's' & 'p' are present.

If $n = 3$ then $l = 0, 1, 2 \Rightarrow 3s, 3p, 3d$ i.e. in $n=3$ shell, three subshell 's', 'p' & 'd' are present.

If $n = 4$ then $l = 0, 1, 2, 3 \Rightarrow 4s, 4p, 4d, 4f$ i.e. in $n=4$ shell, four subshell 's', 'p', 'd' & 'f' are present.

If the value of n is same then the order of energy of the various subshell will be:

$$s < p < d < f$$

$$4s < 3p < 4p < 3d < 4d < 2p < 3s < 2p < 3p < 4s < 3d < 2s < 2p$$

If Value of l is same but value of n is different then the order of energy will be:

$$1s < 2s < 3s < 4s < 5s < 6s$$

$$3d < 4d < 5d < 6d$$

$$4p < 5p < 6p$$

$$\text{The orbital angular momentum} = \sqrt{l(l+1)} \cdot \frac{\hbar}{2\pi} \quad \text{or} \\ \sqrt{l(l+1)\hbar} \quad \left\{ \because \hbar = \frac{\hbar}{2\pi} \right\} \quad \{ \hbar \text{ is called as 'hash'} \}$$

Orbital angular momentum : For s subshell = 0

$$\text{For p Subshell} = \sqrt{2} \cdot \frac{\hbar}{2\pi} \text{ or } \sqrt{2}\hbar.$$

The number of electron in a particular subshell is equal to $2(2l+1)$.

for s subshell number of electrons = $2 e^-$

for p subshell number of electrons = $6 e^-$

for d subshell number of electrons = $10 e^-$

for f subshell number of electrons = $14 e^-$

Shape of the subshell:

s → spherical

p → dumb bell shape

d → double dumb bell shape

f → complex shape

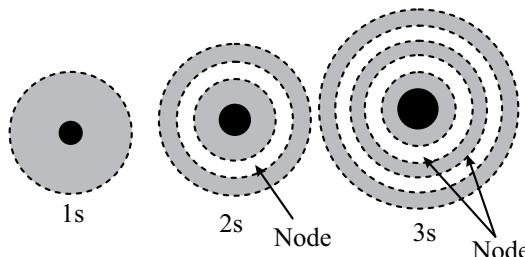
3. Magnetic quantum number /Orientation quantum number (m): given by linde. It represents the shape of different orbitals and the orientation of electron cloud (orbital).

Under the influence of magnetic field each subshell is further subdivided into orbitals (The electron cloud is known as orbital). Magnetic quantum number describe these different distribution of electron cloud.

Value of $m =$ all integral value from $-\ell$ to $+\ell$ including zero. i.e. Value of $m = -\ell \dots 0 \dots +\ell$

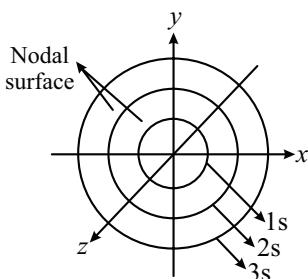
Case-I: If $\ell = 0$ then $m = 0$ it implies that s subshell has only one orbital called as s orbital.

Shapes of s-orbitals: The s-orbitals are spherically symmetrical about the nucleus, i.e., the probability of finding ns electron is same in all directions from the nucleus. 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 figure.



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 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 increases, i.e., the size and energy of s-orbital increases in the order $1s < 2s < 3s \dots$



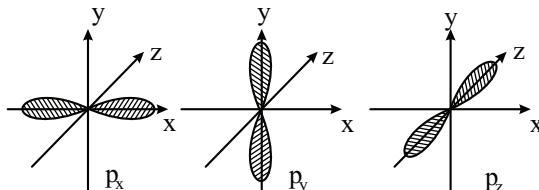
The s orbital of higher energy levels are also symmetrically spherical and can be represented as follows:

Case-II: If $\ell = 1$ (p-subshell) then $m = -1, 0, +1$
It implies that, p subshell have three orbitals called as p_x, p_y and p_z .

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 axis (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 node or nucleus).



The two lobes of each orbital are separated by a plane of zero electron density called nodal plane.

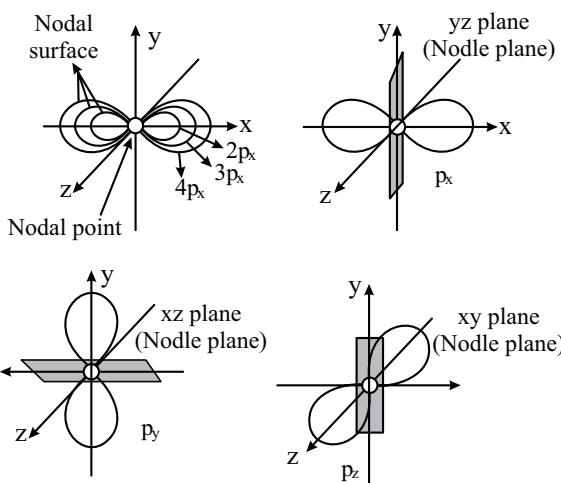
Each p orbital of higher energy level are also dumb bell shape but they have nodal surface.

Nodal surface: Orbital Nodal Surface

$2 p_x$	0	$3 p_x$	1
$4 p_x$	2	$n p_x$	$(n - 2)$

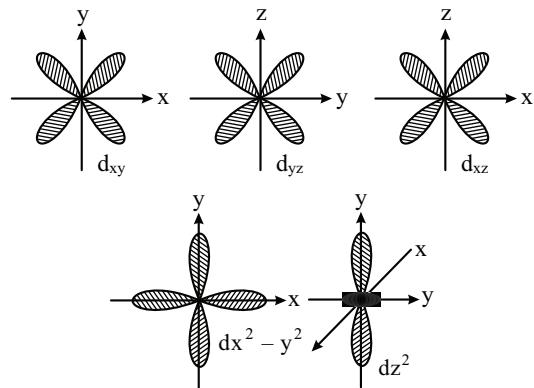
Nodal Plane: Orbital Nodal plane

p_x	y _z plane
p_y	x _z plane
p_z	x _y plane



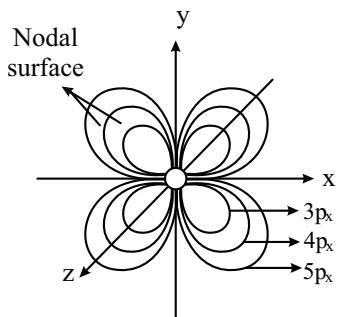
Case-III: When $\lambda = 2$, ' m ' has five values $-2, -1, 0, +1, +2$. It implies that d subshell of any energy shell has five orbitals. All the five orbitals are not identical in shape. Four of the d orbitals $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}$ contain four lobes while fifth orbital d_{z^2} consists of only two lobes. The lobes d_{xy} orbital lie between x and y axis. Similar is the case for d_{yz} and d_{zx} . 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. Geometry of d orbital is Double Dumb bell.

Shape of d-orbitals: It implies that d subshell has 5 orbitals i.e. five electron cloud and can be represented as follows.



Each d-orbital of higher energy level are also double dumbbell shape but they have nodal surface.

In d orbital:



(i) Nodal Point $\rightarrow 1$

(ii) Nodal Surface $\rightarrow 3d_{xy} \rightarrow 0$ Nodal surface
 $4d_{xy} \rightarrow 1$ Nodal surface
 $5d_{xy} \rightarrow 2$ Nodal surface
 $nd_{xy} \rightarrow (n-3)$

Number of nodal surface = $n-\ell-1$

(iii) Nodal plane : $d_{xy} \rightarrow xz \& yz$ nodal plane.
 $d_{xz} \rightarrow xy \& zy$ nodal plane.
 $d_{zy} \rightarrow dzx \& yx$ nodal plane.
 $d_{x^2-y^2} \rightarrow 0$, nodal plane.
 $d_z \rightarrow 0$, nodal plane.

Note: Orbitals of d subshell are Equivalent in energy.

f subshell : When $\ell = 3$ (f subshell)

Then the structure of f-orbital is very complex.

The number of values of f-orbitals in f subshell show that f subshell has 7 orbitals which are equivalent in energy.

Representation of the orbitals :

s subshell \rightarrow

p subshell \rightarrow

d subshell \rightarrow

f

f subshell \rightarrow

4. Spin Quantum number (s): Given by Gold schmidt.

It represents the direction of electron spin around its own axis.

For clock wise spin/spin up (\uparrow) electron $\rightarrow \pm \frac{1}{2}$.

For anticlock wise spin/spin down (\downarrow) electron $\rightarrow \mp \frac{1}{2}$.

Spin angular momentum of an $e^- = \sqrt{s(s+1)} \cdot \frac{\hbar}{2\pi}$.
or $\sqrt{s(s+1)} \hbar$

Each orbital can accomodate 2 electrons with opposite spin or spin paired.

Correct spin paired

Wrong spin paired



Train Your Brain

Example 31: For $5dz^2$, calculate the value of n, l, m and s .

Sol. $n = 5, l = 2, m = 0, s = +\frac{1}{2}$ or $-\frac{1}{2}$

Example 32: Which of the following set of Quantum number is not possible?

(a) $n = 3, l = +2, m = 0, s = +\frac{1}{2}$

(b) $n = 3, l = 0, m = 0, s = -\frac{1}{2}$

(c) $n = 3, l = 0, m = 1, s = +\frac{1}{2}$

(d) $n = 3, l = 1, m = 0, s = -\frac{1}{2}$

Sol. (c) For s-subshell $l = 0$ then should be $m = 0$

Example 33: The orbital angular momentum of an electron is 2s orbital is

(a) $+\frac{1}{2} \cdot \frac{\hbar}{2\pi}$

(b) 0

(c) $\frac{\hbar}{2\pi}$

(d) $\sqrt{2} \frac{\hbar}{4\pi}$

Sol. The orbital angular momentum $= \sqrt{l(l+1)} \frac{\hbar}{2\pi}$.

For 2s orbital, $l = 0$

\therefore Orbital angular momentum $= \sqrt{0(0+1)} \frac{\hbar}{2\pi} = 0$

Example 34: The number of orbitals of g-type

(a) 5

(b) 7

(c) 9

(d) 11

Sol. For g - subshell, $l = 4$.

Therefor no. of orbital $= -l$ to $+l$.

i.e. -4 to $+4$ (including zero).

Hence in g-subshell, 9 orbitals are present.



Concept Application

Rules for Filling Subshell

1. Aufbau Principle.

2. $(n + l)$ rule.

3. Hund's maximum multiplicity principle.

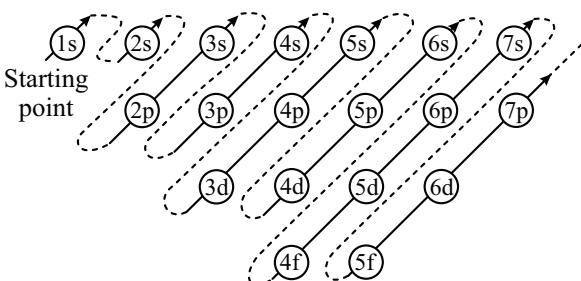
4. Pauli's exclusion principle.

1. **Aufbau Principle:** Aufbau is a German word and its meaning ‘Building up’.

Aufbau principle gives a sequence in which various subshell are filled up depending on the relative order of the energies of various subshell

Principle: The subshell with minimum energy is filled up first when this subshell obtained maximum quota of electrons then the next subshell of higher energy starts filling.

The sequence in which various subshell are filled are as follows.

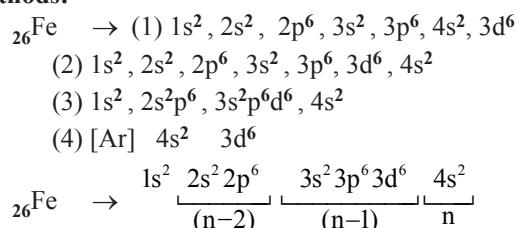


$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14},$
 $5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}, \dots$

For Ex.

${}_1^{\text{H}}$	\rightarrow	$1s^1$
${}_2^{\text{He}}$	\rightarrow	$1s^2$
${}_3^{\text{Li}}$	\rightarrow	$1s^2, 2s^1$
${}_4^{\text{Be}}$	\rightarrow	$1s^2, 2s^2$
${}_5^{\text{B}}$	\rightarrow	$1s^2, 2s^2, 2p^1$
${}_6^{\text{C}}$	\rightarrow	$1s^2, 2s^2, 2p^2$
${}_7^{\text{N}}$	\rightarrow	$1s^2, 2s^2, 2p^3$
${}_8^{\text{O}}$	\rightarrow	$1s^2, 2s^2, 2p^4$
${}_9^{\text{F}}$	\rightarrow	$1s^2, 2s^2, 2p^5$
${}_{10}^{\text{Ne}}$	\rightarrow	$1s^2, 2s^2, 2p^6$
${}_{11}^{\text{Na}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^1$
${}_{12}^{\text{Mg}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2$
${}_{13}^{\text{Al}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^1$
${}_{14}^{\text{Si}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^2$
${}_{15}^{\text{P}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^3$
${}_{16}^{\text{S}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^4$
${}_{17}^{\text{Cl}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^5$
${}_{18}^{\text{Ar}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6$
${}_{19}^{\text{K}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$
${}_{20}^{\text{Ca}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$
${}_{21}^{\text{Sc}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$
${}_{22}^{\text{Ti}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^2$
${}_{23}^{\text{V}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3$
${}_{24}^{\text{Cr}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$ [Exception]
${}_{25}^{\text{Mn}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$
${}_{26}^{\text{Fe}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$
${}_{27}^{\text{Co}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^7$
${}_{28}^{\text{Ni}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8$
${}_{29}^{\text{Cu}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$ [Exception]
${}_{30}^{\text{Zn}}$	\rightarrow	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$

30 Electronic configuration can be written by following different methods:



$n \rightarrow$ Outer most shell or ultimate shell or valence shell.
In this shell e^- are called as valance electron or this is called core charge.

(n-1) → Penultimate shell or core or pre valence Shell

(n-1) \rightarrow Penultimate shell of C
 (n-2) \rightarrow Pre penultimate shell

If we remove the last n shell (ultimate shell) then the remaining shell collectively be called as Kernal

Ex. $^{26}\text{Fe} \rightarrow \underbrace{\text{1s}^2 \text{2s}^2 \text{2p}^6 \text{3s}^2 \text{3d}^6 \text{3p}^6}_{\text{Kernal}} \text{4s}^2$

2. ($n+l$) rule: According to it the sequence in which various subshell are filled up can also be determined with the help of ($n+l$) value for a given subshell.

Principle of ($n+l$) rule: The subshell with lowest ($n+l$) value is filled up first. When two or more subshell have same ($n+l$) value then the subshell with lowest value of n is filled up first.

Sub shell n ℓ $n+\ell$

1s	1	0	1
2s	2	0	2
2p	2	1	3
3s	3	0	3
3p	3	1	4
4s	4	0	4
3d	3	2	5
4p	4	1	5
5s	5	0	5
4d	4	2	6
5p	5	1	6
6s	6	0	6

Order : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}, \dots$

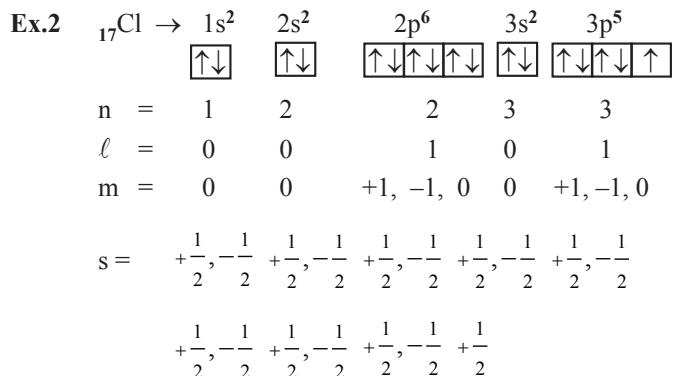
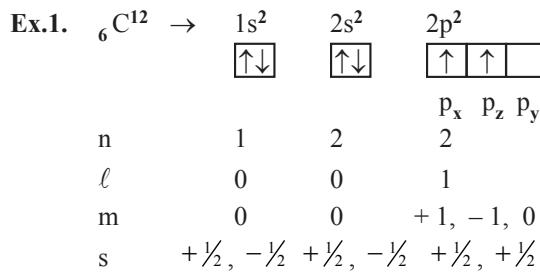
3. Hund's Maximum Multiplicity Rule: (Multiplicity: Many of the same kind).

According to Hund's rule electrons are distributed among the orbitals of subshell in such a way as to give maximum number of unpaired electron with parallel spin.

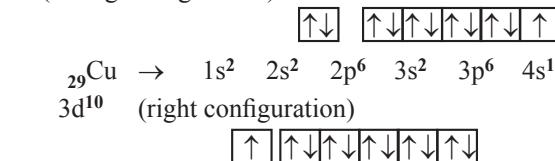
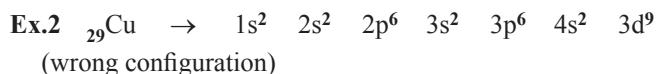
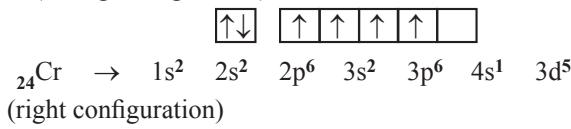
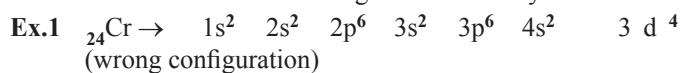
Thus the orbital available in the subshell are first filled singly with parallel spin electron before they begin to pair this means that pairing of electrons occurs with the introduction of second electron in 's' subshell, fourth electron in 'p' subshell, 6th electron in 'd' Subshell & 8th e⁻ in 'f' subshell.

Ex. ${}^5B \rightarrow$	$1s^2$	$2s^2$	$2p^1$
			
${}^6C \rightarrow$	$1s^2$	$2s^2$	$2p^2$
			
${}^7N \rightarrow$	$1s^2$	$2s^2$	$2p^3$
			
${}^8O \rightarrow$	$1s^2$	$2s^2$	$2p^4$
			
${}^9F \rightarrow$	$1s^2$	$2s^2$	$2p^5$
			
${}^{10}Ne \rightarrow$	$1s^2$	$2s^2$	$2p^6$
			

4. Pauli's Exclusion principle: In 1925 Pauli stated that no two electron in an atom can have same values of all four quantum numbers, i.e. An orbital can accommodate maximum 2 electrons with opposite spin.



Exception of Aufbau principle: In some cases it is seen that the electronic configuration is slightly different from the arrangement given by Aufbau principle. A simple reason behind this is that half filled & full filled subshell have got extra stability.



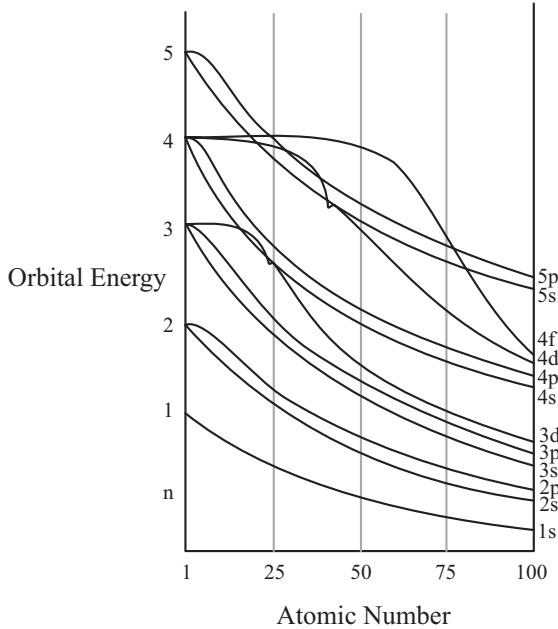
Symmetrical Distribution of Electrons

- ❖ It is well known that symmetry leads to stability.
- ❖ The completely filled or half-filled sub-shells have symmetrical distribution of electrons in them and are therefore more stable.
- ❖ Electrons in the same sub-shell (here 3d) have equal energy but different spatial distribution.
- ❖ Consequently, their shielding of one another is relatively strongly attracted by the nucleus.

Exchange Energy

- ❖ The stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a sub-shell.
- ❖ These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy.

- ❖ The number of exchanges that can take place is maximum when the sub-shell is either half-filled or completely filled.
 - ❖ As a result the exchange energy is maximum and so is the stability.
 - ❖ You may notice that the exchange energy is at the basis of Hund's rule that electrons which enter orbitals of equal energy have parallel spins as far as possible.
 - ❖ In other words, the extra stability of half-filled and completely filled sub-shell is due to:
 - ❖ Relatively small shielding
 - ❖ Smaller coulombic repulsion energy
 - ❖ Larger exchange energy
 - ❖ Symmetrical distribution of electrons

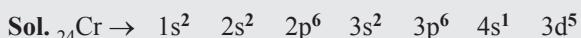


Variation of orbital energy with atomic number

Variation of orbital energy with atomic number

Train Your Brain

Example 35: Calculate the number of unpaired e^- in Cr.



In ^{24}Cr , 6e⁻ are unpaired.

Example 36: The number of unpaired e^- in Cr^{+3} :



In Cr^{+3} , $3e^-$ are unpaired.

Example 37: The number of unpaired e^- in 3d subshell of Cr^{+3}



Therefore number of unpaired electron in 3d subshell is 3.

Example 38: The number of unpaired e^- in Fe^{+2} & Fe^{+3}



$$\text{Fe}^{+3} \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^5 = 5 \text{ unpaired e}^-$$



Concept Application

Set	n	ℓ	m	s
(i)	1	0	1	$+\frac{1}{2}$
(ii)	3	0	0	$-\frac{1}{2}$
(iii)	1	2	2	$+\frac{1}{2}$
(iv)	4	3	-3	$+\frac{1}{2}$
(v)	5	2	1	$-\frac{1}{2}$
(vi)	3	2	1	0

- (a) (i), (iii) (b) (i), (ii), and (vi)
(c) (i), (iii), and (vi) (d) (i), (iii), and (iv)

33. The total spin resulting from a d⁷ configuration is :
(a) 1 (b) 2
(c) 5/2 (d) 3/2

34. Given is the electronic configuration of element X:
K L M N

The number of electrons present with $\ell = 2$ in an atom of element X is :

THE QUANTUM/WAVE MECHANICAL MODEL

- ❖ Quantum mechanics is a theoretical science that deals with the study of the motions of the microscopic objects that have both observable wave-like and particle-like properties.
 - ❖ It specifies the laws of motion that these objects obey.
 - ❖ When quantum mechanics is applied to macroscopic objects (for which wave like properties are insignificant) the results are the same as those from the classical mechanics.
 - ❖ Quantum mechanical model of atom is the picture of the structure of the atom, which emerges from the application of the Schrödinger equation to atoms.

- For a particle whose energy does not vary with time, the Schrodinger equation may be written as

$$\hat{H}\Psi = E\Psi$$

- where \hat{H} = Hamiltonian or Total energy operator, ψ = wave function

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m(E - V)}{h^2} \psi = 0$$

where x,y and z are Cartesian Co-ordinates, m = mass of the electron,

E = Total energy of the electron, V = PE of the electron,

ψ = Wave function of the electron

- For a given system for which V and m are known, we can use the Schrödinger equation to obtain value of E (the allowed energies of the particle) & ψ (the wave function).

- For H-atom, PE (V) = $-\frac{Ke^2}{r}$

- Schrodinger's wave equation becomes

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m \left(E + \frac{Ke^2}{r} \right)}{h^2} \psi = 0$$

- The wave function itself has no physical meaning, but ψ^2 is a probability density and for this to be the case, ψ must have certain properties:

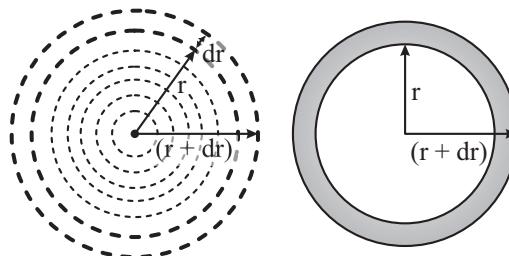
- It must be finite for all values of x;
- It can only have one value for any value of x;
- And $\frac{d\psi}{dx}$ must vary continuously as x varies.
- ψ must be continuous, have a continuous slope, be single-valued, & be square integrable.
- The results (solutions) of wave equation are
 - The wave function is a solution of the Schrodinger equation and describes the behavior of an electron in region of space called the atomic orbital.
 - We can find energy values that are associated with particular wave functions.
 - The quantization of energy levels arises naturally from the Schrodinger equation.
 - A wave function is a mathematical function that contains detailed information about the behavior of an electron.
 - An atomic wave function consists of a radial component, R (r), and an angular component, A (β, ϕ).
 - The region of space defined by a wave function is called an atomic orbital.

- "For a three dimensional wave function of a particle, if the wave function of a particle has the value ψ at some point, then probability of finding a particle in a small volume (dV) around that point is $|\psi|^2 dV$ ".

- The wave function ψ is a probability amplitude in the sense that its square modulus ($|\psi|^2$) is a probability density.
- The physical significance of ψ is difficult to understand, but $|\psi|^2$ has a clear physical significance of being the probability density (probability per unit volume) of the location of particle.

Radial Probability Function

- According to Max Born, probability of finding an electron in a small volume dV is $|\psi|^2 dV$.
- Radial probability distribution function = $R^2 dV$. (where R = radial wave function)
- In order to find the value of dV, the entire space of the electron orbital around the nucleus is supposed to be divided into small imaginary concentric shells of very small thickness dr, each.
- Let us find out the volume of the space in between two such shells.



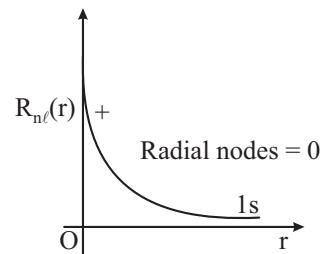
RADIAL WAVE FUNCTION FOR H-LIKE ATOMS

- $R_{n,\ell}$ = Constant \times polynomial \times Exponential.

(A) $R_{n,\ell}(r)$ v/s r plots:

(i) 1s-orbital:

$$R_{1,0} = 2 \left(\frac{Z}{a_0} \right)^{3/2} \times 1 \times e^{-Zr/a_0}$$



- 1s - orbital has a finite value of $R_{n,\ell}(r)$ at nucleus.

(ii) 2s-orbital:

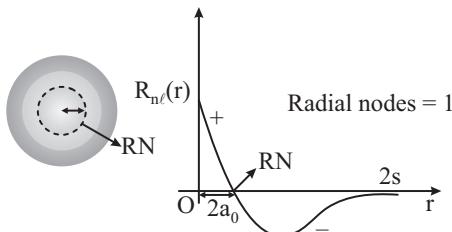
$$R_{2,0} = \left(\frac{Z}{a_0} \right)^{3/2} \frac{1}{2\sqrt{2}} \times \left(2 - \frac{Zr}{a_0} \right) \times e^{-Zr/2a_0}$$

(a) If $2 > \frac{Zr}{a_0}$, then $R_{2,0}$ is + ve.

(b) If $\frac{Zr}{a_0} > 2$, then $R_{2,0}$ is - ve.

(c) If $\frac{Zr}{a_0} = 2$, then $R_{2,0}$ is 0.

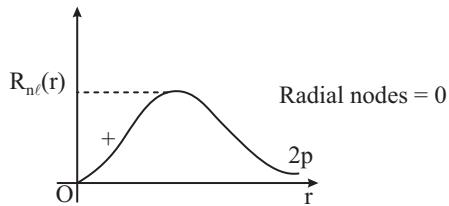
$$\text{At Radial node, } r = \frac{2a_0}{Z}$$



2s - orbital has a finite value of $R_{n,\ell}(r)$ at nucleus.
2s - orbital also decays exponentially but its decay slower than 1s - orbital.

(iii) 2p-subshell:

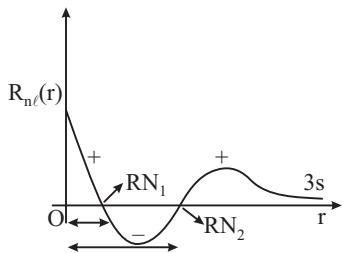
$$R_{2,1} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{2\sqrt{6}} \times \left(\frac{Zr}{a_0}\right) \times e^{-Zr/2a_0}$$



2p - orbital has zero value of $R_{n,\ell}(r)$ at nucleus.
2p - orbital has a maxima in the $R_{n,\ell}(r)$ v/s r plot.

(iv) 3s-orbital:

$$R_{3,0} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{2}{81\sqrt{3}} \times \left(27 - 18\frac{Zr}{a_0} + \frac{2Z^2r^2}{a_0^2}\right) \times e^{-Zr/3a_0}$$

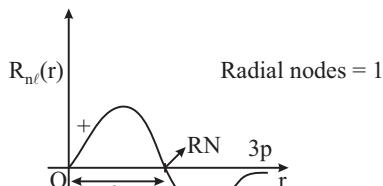


Radial nodes = 2

3s - orbital has a finite value of $R_{n,\ell}(r)$ at nucleus.

(v) 3p-subshell:

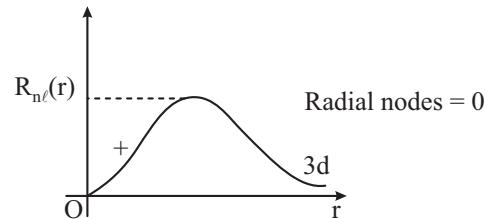
$$R_{3,1} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{4}{81\sqrt{6}} \times \left(6\frac{Zr}{a_0} - \frac{Z^2r^2}{a_0^2}\right) \times e^{-Zr/3a_0}$$



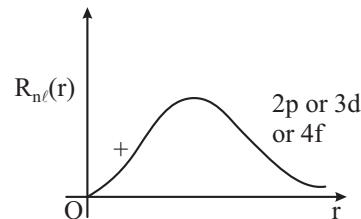
3p - orbital has zero value of $R_{n,\ell}(r)$ at nucleus.

(vi) 3d-subshell:

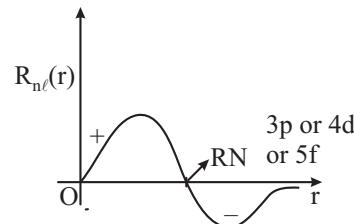
$$R_{3,2} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{4}{81\sqrt{30}} \times \frac{Z^2r^2}{a_0^2} \times e^{-Zr/3a_0}$$



3d - orbital has zero value of $R_{n,\ell}(r)$ at the nucleus.



peak height: 2p > 3d ? 4f

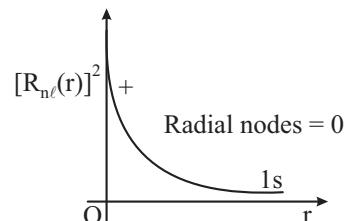


- ❖ For all orbitals other than s-orbital, $R_{n,\ell}(r) = 0$ at the nucleus.
- ❖ For all 1s - orbitals, $R_{n,\ell}(r)$ is always positive.
- ❖ For the first orbital of other types (i.e. 2p, 3d, 4f etc), $R_{n,\ell}(r)$ is +ve everywhere except at the origin.
- ❖ For the second orbital of a given type (i.e. 2s, 3p, 4d, 5f etc.), $R_{n,\ell}(r)$ may be + ve or - ve but the radial wave function has only 1 sign change, i.e. they have 1 radial node.
- ❖ For the third orbital of a given type (i.e. 3s, 4p, 5d, 6f etc.), $R_{n,\ell}(r)$ may have 2 sign changes i.e. they have 2 radial nodes.

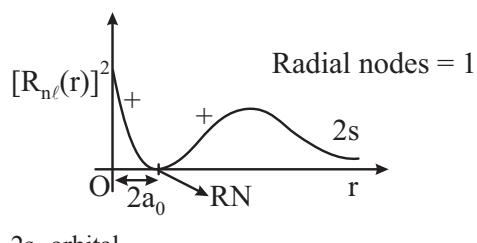
(B) $[R_{n,\ell}(r)]^2$ v/s r plots:

$[R_{n,\ell}(r)]^2$ would always be +ve, irrespective of the sign of $R_{n,\ell}(r)$ for a given value of r. R^2 represents the probability density of finding electron at a particular point in space.

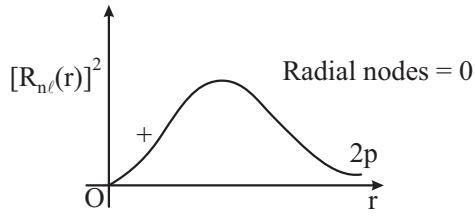
(i) 1s - orbital:



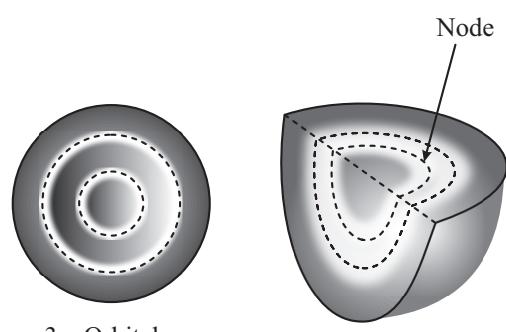
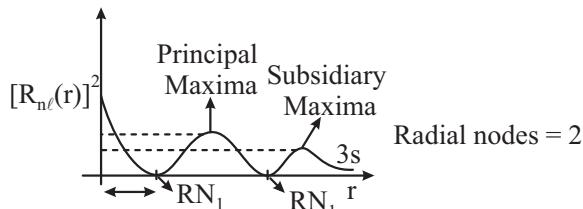
(ii) 2s - orbital:



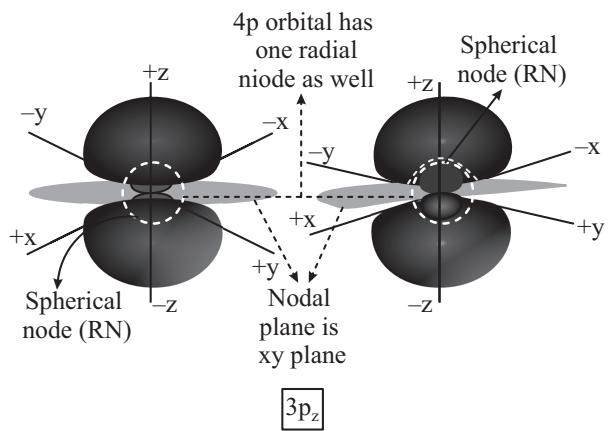
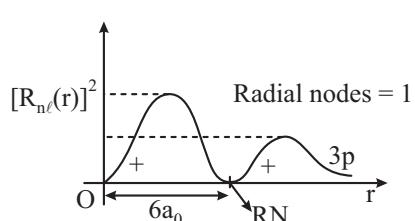
(iii) 2p - subshell:



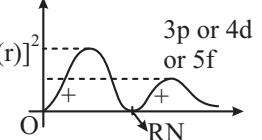
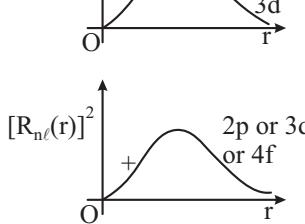
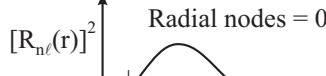
(iv) 3s - orbital:



(v) 3p-subshell:



(vi) 3d-subshell:



- ❖ Note: first maxima is higher than second & second is higher than third.

- ❖ $R_{n,l}(r)$ v/s r plot, R^2 v/s r plot & $4\pi r^2 R^2$ v/s r plot are all same for '2p' orbital, '3d' orbital, '4f' orbital etc.

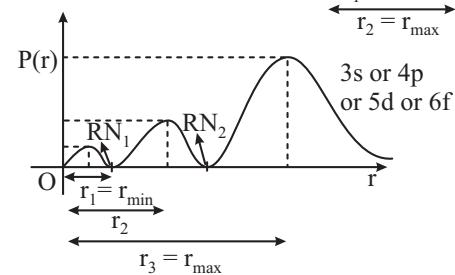
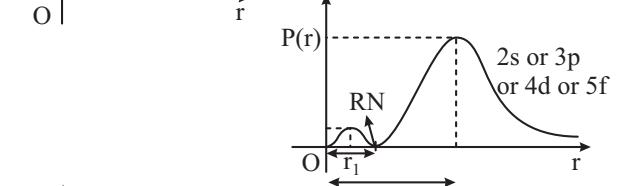
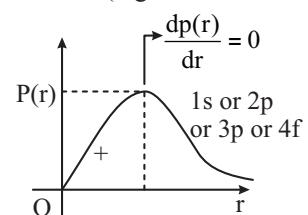
(C) $4\pi r^2 [R_{n,l}(r)]^2$ v/s r plots:

- ❖ Radial distribution function or radial probability distribution function (RPDF)

$$= p(r) dr = 4\pi r^2 [R_{n,l}(r)]^2 dr$$

$$p(r) = 4\pi^2 [R_{n,l}(r)]^2$$

The radial distribution is the probability function of choice to determine the most likely radius to find the electron for a given orbital (regardless of its direction).





Train Your Brain

Example 39: The Schrodinger wave equation for hydrogen atom is

$$\Psi_{2s} = \frac{1}{4\sqrt{2}\pi} \left(\frac{1}{a_0} \right)^{3/2} \left(2 - \frac{r_0}{a_0} \right) e^{-r_0/a_0}$$

Where a_0 is Bohr's radius. If the radial node in 2s be at r_0 , then find r_0 in terms of a_0 .

Sol.

$\Psi_{2s}^2 = \text{Probability of finding electron within } 2s \text{ sphere}$

$\Psi_{2s}^2 = 0 \text{ at node}$

$$\therefore \frac{1}{32\pi} \left(\frac{1}{a_0} \right)^3 \left(2 - \frac{r_0}{a_0} \right)^2 e^{-\frac{2r_0}{a_0}} = 0$$

$$\left(2 - \frac{r_0}{a_0} \right)^2 = 0; \left(2 - \frac{r_0}{a_0} \right) = 0$$

$$2 = \frac{r_0}{a_0}$$

$$\therefore r_0 = 2a_0$$

Example 40: The Schrodinger wave equation for hydrogen atom is

$$\Psi(\text{radial}) = \frac{1}{16\sqrt{4}} \left(\frac{Z}{a_0} \right)^{3/2} (\sigma - 1)(\sigma^2 - 8\sigma + 12) e^{-\sigma/2}$$

❖ Where a_0 and Z are the constant in which answer can be expressed and $\sigma = \frac{2Zr}{a_0}$. Minimum and maximum position of radial nodes from nucleus are ... respectively.

(a) $\frac{a_0}{Z}, \frac{3a_0}{Z}$

(b) $\frac{a_0}{2Z}, \frac{a_0}{Z}$

(c) $\frac{a_0}{2Z}, \frac{3a_0}{Z}$

(d) $\frac{a_0}{2Z}, \frac{4a_0}{Z}$

Sol. At the node, Since $\psi^2 = 0$, thus $\psi = 0$.

(i) $(\sigma - 1) = 0, \sigma = 1 \quad \therefore r_0 = \frac{a_0}{2Z}$

(ii) $(\sigma^2 - 8\sigma + 12) = 0 \quad (\sigma^2 - 6\sigma - 2\sigma + 12) = 0$
 $(\sigma - 6)(\sigma - 2) = 0; \sigma = 6 = \frac{2Zr_0}{a_0};$

$$\therefore r_0 = \frac{3a_0}{Z}$$

Radial nodes are at, $\frac{a_0}{2Z}, \frac{a_0}{Z}$ and $\frac{3a_0}{Z}$.



Concept Application

35. 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 $a_0 = 0.529 \text{ \AA}$; Z = atomic number,
 r = radial distance from nucleus.

The radial node of orbital is at distance from nucleus.

36. The correct time independent Schrödinger's wave equation for an electron with E as total energy and V as potential energy is :

$$(a) \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2}{mh^2}(E - V)\psi = 0$$

$$(b) \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi m}{h^2}(E - V)\psi = 0$$

$$(c) \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

$$(d) \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi m^2}{h}(E - V)\psi = 0$$

Rutherford's Scattering Experiment

$Q = ne$ (charge is quantized)

$$\text{P.E.} = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}$$

Mass Number and Atomic Number

Mass number of an element = No. of protons (Z) + No. of neutrons (n).

Distance of Closest Approach

$$\text{Closest distance (r)} = \frac{4KZe^2}{m_\alpha v_\alpha^2}$$

Wave and its Characteristics

$$\bar{v} = \frac{1}{\lambda}$$

$$v = v \times \lambda$$

$$E_0 = hv \quad (v - \text{Frequency of light})$$

$$E_0 = \frac{hc}{\lambda} \quad (c - \text{speed of light})$$

Photoelectric Effect

$$hv = hv_0 + \frac{1}{2} m_e v^2$$

Bohr's Model of Atom

$$\triangleright \frac{mv^2}{r} = \frac{Ke^2 Z}{r^2}$$

$$\triangleright mvr = \frac{nh}{2\pi}$$

$$\triangleright \frac{hc}{\lambda} = \Delta E$$

$$\triangleright v = \frac{\Delta E}{h}$$

$$\triangleright r = \frac{n^2 h^2}{4\pi^2 m K Z e^2}$$

$$\triangleright r_n = 0.529 \times \frac{n^2}{Z} \text{ \AA}$$

$$\triangleright v = \frac{2\pi Z e^2 K}{nh}$$

$$\triangleright v_n = 2.18 \times 10^6 \times \frac{Z}{n} \text{ m/sec}$$

$$\triangleright T = \frac{2\pi r}{v}$$

$$\triangleright f = \frac{v}{2\pi r}$$

$$\triangleright \text{T.E.} = E_n = -\frac{2\pi^2 m e^4 k^2}{h^2} \left(\frac{z^2}{n^2} \right)$$

$$\triangleright E_n = -13.6 \frac{Z^2}{n^2} \text{ eV / atom}$$

$$\triangleright E_n = -2.18 \times 10^{-18} \frac{Z^2}{n^2} \text{ J/atom}$$

$$\triangleright \text{T.E.} = \frac{1}{2} \text{ P.E.}$$

$$\triangleright \text{T.E.} = -\text{K.E.}$$

Emission Spectrum of Hydrogen

$$\triangleright \frac{1}{\lambda} = \bar{v} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$R = \text{Rydberg constant} = 1.09678 \times 10^7 \text{ m}^{-1}$$

- Number of different line produce = $\frac{\Delta n(\Delta n + 1)}{2}$, where Δn
 $= n_2 - n_1$.
 n_2 = higher energy orbit, n_1 = lower energy orbit.
 - For single isolated atom max. number of spectral lines observed = $(n - 1)$.

De-Broglie's Hypothesis

$$\lambda = \frac{h}{mv}$$

$$\lambda = \frac{h}{\sqrt{2emV}}$$

$$\lambda = \frac{12.3}{\sqrt{V}} \text{ Å}$$

Heisenberg's Uncertainty

$$\nabla \Delta x \cdot \Delta p \geq \frac{h}{4\pi} \text{ or } \Delta x \cdot (m\Delta v) \geq \frac{h}{4\pi}$$

$$\triangleright \quad \Delta E \cdot \Delta t \geq \frac{\hbar}{4\pi}$$

Schrodinger's Wave Equation for Hydrogenic Atom

$$\nabla \cdot \frac{\delta^2 \psi}{\delta x^2} + \frac{\delta^2 \psi}{\delta y^2} + \frac{\delta^2 \psi}{\delta z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

$$\Psi(r, \theta, \phi) = R(r) \cdot Y(\theta, \phi)$$

$$R(r) = R(n, \ell) \propto \left(\frac{2\pi r}{na_0} \right)^\ell e^{-\pi r/na_0}$$

$$Y(\theta, \phi) = Y(\ell, m) \propto \sin^{|m|} \theta \cdot \cos^{\ell-|m|} \theta \cdot e^{im\phi}$$

if $\psi = e^{-\alpha x^2}$, Probability density = $|\psi|^2 = e^{-2\alpha x^2}$

for most probable $\frac{d|\psi|^2}{dx} = 0$

- Radial nodes = $n - \ell - 1$,
 - Angular nodes = ℓ ,
 - Total nodes = $n - 1$

Quantum Numbers

- ❖ Number of subshell present in n^{th} shell = n .
 - ❖ Number of orbitals present in n^{th} shell = n^2 .
 - ❖ The maximum number of electrons in a principal energy shell = $2n^2$.
 - ❖ Angular momentum of any orbit = $\frac{nh}{2\pi}$.
 - ❖ Number of orbitals in a subshell = $2\ell + 1$
 - ❖ Maximum number of electrons in particular subshell = $2 \times (2\ell + 1)$.
 - ❖ $L = \frac{h}{2\pi} \sqrt{\ell(\ell+1)} = \hbar \sqrt{\ell(\ell+1)} \left[\hbar = \frac{h}{2\pi} \right]$.
 - ❖ Orbitals present in a main energy level is ' n^2 '.
 - ❖ $\mu = \sqrt{n(n+2)}$ B.M. .
 - ❖ Spin angular momentum = $\frac{h}{2\pi} \sqrt{s(s+1)}$.
 - ❖ Maximum spin of atom = $\frac{1}{2} \times \text{No. of unpaired electron}$.



Solved Examples

1. The bond dissociation energy of Cl–Cl bond in chlorine gas is 240 kJ/mol. Calculate the longest wavelength of EMR needed to dissociate bond. Assume one photon may dissociate only one bond.

$$\text{Sol. } E = \frac{240 \times 10^3}{6 \times 10^{23}} = \frac{1 \times 6.626 \times 10^{-34} \times 3 \times 10^8}{\lambda}$$

2. A near ultra violet photon of wavelength 300 nm is absorbed by a gas and then emitted as two photons. One photon is of red light with wavelength 760 nm. What would be the wavelength of the second photon ?

Sol. It may noted that energy of photon which adsorbed is emitted as sum of the energy of two photons.

$$\text{Energy absorbed } hv = \frac{hc}{\lambda}$$

3. The ionization energy of hydrogen atom is 13.6 eV. What will be the ionization energy of $\text{He}^+ -$?

Sol. He^+ is a hydrogen like species i.e. the electron is ionised from first orbit.

$$\therefore \text{Ionization energy of } \text{He}^+ = \frac{Z^2 E_H}{n^2}$$

$$= \frac{4 \times 13.6}{1^2} = 54.4 \text{ eV}$$

4. The ionization energy of H-atm is 13.6 eV. The ionization energy of Li^{+2} ion will be:

Sol. (d) E_1 for $\text{Li}^{+2} = E_1$ for $\text{H} \times Z^2$ [for Li, Z = 3]

$$= 122.4 \text{ eV}$$

5. 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 .

Sol. $R(r) = 0$

$$\left[2 - \frac{r}{a_0} \right] e^{\frac{r}{2a_0}} = 0 \Rightarrow 2 - \frac{r}{a_0} = 0 \Rightarrow r = 2a_0$$

6. (a) The Schrodinger wave equation for hydrogen atom is

$$\Psi_{2s} = \frac{1}{4(2\pi)^{1/2}} \left(\frac{1}{2} \right)^{3/2} \left(2 - \frac{r_0}{a_0} \right) e^{-r/a}$$

Where a_0 is Bohr's radius. Let the radial node in 2s be at r_0 . Then find r_0 in terms of a_0 .

(b) A base ball having mass 10 g and projected with speed of 100 m/s. Find out the value of wavelength of base ball.

Sol. (a) $r_0 = 2a_0$, (b) $6.626 \times 10^{-25} \text{ Å}$

$$\Psi_{2s} = \frac{1}{4(2\pi)^{1/2}} \left(\frac{1}{a_0} \right)^{3/2} \left(2 - \frac{r_0}{a_0} \right) e^{-r/a}$$

$$(a) 2 - \frac{r_0}{a_0} = 0$$

$$(b) \lambda = \frac{h}{mv}$$

$$\frac{r_0}{a_0} = 2$$

$$= \frac{6.626 \times 10^{-34}}{(0.1)(100)}$$

$$r_0 = 2a_0$$

$$= 6.626 \times 10^{-25} \text{ Å}$$

7. Calculation of different types of maximum possible radiations which can be observed in (from higher energy level to lower energy level).

Sol. $n_2 = n, \quad n_1 = 1$

Total no. of radiation obtained having difference wave lengths = Transition ending at 1st level + Transition ending at 2nd level + + Transition ending at $(n-1)$ energy levels.

= Total no. of radiation in Lyman series + total no. of radiation in Balmer series + Total no. of radiation in $(n-1)$ series.

$$= (n-1) + (n-2) + (n-3) + \dots + 2 + 1$$

$$= \frac{(n-1)(n-1+1)}{2} \Rightarrow \frac{n(n-1)}{2}$$

$$= (n_2 - n_1) + n_2 - (n_1 + 1) + \dots + 2 + 1$$

Total no. of different radiation

$$= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2} = \frac{N(N+1)}{2}$$

N = difference in higher energy level and lower energy level.

8. The energy level of an atom for 1st, 2nd and third levels are $E, 4E_{1 \rightarrow 3}, 2E$ respectively. If photon of wavelength λ is emitted for a transition 3 to 1. Calculate the wavelength for transition 2 to 1 in terms of λ .

Sol. Energy of photon released = $E_3 - E_1$

... (i)

As we know that energy of photon is given by $= \frac{hc}{\lambda}$

where λ wavelength of photon
from (1)

$$\frac{hc}{\lambda} = E_3 - E_1 = E \Rightarrow \lambda = \frac{hc}{E} \quad \dots \text{(ii)}$$

On transition from $2 \rightarrow 1$ energy level.

Energy of photon released = $E_2 - E_1$

Let, wavelength of photon released be λ'

$$\Rightarrow \text{Energy of photon released} = \frac{hc}{\lambda'} \quad \dots \text{(iii)}$$

From (iii)

$$E_2 - E_1 = \frac{hc}{\lambda},$$

$$\Rightarrow 3E = \frac{hc}{\lambda},$$

$$\Rightarrow \lambda' = \frac{hc}{3E} = \frac{1}{3} \left(\frac{hc}{E} \right)$$

$$\Rightarrow \lambda' = \frac{1}{3} (\lambda) \text{ (from (ii))}$$

$$\Rightarrow \lambda' = \frac{1}{3}$$

Hence, wavelength of photon emitted for transition $2 \rightarrow 1$ in $\frac{\lambda}{3}$.

9. Two electromagnetic radiations have wave numbers in the ratio 3:3. Their energies per quanta will be in the ratio

$$(a) 3:2 \quad (b) 9:4$$

$$(c) 4:9 \quad (d) 2:3$$

Sol. $\frac{v_1}{v_2} = \frac{2}{3}$ (given)

We know—

$$E = \frac{nhc}{\lambda} \text{ or } E = nhc \bar{v}$$

Where \bar{v} = wave number

$$\therefore \frac{n_1}{E_2} = \frac{hc\bar{v}_1}{hc\bar{v}_2} \text{ or } \frac{E'_1}{E'_2} = \frac{\bar{v}_1}{\bar{v}_2} = \frac{2}{3}$$

n_2

Where, E' = Energy per quanta

10. Hydrogen like species is observed to emit 6 wavelengths originating from all possible transitions between a group of levels these energy levels have energy between -0.85 eV and -0.544 eV (including both these energy levels) calculate:

- (i) The quantum number of levels between which transition is taking place.

- (ii) Find the atomic number of species.

Sol. (i) To bind the atomic number of the atom we have

$$n \frac{(n-1)}{2} = 6$$

$$n(n-1) = 12$$

$$n^2 - n - 12 = 0$$

$$n^2 - 4n - 2n - 12 = 0$$

$$n(n-4) - 3(n-4) = 0$$

$$(n-4)(n-3) = 0$$

$$n = 4, 3$$

$$n = 4$$

i.e transition is taking place from

$$m \rightarrow m + 3$$

$$E_m = 0.85 \text{ eV}$$

$$E_{m+3} = -0.544 \text{ eV}$$

$$-0.85 = -13.6 \times \frac{z^2}{m^2} \text{ or, } z/m = 0.25 \quad \dots (\text{i})$$

$$-0.544 = -13.6 \times \frac{z^2}{(m+3)^2}$$

$$\text{on solving, } \frac{z}{m+3} = 0.2 \quad \dots (\text{ii})$$

on solving (i) & (ii)

$$z = 3, m = 12$$

$$(\text{ii}) \Delta E_{\max} = -0.544 - (-0.85) = 0.306 \text{ eV}$$

$$\lambda_{\min} = \frac{hc}{\Delta E_{\max}} = \frac{1241}{0.306} = 4052.3 \text{ nm}$$

- 11.** Arrange the particle in their increasing order of specific charge ratio.



$$\text{Sol. } \text{Na}^+ = \frac{1}{23}; \text{Li}^+ = \frac{1}{7}; \text{F}^- = \frac{1}{19}; \text{Mg}^{2+} = \frac{2}{24} = \frac{1}{12}; \text{Al}^{3+} = \frac{3}{27} = \frac{1}{9}$$

$$\text{Na}^+ < \text{F}^- < \text{Mg}^{2+} < \text{Al}^{3+} < \text{Li}^+$$

- 12.** Which of the following pairs have same specific charge $\left(\frac{e}{m}\right)$?

- (a) electron & proton
- (b) electron & positron
- (c) proton & deuteron
- (d) α -particle & deuteron
- (e) proton & positron

Sol. (b,d) $M_e = M_{\text{positron}}$

$$M_\alpha = m_{\text{deuteron}}$$

- 13.** Through what potential difference an α -particle should be accelerated to have speed $5 \times 10^6 \text{ m/s}$.

$$\text{Sol. } qV = \frac{1}{2}mv^2$$

$$(2 \times 1.6 \times 10^{-19} \times V) = \frac{1}{2} \times 4 \times 1.66 \times 10^{-27} \times (5 \times 10^6)^2$$

$$V = 0.26 \text{ MV}$$

- 14.** The distance of closest approach of an α -particle fired towards a nucleus with momentum ' P ' is r . What will be the distance of closest approach when the momentum of the α -particle is $2P$?

- (a) $1r$
- (b) $4r$
- (c) $r/2$
- (d) $r/4$

Sol. We know—

$$K.E. = \frac{p^2}{2m} \quad \dots (\text{i})$$

$$\text{and K. E.} = \frac{Kq_1q_2}{r} \quad \dots (\text{ii})$$

from (i) and (ii)

$$\frac{p^2}{2m} = \frac{kq_1q_2}{r}$$

As m, k, q_1 and q_2 are constant

$$p^2 \propto \frac{1}{r} \text{ or } r \propto \frac{1}{p^2}$$

$$\text{Now } \frac{r_2}{r_1} = \frac{P_1^2}{P_2^2}$$

$$\text{given } r_1 = r, P_1 = P, P_2 = 2P$$

$$\therefore \frac{r_2}{r} = \frac{P^2}{4P^2} \text{ or } r_2 = \frac{r}{4}$$

- 15.** Wavelength of photon which have energy equal to average of energy of photons with $\lambda_1 = 4000 \text{ \AA}$ and $\lambda_2 = 6000 \text{ \AA}$ will be:

- (a) 5000 \AA
- (b) 4800 \AA
- (c) 9600 \AA
- (d) 2400 \AA

Sol. According to question $E = \frac{E_1 + E_2}{2}$

$$\text{or } \frac{hc}{\lambda} = \frac{\frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}}{2}$$

$$\text{or } \frac{1}{\lambda} = \left(\frac{\frac{1}{4000} + \frac{1}{6000}}{2} \right)$$

$$\text{or } \lambda = 4800 \text{ \AA}$$

- 16.** The force of attraction on electron by the nucleus is directly proportional to

- (a) $\frac{n^3}{Z^4}$
- (b) $\frac{Z^3}{n^4}$
- (c) $\frac{n^4}{Z^2}$
- (d) $\frac{Z^2}{n^4}$

(iii) Orbit = 2nd

$$\therefore E = -13.6 \times \frac{Z^2}{n^2}$$

$$\therefore 3.4 = -13.6 \times \frac{1^2}{n^2}$$

$$\Rightarrow n^2 = \frac{-13.6}{-3.4} = 4$$

i.e. n = 2

$$(iv) r = 0.529 \times \frac{n^2}{Z} \text{\AA}$$

$$r = 0.529 \times \frac{(2)^2}{1} \text{\AA}$$

$$= 0.529 \times 4 \text{\AA} = 2.16 \text{\AA}$$

24. 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.

Sol. 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

$$\text{so, } E_2 - E_1 = -3.4 + 13.6 = 10.2 \text{ eV}$$

25. In a hydrogen spectrum if electron moves from 6th to 2nd by transition in multi steps then find out the number of lines in spectrum

Sol. Total number of line = 4 + 3 + 2 + 1 + 0 = 10

$$\begin{aligned} \text{Total number of lines} &= \frac{(n_2 - n_1)[(n_2 - n_1) + 1]}{2} \\ &= \frac{(6-2)(4+1)}{2} = 10 \end{aligned}$$

26. In the spectrum of H⁺ ion the wavelength of α line of Balmer series is x Å. What is the wavelength of α line of Paschen series.

$$\text{Sol. } \frac{1}{\lambda_1} = Rz^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$$

$$\frac{1}{\lambda_2} = Rz^2 \left(\frac{1}{3^2} - \frac{1}{5^2} \right)$$

$$\frac{\lambda_2}{\lambda_1} = \frac{\frac{1}{2^2} - \frac{1}{3^2}}{\frac{1}{3^2} - \frac{1}{5^2}} \Rightarrow \frac{\lambda_2}{x} = \frac{5}{16} \times \frac{25}{4}$$

$$\lambda_2 = \frac{125}{64} x \text{\AA}$$

27. A sample of He⁺ ions in ground state absorbs the radiation of x Å subsequently, the sample emit radiation of 6 different wavelength. Calculate the value of x.

$$\text{Sol. } \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2} = 6 \quad \text{given, } n_1 = 1$$

$$\frac{(n-1)(n-1+1)}{2} = 6$$

On solving

n = 4 or n = 3

6 different wavelength will be obtained only from n = 4

$$\frac{1}{x} = R_H \times z^2 \left(\frac{1}{1^2} - \frac{1}{4^2} \right)$$

$$\frac{1}{x} = R_H \times z^2 \left(\frac{1}{11} - \frac{1}{16} \right)$$

$$\frac{1}{x} = R_H \times \frac{4 \times 15}{16 \times 4}$$

$$\text{or } n = \frac{4}{15R_H} \quad \text{or } n = \frac{4}{15 \times 1.09678 \times 10^7 m^{-1}}$$

$$\text{or } n = 243 \text{\AA}$$

28. The orbital angular momentum of an electron is $\sqrt{3} \frac{h}{\pi}$.

Which of the following may be the permissible value of angular momentum of this electron revolving in unknown Bohr orbit?

$$(a) \frac{h}{\pi} \qquad (b) \frac{h}{2\pi}$$

$$(c) \frac{3h}{2\pi} \qquad (d) \frac{2h}{\pi}$$

$$\text{Sol. Orbital angular momentum} = \sqrt{l(l+1)} \frac{h}{2\pi}$$

$$\text{Orbital angular momentum} = \sqrt{3} \frac{h}{\pi}$$

$$\therefore \sqrt{l(l+1)} \times \frac{h}{2\pi} = \sqrt{3} \frac{h}{\pi}$$

On Solving above equation, we get l = -4 and 3 (-4 not allowed as l < 0)

For l = 3, n = 4, 5, 6 (Possible)

Therefor possible angular momentum

$$= \frac{4h}{2\pi}, \frac{5h}{2\pi}, \frac{6h}{2\pi}, \frac{7h}{2\pi}, \dots$$



Exercise-1 (Topicwise)

DISCOVERY OF SUB ATOMIC PARTICLES, ATOMIC MODELS, NUCLEUS

1. The fraction of volume occupied by the nucleus with respect to the total volume of an atom is:
 - (a) 10^{-15}
 - (b) 10^{-5}
 - (c) 10^{-30}
 - (d) 10^{-10}
2. The approximate size of the nucleus of $^{64}_{28}\text{Ni}$ is:
 - (a) 3 fm
 - (b) 4 fm
 - (c) 5 fm
 - (d) 2 fm
3. The ratio of e/m for a cathode ray:
 - (a) Varies with a gas in a discharge tube.
 - (b) Is fixed.
 - (c) Varies with different electrodes.
 - (d) Is maximum if hydrogen is taken.
4. Cathode rays have:
 - (a) Mass only
 - (b) Charge only
 - (c) No mass and no charge
 - (d) Mass and charge both
5. Which is the correct statement about proton?
 - (a) It is a nucleus of deuterium.
 - (b) It is an ionised hydrogen molecule.
 - (c) It is an ionised hydrogen atom.
 - (d) It is an α -particle.
6. Rutherford's experiment on scattering of α -particles showed for the first time that the atom has:
 - (a) Electrons
 - (b) Protons
 - (c) Neutrons
 - (d) Nucleus
7. 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 very high velocity.
8. Increasing order (lowest first) for the values of e/m (charge/mass) for electron (e), proton (p), neutron (n) and α -particle (α) is:
 - (a) e, p, n, α
 - (b) n, p, e, α
 - (c) n, p, α , e
 - (d) n, α , p, e
9. Nucleons are:
 - (a) Protons and neutrons.
 - (b) Neutrons and electrons.
 - (c) Protons and electrons.
 - (d) Protons, neutrons and electrons.

10. The discovery of neutron came very late because:
 - (a) It is present in nucleus.
 - (b) It is a fundamental particle.
 - (c) It does not move.
 - (d) It does not carry any charge.
 11. Atomic number of an element represents:
 - (a) Number of neutrons in the nucleus.
 - (b) Atomic mass of an element.
 - (c) Valency of an element.
 - (d) Number of protons in the nucleus.
 12. The highest value of e/m of anode rays has been observed when the discharge tube is filled with:
 - (a) Nitrogen
 - (b) Oxygen
 - (c) Hydrogen
 - (d) Helium
- ### QUANTUM THEORY OF LIGHT & PHOTOELECTRIC EFFECT
13. The MRI (magnetic resonance imaging) body scanners used in hospitals operate with 400 MHz radio frequency. The wavelength corresponding to this radio frequency is:
 - (a) 0.75 m
 - (b) 0.75 cm
 - (c) 1.5 m
 - (d) 2 cm
 14. Electromagnetic radiations of wavelength 242 nm is just sufficient to ionise Sodium atom. Then the ionisation energy of Sodium in kJ mole⁻¹ is:
 - (a) 494.65
 - (b) 400
 - (c) 247
 - (d) 600
 15. A bulb of 40 W is producing a light of wavelength 620 nm with 80% of efficiency then the number of photons emitted by the bulb in 20 seconds are ($1\text{eV} = 1.6 \times 10^{-19} \text{ J}$, $hc = 12400 \text{ eV Å}$):
 - (a) 2×10^{18}
 - (b) 10^{18}
 - (c) 10^{21}
 - (d) 2×10^{21}
 16. Light of wavelength λ falls on metal having work function hc/λ_0 . Photoelectric effect will take place only if :
 - (a) $\lambda \geq \lambda_0$
 - (b) $\lambda \geq 2\lambda_0$
 - (c) $\lambda \leq \lambda_0$
 - (d) $\lambda \leq \lambda_0/2$
 17. A light whose frequency is equal to $6 \times 10^{14} \text{ Hz}$ is incident on a metal whose work function is 2 eV ($h = 6.63 \times 10^{-34} \text{ Js}$, $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$). The maximum energy of electrons emitted will be:
 - (a) 2.49 eV
 - (b) 4.49 eV
 - (c) 0.49 eV
 - (d) 5.49 eV

BOHR MODEL

- 22.** Which is the correct relationship:

 - E_1 of H = $1/2 E_2$ of He^+ = $1/3 E_3$ of Li^{2+} = $1/4 E_4$ of Be^{3+}
 - $E_1(\text{H}) = E_2(\text{He}^+) = E_3(\text{Li}^{2+}) = E_4(\text{Be}^{3+})$
 - $E_1(\text{H}) = 2E_2(\text{He}^+) = 3E_3(\text{Li}^{2+}) = 4E_4(\text{Be}^{3+})$
 - No relation

23. If velocity of an electron in 1st orbit of H atom is V, what will be the velocity of electron in 3rd orbit of Li^{+2} ?

 - V
 - $V/3$
 - $3 V$
 - $9 V$

24. In a certain electronic transition in the hydrogen atoms from an initial state (1) to a final state (2), the difference in the orbital radius ($r_1 - r_2$) is 24 times the first Bohr radius. Identify the transition:

 - $5 \rightarrow 1$
 - $25 \rightarrow 1$
 - $8 \rightarrow 3$
 - $6 \rightarrow 5$

25. S₁ : Potential energy of the two opposite charge system increases with the decrease in distance.
S₂ : When an electron make transition from higher orbit to lower orbit it's kinetic energy increases.
S₃ : When an electron make transition from lower energy to higher energy state its potential energy increases.
S₄ : 11eV photon can free an electron from the 1st excited state of He^+ -ion.

 - T T T T
 - F T T F
 - T F F T
 - F F F F

- 26.** Energy of Bohr orbit:

 - Increases as we move away from the nucleus.
 - Decreases as we move away from the nucleus.
 - Remains the same as we move away from the nucleus.
 - None of the above.

27. The radius of the first orbit of H-atom is r . Then, the radius of the first orbit of Li^{2+} will be:

 - $r/9$
 - $r/3$
 - $3r$
 - $9r$

28. According to Bohr theory, the angular momentum for an electron of 5 th orbit is:

 - $5 h/\pi$
 - $2.5 h/\pi$
 - $5 \pi/h$
 - $25 h/\pi$

29. Which of the following electron transitions in hydrogen atom will require largest amount of energy?

 - from $n = 1$ to $n = 2$
 - from $n = 2$ to $n = 3$
 - from $n = \infty$ to $n = 1$
 - from $n = 3$ to $n = 5$

30. $E_n = -313.6/n^2$ kcal/mol. If the value of $E = -34.84$ kcal/mol, to which value does 'n' correspond?

 - 4
 - 3
 - 2
 - 1

31. If the velocity of an electron in the first Bohr orbit of a hydrogen atom is V , then its velocity in the third Bohr orbit will be:

 - $V/9$
 - $V/3$
 - $9 V$
 - $3 V$

32. The ratio of the radius of Bohr first orbit for the electron orbiting the hydrogen nucleus to that of the electron orbiting the deuterium nucleus (mass nearly twice that of H nucleus) is approximately:

 - 1 : 1
 - 1 : 2
 - 2 : 1
 - 1 : 4

33. An electron in H-atom in its ground state absorbs 1.50 times as much as energy as the minimum required for its escape (13.6 eV) from the atom. Thus KE given to emitted electron is:

 - 13.6 eV
 - 20.4 eV
 - 34.0 eV
 - 6.8 eV

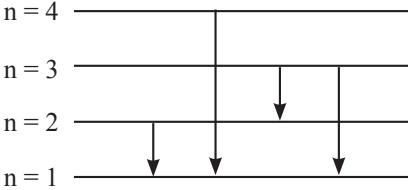
34. Bohr's theory is not valid for the species:

 - H atom
 - He^+ ion
 - Li^+ ion
 - Li^{2+} ion

35. If r_1 is the radius of the first orbit of hydrogen atom, then the radii of second, third and fourth orbitals in terms of r_1 are:

 - r_1^2, r_1^3, r_1^4
 - $8r_1, 27r_1, 64r_1$
 - $4r_1, 9r_1, 16r_1$
 - $2r_1, 6r_1, 8r_1$

SPECTRUM

- 37.** Total no. of lines in Lyman series of H spectrum will be (where n = no. of orbits):
 (a) n (b) n - 1
 (c) n - 2 (d) n(n + 1)
- 38.** No. of visible lines when an electron returns from 5th orbit upto ground state in H spectrum:
 (a) 5 (b) 4
 (c) 3 (d) 10
- 39.** Suppose that a hypothetical atom gives a red, green, blue and violet line spectrum. Which jump according to figure would give off the red spectral line?
- 
- (a) 3 → 1 (b) 2 → 1
 (c) 4 → 1 (d) 3 → 2
- 40.** The difference between the wave number of 1st line of Balmer series and last line of paschen series for Li²⁺ ion is:
 (a) $\frac{R}{36}$ (b) $\frac{5R}{36}$
 (c) 4R (d) $\frac{R}{4}$
- 41.** The spectral lines corresponding to the radiation emitted by an electron jumping from higher orbits to first orbit belong to:
 (a) Paschen series (b) Balmer series
 (c) Lyman series (d) None of these
- 42.** For the Paschen series, the value of n₁ and n₂ in the expression $\Delta E = R_M \times c \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$ is:
 (a) n₁ = 1, n₂ = 2, 3, 4... (b) n₁ = 2, n₂ = 3, 4, 5...
 (c) n₁ = 3, n₂ = 4, 5, 6... (d) n₁ = 4, n₂ = 5, 6, 7...
- 43.** If the series limit of wavelength of the Lyman series for the hydrogen atoms is 912 Å, then the series limit of wavelength for the Balmer series of the hydrogen atom is:
 (a) 912 Å (b) 912×2 Å
 (c) 912×4 Å (d) $912/2$ Å
- 44.** The shortest λ for the Lyman series of hydrogen atom is ... (Given $R_H = 109678 \text{ cm}^{-1}$)
 (a) 911.7 Å (b) 700 Å
 (c) 600 Å (d) 811 Å
- 45.** The frequency of first line of Balmer series in hydrogen atom is v_o . The frequency of corresponding line emitted by singly ionised helium atom is:
 (a) $2v_o$ (b) $4v_o$
 (c) $v_o/2$ (d) $v_o/4$
- 46.** Which of the following statement is not true?
 (a) Lyman spectral series of hydrogen atom lies in the ultraviolet region of electromagnetic radiation.
 (b) Balmer spectral series of hydrogen atom lies in the visible region of electromagnetic radiation.
 (c) Paschen spectral series of hydrogen atom lies in the visible region of electromagnetic radiation.
 (d) Brackett spectral series of hydrogen atom lies in the infrared region of electromagnetic radiation.
- 47.** The first emission line of Balmer series in H spectrum has the wave number equal to:
 (a) $\frac{9R_H}{400} \text{ cm}^{-1}$ (b) $\frac{7R_H}{144} \text{ cm}^{-1}$
 (c) $\frac{3R_H}{4} \text{ cm}^{-1}$ (d) $\frac{5R_H}{36} \text{ cm}^{-1}$
- 48.** When an electron de-excites from higher orbit in H-atom, two radiations are emitted out in Paschen and Lyman series. The wavelength of radiation emitted out in Lyman series is:
 (a) $\frac{8R}{9}$ (b) $\frac{3R}{4}$
 (c) $\frac{4}{3R}$ (d) $\frac{9}{8R}$

De-BROGLIE WAVELENGTH AND HEISENBERG UNCERTAINTY PRINCIPLE

- 49.** 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) $\frac{x}{2}$
- 50.** de-Broglie wavelength of electron in second orbit of Li²⁺ ion will be equal to de-Broglie of wavelength of electron in:
 (a) n = 3 of H-atom (b) n = 4 of C⁵⁺ ion
 (c) n = 6 of Be³⁺ ion (d) n = 3 of He⁺ ion
- 51.** de-Broglie equation describes the relationship of wavelength associated with the motion of an electron and its:
 (a) Mass (b) Energy
 (c) Momentum (d) Charge
- 52.** A body of mass 'x' kg is moving with velocity of 100 m sec⁻¹. Its de-Broglie wavelength is 6.62×10^{-35} m. Hence 'x' is ($h = 6.62 \times 10^{-34}$ J sec):
 (a) 0.25 kg (b) 0.15 kg
 (c) 0.2 kg (d) 0.1 kg
- 53.** The wavelengths of electron waves in two orbits is 3:5. The ratio of kinetic energy of electrons will be:
 (a) 25 : 9 (b) 5 : 3
 (c) 9 : 25 (d) 3 : 5
- 54.** A ball of mass 200 g moving with a velocity of 10 m sec⁻¹. If the error in measurement of velocity is 0.1%, the uncertainty in its position is:
 (a) 3.3×10^{-31} m (b) 3.3×10^{-27} m
 (c) 5.3×10^{-25} m (d) 2.64×10^{-32} m

56. Which of the following particles moving with same velocity would be associated with smallest de-Broglie wavelength?

(a) Hydrogen molecule (b) Oxygen molecule
(c) Helium molecule (d) Nitrogen molecule

QUANTUM NUMBERS & ELECTRONIC CONFIGURATION

QUANTUM MECHANICAL MODEL OF ATOM, SHRODINGER WAVE EQUATION AND ORBITAL CONCEPT

63. The maximum radial probability in 1s-orbital occurs at a distance when: $[r_0 = \text{Bohr radius}]$

 - $r = r_0$
 - $r = 2r_0$
 - $r = \frac{r_0}{2}$
 - $2r = \frac{r_0}{2}$

64. The maximum probability of finding electron in the d_{xy} orbital is :

 - Along the x-axis.
 - Along the y-axis.
 - At an angle of 45° from the x and y axis.
 - At an angle of 90° from the x and y axis.

65. $3p_y$ orbital has.....nodal plane :

 - XY
 - YZ
 - ZX
 - All of these

66. A 3p-orbital has:

 - Two non-spherical nodes.
 - Two spherical nodes.
 - One spherical and one non spherical nodes.
 - One spherical and two non spherical nodes.

67. According to Schrodinger model nature of electron in an atom is as:

 - Particle only.
 - Wave only.
 - Particle and wave nature simultaneous.
 - Sometimes waves and sometimes particle.

68. Consider the following statements:

 - Electron density in the XY plane in $3d_{x^2-y^2}$ orbital is zero.
 - Electron density in the XY plane in $3d_z^2$ orbital is zero.
 - 2s orbital has one nodal surface.
 - For $2p_z$ orbital, XY is the nodal plane.

Which of these are incorrect statements?

 - A & C
 - D & C
 - Only B
 - A, B

69. Which of the following d-orbitals has dough-nut shape ?

 - d_{xy}
 - d_{yz}
 - $d_{x^2-y^2}$
 - d_{z^2}

70. The permissible solution to the Schrodinger wave equation gave an ideal of quantum number:

 - 4
 - 3
 - 2
 - 1



Exercise-2 (Learning Plus)

- 15.** An electron, a proton and an alpha particle have kinetic energies of $16E$, $4E$ 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) $\lambda_\alpha > \lambda_e >> \lambda_p$
- 16.** In an atom, two electrons move around the nucleus in circular orbits of radii R and $4R$. The ratio of the time taken by them to complete one revolution is:
- (a) $1 : 4$ (b) $4 : 1$
 (c) $1 : 8$ (d) $8 : 7$
- 17.** A 3p-orbital has:
- (a) Two non-spherical nodes.
 (b) Two spherical nodes.
 (c) One spherical and one non-spherical node.
 (d) One spherical and two non-spherical nodes.
- 18.** The difference in angular momentum associated with the electron in two successive orbits of hydrogen atom is:
- (a) h/p (b) $h/2p$
 (c) $h/2$ (d) $(n - 1)h/2p$
- 19.** An α -particle is accelerated from rest through a potential difference of 6.0 V . Its de Broglie wavelength is:
- (a) 5 \AA (b) 4.15 pm
 (c) 414.6 \AA (d) 5 nm
- 20.** A photon of 2.55 eV is emitted out by an electronic transition in hydrogen atom. The change in de Broglie wavelength of the electron is:
- (a) 3.32 \AA (b) 4.98 \AA
 (c) 6.64 \AA (d) 9.96 \AA
- 21.** An electron that has the quantum numbers $n = 3$ and $m = 2$:
- (a) Must have spin quantum number value $+1/2$
 (b) Must have $l = 2, 3$ or 4
 (c) Must have $l = 0, 1$ or 2
 (d) Must have $l = 2$
- 22.** Electronic configuration of an element is $1s^2, 2s^1, 2p^2$. It is:
- (a) Ground state configuration of B ($Z = 5$).
 (b) Excited state configuration of B.
 (c) Ground state configuration of C^+ ion ($Z = 6$).
 (d) Impossible configuration.
- 23.** What is the most probable distance of a $1s$ -electron in a He^+ ion. The wave function for $1s$ -orbital is given by
- $$\Psi = \sqrt{\left(\frac{Z^3}{\pi a_0^3}\right)} e^{-Zr/a_0}, \text{ where } a_0 = \text{radius of first Bohr's orbit in H-atom} = 52.9\text{ pm.}$$
- (a) 52.9 pm (b) 13.25 pm
 (c) 6.61 pm (d) 26.45 pm
- 24.** The dissociation energy of H_2 is 429.0 kJ/mol . If H_2 is dissociated by illumination with radiation of wavelength 270.0 nm , then what percentage of radiant energy will be converted into kinetic energy? ($h = 6.6 \times 10^{-34}\text{ Js}$, $N_A = 6 \times 10^{23}$)
- (a) 1.25% (b) 3.26%
 (c) 5.0% (d) 7.5%
- 25.** The magnitude of the orbital angular momentum of an electron is given by $L = \sqrt{5} h/\pi$. How many orbitals of this kind are possible, belonging to an orbit?
- (a) 4 (b) 5
 (c) 11 (d) 9
- 26.** Which of the ions is not having the configuration of Ne ?
- (a) Cl^- (b) F^-
 (c) Na^+ (d) Mg^{2+}
- 27.** In a given atom, no two electrons can have the same values for all the four quantum numbers. This is called:
- (a) Hund's rule (b) Pauli's exclusion principle
 (c) Uncertainty principle (d) Aufbau principle
- 28.** How many electrons can fit into the orbitals that comprise the 3rd quantum shell, $n = 3$?
- (a) 2 (b) 8
 (c) 18 (d) 32
- 29.** Which of the following sets of quantum numbers is correct for an electron in $4f$ -orbital?
- (a) $n = 4, l = 3, m = +4; s = +1/2$
 (b) $n = 4, l = 4, m = -4, s = -1/2$
 (c) $n = 4, l = 3, m = +1, s = +1/2$
 (d) $n = 3, l = 2, m = -2, s = +1/2$
- 30.** In any subshell, the maximum number of electrons having same values of spin quantum number is:
- (a) $\sqrt{l(l+1)}$ (b) $l+2$
 (c) $2l+1$ (d) $4l+2$
- 31.** Total number of ' m ' values for $n = 4$ is:
- (a) 8 (b) 16
 (c) 12 (d) 20
- 32.** The electronic configuration of an atom/ion can be defined by which of the following?
- (a) Aufbau principle.
 (b) Pauli's exclusion principle.
 (c) Hund's rule of maximum multiplicity.
 (d) All of these.
- 33.** According to Aufbau principle, the correct order of energy of $3d$, $4s$ and $4p$ -orbitals is:
- (a) $4p < 3d < 4s$ (b) $4s < 4p < 3d$
 (c) $4s < 3d < 4p$ (d) $3d < 4s < 4p$
- 34.** The orbital diagram in which 'Aufbau principle' is violated, is:
- (a) (b)
 (c) (d)

35. An ion which has 18 electrons in the outermost shell is:

 - K^+
 - Cu^+
 - Cs^+
 - Th^{4+}

36. A strong argument for the particle nature of cathode rays is:

 - They can rotate paddle wheel.
 - They can propagate in vacuum.
 - They cast shadows.
 - They are deflected by electric and magnetic fields.

37. Three isotopes of an element have mass numbers, M , $(M + 1)$ and $(M + 2)$. If the mean mass number is $(M + 0.5)$, then which of the following ratios may be accepted for M , $(M + 1)$, $(M + 2)$ in that order?

 - $1 : 1 : 1$
 - $4 : 1 : 1$
 - $3 : 2 : 1$
 - $2 : 1 : 1$

38. Which of the following statements is not correct?

 - The shape of an atomic orbital depends on the azimuthal quantum number.
 - The orientation of an atomic orbital depends on the magnetic quantum number.

39. Gases begin to conduct electricity in discharge tube at low pressure because:

 - At low pressures, gases turn to plasma.
 - Colliding electrons can acquire higher kinetic energy due to increased mean free path leading to ionisation of atoms.
 - Atoms break up into electrons and protons.
 - The electrons in atoms can move freely at low pressure.

40. The uncertainty in momentum of an electron is $1 \times 10^{-5} \text{ kg ms}^{-1}$. The uncertainty in its position will be ($\hbar = 6.62 \times 10^{-34} \text{ kg m}^2\text{s}$):

 - $1.05 \times 10^{-28} \text{ m}$
 - $1.05 \times 10^{-26} \text{ m}$
 - $5.27 \times 10^{-30} \text{ m}$
 - $5.25 \times 10^{-28} \text{ m}$



Exercise-3 (JEE Advanced Level)

MULTIPLE CORRECT TYPE QUESTIONS

- The radius of the following orbits are double as that of the first Bohr's orbit of hydrogen atom.
(a) He^+ ($n = 2$) (b) Be^{+3} ($n = 2$)
(c) O^{+7} ($n = 4$) (d) C^{+5} ($n = 3$)
 - Which are correct statements?
(a) Hund's rule deals with degenerate orbitals.
(b) Pauli exclusion principle stated as only two electrons may exist in the same orbital and these electrons must have opposite spin.
(c) In ground state of atom the orbitals are filled on the basis of increasing $(n + l)$ value.
(d) The maximum number of electrons in the subshell with principal quantum number 'n' is equal to $2n^2$?
 - Which statements are correct?
(a) ψ (orbital wave function) a mathematical function of co-ordinates of the electron.
(b) ψ^2 represents probability density of electron at a point.
(c) Schrodinger wave equation play same role in quantum mechanism as Newton's Law of motion do in classical mechanism.
(d) Radial probability density $[R^2(r)]$ is maximum close to nucleus but total probability is least.

4. Which of the following statements are correct about the cathode ray experiment?

 - (a) The cathode rays starts from anode and move towards cathode.
 - (b) Television picture tubes are cathode ray tubes and pictures result due to fluorescence on the television screen coated with certain fluorescent materials.
 - (c) In the presence of magnetic or electric field, the behaviour of cathode rays are similar to negatively charged particles.
 - (d) The characteristics of cathode rays does not depend upon the material of electrodes but nature of gas present in the cathode ray tube.

5. Choose the correct statements from among the following:

 - (a) The total number of spherical nodes in an orbital are $n - l - 1$.
 - (b) The total number of angular nodes in an orbital are l .
 - (c) The number of maxima in an orbital is $(n - l)$.
 - (d) A node is a point in space where the wave function ψ has zero amplitude.

6. The energy of an electron in the first Bohr's orbit of H-atom is -13.6 eV . The possible energy value(s) of the excited state(s) for electrons in Bohr's orbits to hydrogen is:

 - (a) -3.4 eV
 - (b) -10.2 eV
 - (c) -1.51 eV
 - (d) -0.85 eV

7. Which of the following statement(s) is/are correct?
- The ratio of the radii of the first three Bohr orbits of hydrogen atom is 1:8:27.
 - The ratio of magnitude of total energy: kinetic energy: potential energy for electron in any orbit of hydrogen atom is 1:1:2.
 - The frequency of a green light is 6×10^{14} Hz, then its wavelength is 500 nm.
 - The ratio of de Broglie wavelength of a H-atom, He-atom and CH_4 -molecule moving with equal kinetic energy is 4:2:1.
8. When photons of energy 4.25 eV strikes the surface of a metal 'A', the ejected photoelectrons have maximum kinetic energy T_A (in eV) and de Broglie wavelength λ_A . The maximum kinetic energy of photoelectrons liberated from another metal 'B' by photons of energy 4.20 eV is T_B ($= T_A - 1.50$ eV). If the de Broglie wave length of these photoelectrons is λ_B ($= 2\lambda_A$), then
- the work function of 'A' is 2.25 eV
 - the work function of 'B' is 3.70 eV
 - $T_A = 2.00$ eV
 - $T_B = 2.75$ eV

9. Which is/are correct for sodium atom in the ground state?
- There is only one unpaired electron.
 - There are five pairs of electrons.
 - 6 electrons are of one spin and other 5 of opposite spin.
 - There are ten electrons in the same spin.

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 10 to 13): The wave function for an atomic orbital of single electron atom or ion is

$$\Psi(r, \theta, \phi) = \frac{2}{3} \left(\frac{Z}{3a_0} \right)^{3/2} (1-\sigma)(12-8\sigma+\sigma^2) \cdot \sigma \cdot e^{-\sigma/2} \cdot \cos \theta$$

where $\sigma = \left(\frac{2Zr}{na_0} \right)$ and $a_0 = 0.529$ Å. All other parameters have their usual meaning.

- The number of radial and angular nodes for the orbital is, respectively,
- 4p
- 5p
- 5d
- 5f
- If θ is the angle measured from Z-axis, then the orbital should be:
- p_x
- p_y
- p_z
- d_{z^2}
- The maximum distance of radial node from the nucleus is:
- $\frac{a_0}{Z}$
- $\frac{3a_0}{Z}$
- $\frac{6a_0}{Z}$
- $\frac{15a_0}{Z}$

MATCH THE COLUMN TYPE QUESTIONS

14. Frequency = f, Time period = T, Energy of n^{th} orbit = E_n , radius of n^{th} orbit = r_n , Atomic number = Z, Orbit number = n

Column-I		Column-II	
A.	f	p.	n^3
B.	T	q.	Z^2
C.	E_n	r.	$\frac{1}{n^2}$
D.	$\frac{1}{r_n}$	s.	Z

- $A \rightarrow (q); B \rightarrow (p); C \rightarrow (q,r); D \rightarrow (r,s)$
- $A \rightarrow (r); B \rightarrow (p); C \rightarrow (q,r); D \rightarrow (r,s)$
- $A \rightarrow (q); B \rightarrow (p); C \rightarrow (q,r); D \rightarrow (q, s)$
- $A \rightarrow (q); B \rightarrow (p); C \rightarrow (s,r); D \rightarrow (r,s)$

15. Match List-I with List-II and select the correct answer using the codes given below in the lists (n, ℓ and m are respectively the principal, azimuthal and magnetic quantum no.)

List-I		List-II	
A.	Number of value of l for an energy level (n)	p.	$0, 1, 2, \dots, (n-1)$
B.	Values of ℓ for a particular type of orbit	q.	$+\ell$ to $-\ell$ through zero
C.	Number of value of m for $\ell = 2$	r.	5
D.	Values of 'm' for a particular type of orbital	s.	n

- $A \rightarrow (r); B \rightarrow (p); C \rightarrow (s); D \rightarrow (q)$
- $A \rightarrow (s); B \rightarrow (q); C \rightarrow (r); D \rightarrow (p)$
- $A \rightarrow (s); B \rightarrow (p); C \rightarrow (r); D \rightarrow (q)$
- $A \rightarrow (r); B \rightarrow (p); C \rightarrow (s); D \rightarrow (q)$

16. Match the column & choose the correct option among the options given.

(Note: Each statement in column-I has one or more matches in column-II.)

Column-I (For mono electronic species)		Column-II	
A.	Radius of nth orbit	p.	inversely proportional to Z
B.	Energy of electron in n^{th} orbit	q.	inversely proportional to n^2
C.	Velocity of electron in nth orbit	r.	inversely proportional to n
D.	Angular momentum of electron	s.	proportional to n

- (a) A → (p); B → (q); C → (r); D → (s)
 (b) A → (p,r); B → (q); C → (r); D → (s)
 (c) A → (p,q); B → (p,r); C → (r); D → (s)
 (d) A → (p,q); B → (q); C → (s); D → (r)

17. Match the column & choose the correct option among the options given.

(Note: Each statement in column-I has one or more matches in column-II.)

Column-I		Column-II	
A.	5 → 1 transition in H atom	p.	spectral line in IR region
B.	7 → 3 transition in H atom	q.	spectral line in visible region
C.	Last line of Balmer series in H atom	r.	spectral line ultra violet region
D.	4 → 2 transition in He ₊ ion	s.	spectral line will be observed one

- (a) A → (r,s); B → (q,s); C → (r,s); D → (p,s)
 (b) A → (r,s); B → (p,s); C → (q,s); D → (r,s)
 (c) A → (r,s); B → (r,s); C → (p,s); D → (r,s)
 (d) A → (r,s); B → (r); C → (p,s); D → (q,s)

18. Match the column & choose the correct option among the options given.

(Note: Each statement in column-I has only one match in column-II.)

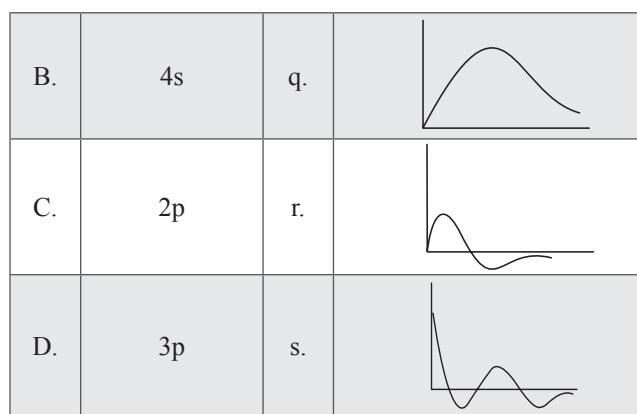
Column-I		Column-II	
A.	Orbit angular momentum	p.	$\sqrt{n(n+2)}$
B.	Orbital angular momentum	q.	$\frac{nh}{2\pi}$
C.	Spin angular momentum	r.	$\sqrt{s(s+1)h}$
D.	Magnetic moment	s.	$\sqrt{l(l+1)h}$
		t.	$\sqrt{n(n+1)h}$

- (a) A → (p); B → (r); C → (s); D → (q)
 (b) A → (p); B → (s); C → (r); D → (q)
 (c) A → (q); B → (s); C → (r); D → (p)
 (d) A → (q); B → (r); C → (s); D → (p)

19. Match the columns & choose the correct option among the options given.

(Note: Each statement in column-I has only one match in column-II.)

Column-I (Orbital)		Column-II (R vs. r Graph)	
A.	3s	p.	



- (a) A → (q); B → (s); C → (q); D → (r)
 (b) A → (p); B → (q); C → (s); D → (r)
 (c) A → (r); B → (s); C → (q); D → (q)
 (d) A → (p); B → (s); C → (q); D → (r)

20. 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.

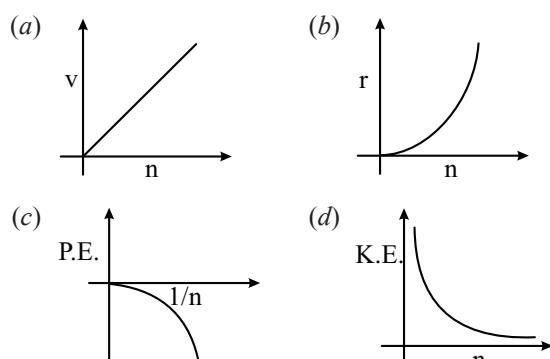
21. Select the correct curve(s):

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.



22. Which is/are **correct** statement:

- (a) The difference in angular momentum associated with the electron present in consecutive orbits of H- atom is $(n-1)\frac{h}{2\pi}$.
 (b) Energy difference between energy levels will be changed if, P. E. at infinity assigned value other than zero.
 (c) Frequency of spectral line in a H-atom is in the order of $(2 \rightarrow 1) < (3 \rightarrow 1) < (4 \rightarrow 1)$.
 (d) On moving away from the nucleus, kinetic energy of electron decreases.

23. If there are only two H-atoms, each is in 3rd excited state then:
- Maximum number of different photons emitted is 4.
 - Maximum number of different photons emitted is 3.
 - Minimum number of different photons emitted is 1.
 - Minimum number of different photons emitted is 2.
24. The qualitative order of de-Broglie wavelength for electron, proton and α particle is $\lambda_e > \lambda_p > \lambda_\alpha$ if:
- If kinetic energy is same for all particles.
 - If the accelerating potential difference 'V' is same for all the particles (from rest).
 - If velocities are same for all particles.
 - None of the above.
25. In the experiment on photoelectric effect using light having frequency greater than the threshold frequency, the photocurrent will certainly increase when:
- Anode voltage is increased.
 - Area of cathode surface is increased.
 - Intensity of incident light is increased.
 - Distance between anode and cathode is increased.
26. An electron in hydrogen atom first jumps from second excited state to first excited state and then, from first excited state to ground state. Let the ratio of wavelength, momentum and energy of photons in the two cases by x, y and z, then select the wrong answers:
- $z = 1/x$
 - $x = 9/4$
 - $y = 5/27$
 - $z = 5/27$
27. Choose the correct statement among the following:
- Radial distribution function ($\psi^2 \cdot 4\pi r^2 dr$) give probability at a particular distance along any chosen direction.
 - $\psi^2(r)$ give probability density at a particular distance over a spherical surface.
 - For 's' orbitals $\psi(r)\psi(\theta)\psi(\phi) = \psi(x, y, z)$ is independent of θ and ϕ .
 - '2p' orbital with quantum numbers. $n = 2, l = 1, m = 0$, also shows angular dependence.
28. Which of the following statements is/are correct for an electron of quantum numbers $n = 4$ and $m = 2$?
- The value of l may be 2.
 - The value of l may be 3.
 - The value of s may be +1/2.
 - The value of l may be 0, 1, 2, 3.
29. Which of the following statement(s) is (are) correct?
- The electronic configuration of Cr is [Ar] (3d)⁵ (4s)¹. (Atomic number of Cr = 24)
 - The magnetic quantum number may have negative values.
 - In silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (Atomic number of Ag = 47)
 - None of these

NUMERICAL TYPE QUESTIONS

30. What is likely to be orbit number for a circular orbit of diameter 20 nm of the hydrogen atom if we assume Bohr orbit to be the same as that represented by the principal quantum number?
31. Number of possible spectral lines which may be emitted in Bracket series in H atom if electrons present in 9th excited level returns to ground level, are _____.
32. In a sample of H-atom electrons make transition from 5th excited state to ground state, producing all possible types of photons, then number of lines in infrared region are _____.
33. The maximum number of 3d-electrons having spin quantum number $s = +1/2$ are _____.
34. Magnetic moment of X^{3+} ion of 3d series is $\sqrt{35}$ BM. What is atomic number of X^{3+} ?
35. The work function (ϕ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metal is
- | | | | | | | | | | |
|-------------|-----|-----|-----|-----|-----|-----|-----|-----|------|
| Metal | Li | Na | K | Mg | Cu | Ag | Fe | Pt | W |
| ϕ (eV) | 2.4 | 2.3 | 2.2 | 3.7 | 4.8 | 4.3 | 4.7 | 6.3 | 4.75 |
36. The quantum number n corresponding to the excited state of He^+ ion if on transition to the ground state that ion emits two photons in succession with wavelengths 108.5 and 30.4 nm is
37. 'a particle' of 3.6 MeV are fired towards nucleus ${}^A_Z X$, at point of closest separation distance between 'a particle' and ' X ' is 1.6×10^{-14} m. Calculate atomic number of ' X ' [Given: $1/4\pi e_0 = 9 \times 10^9$ in S.I. units]
38. The atomic number of hydrogen-like ion has the wavelength difference between the first line of Balmer and Lyman series equal to 59.3 nm.
39. Photons of same energy were allowed to strike on two different samples of hydrogen atoms, one having each atom in ground state and other in a particular excited state of orbit number n. The photonic beams ionize the hydrogen atoms in both the samples. If the difference in maximum kinetic energy of emitted photoelectron from both the samples is 12.75 eV, then the value of n is.
40. The angular momentum of an electron in a Bohr's orbit of H-atom is 3.1652×10^{-34} kg-m²/sec. Calculate the wavenumber in terms of Rydberg constant (R) of the spectral line emitted when an electron falls from this level to the ground state.[Use $h = 6.626 \times 10^{-34}$ Js]
41. A photon having $\lambda = 960 \text{ \AA}$ causes the ionization of a nitrogen atom. Give the I.E. per mole of nitrogen in KJ. (Use : $hc = 1240 \text{ eV} \times \text{nm}$ and $1 \frac{\text{eV}}{\text{atom}} = 96.0 \text{ kJ/mol}$)
42. The work function for a metal is 40 eV. To emit photo electrons of zero velocity from the surface of the metal the wavelength of incident light should be x nm.
43. If first ionization potential of a hypothetical atom is 16 V, then the first excitation potential will be :

44. Electrons in the H-atoms jump from some higher level upto 3rd energy level. If three spectral lines are possible for the transition, find the initial position of electron.

45. An electron in Li²⁺ ion makes a transition from higher state n₂ to lower state n₁ = 6. The emitted photons is used to ionize an electron in H-atom from 2nd excited state. The electron on leaving the H-atom has a de-Broglie wavelength $\lambda = 12.016 \text{ \AA}$. Find the value of n₂.

Note: Use $(12.016)^2 = \frac{150 \times 144}{13.6 \times 11}$, $\lambda_A = \sqrt{\frac{150}{KE_{\text{eV}}}}$

46. In a hypothetical H-atom the mass of electron & its charge is double of what we consider then calculate the total energy (in eV) of electron in the 1st orbit of such a hypothetical H-atom?
 [Assuming all others concepts and parameter to be same as we considered in Bohr's model.]

47. In H-spectrum, longest wavelength of Lyman is 120 nm and shortest wavelength of Balmer is 360 nm. From this data, find longest wavelength of photon, that can ionize this H-atom.

48. A proton and an electron, both at rest initially, combine to form a H-atom in ground state. A single photon is emitted in this process. Find the wavelength (in nm) of this photon. (use : $hc = 1237.6 \text{ eV} \times \text{nm}$)

49. The ionisation energy of the hydrogen atom is given to be 13.6 eV. A photon falls on a hydrogen atom which is initially in the ground state and excites it to the (n = 4)state. Calculate the wavelength (in Å) of the photon.

50. The diameter of a dust particle of mass 10^{-3} gm is 2 Å. If uncertainty in speed of this particle is $\frac{3.31}{\pi} \times 10^{-3} \text{ m/s}$, then find minimum uncertainty in its position.

51. The vapours of Hg absorb some electrons accelerated by a potential difference of 4.5 eV, as a result of which 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. (in m⁻¹) of the light.

52. Mr. Alakh Pandey has to decode a number "ABCDEF" where each alphabet is represented by a single digit. Suppose an orbital whose radial wave function is represented as;

$$\Psi_{(r)} = k_1 \cdot e^{-r/k_2} (r^2 - 5k_3 r + 6k_3^2).$$
 From the following information given about each alphabet then write down the answers in the form of "ABCDEF", for above orbital.
 Info A = Value of n where "n" is principal quantum number.
 Info B = No. of angular nodes.
 Info C = Azimuthal quantum number of subshell to orbital belongs.
 Info D = No. of subshells having energy between (n + 5)s to (n + 5)p where n is principal quantum number.
 Info E = Orbital angular momentum of given orbital.
 Info F = Radial distance of the spherical node which is farthest from the nucleus. (Assuming $k_1 = 1$).



Exercise-4 (Past Year Questions)

JEE MAIN

(a) $\lambda \propto \frac{1}{(v - v_0)}$

(b) $\lambda \propto \frac{1}{(v - v_0)^{\frac{1}{4}}}$

(c) $\lambda \propto \frac{1}{(v - v_0)^{\frac{3}{2}}}$

(d) $\lambda \propto \frac{1}{(v - v_0)^{\frac{1}{2}}}$

6. Heat treatment of muscular pain involves radiation of wavelength of about 900 nm.

Which spectral line of H atom is suitable for this purpose?

$[R_H = 1 \times 10^5 \text{ cm}^{-1}, h = 6.6 \times 10^{-34} \text{ Js} = 3 \times 10^8 \text{ ms}^{-1}]$

(2019)

- (a) Paschen, $\infty \rightarrow 3$ (b) Paschen, $5 \rightarrow 3$
 (c) Balmer, $\infty \rightarrow 2$ (d) Lyman, $\infty \rightarrow 1$

7. For emission line of atomic hydrogen from $n_i = 8$ to $n_f = n$, the plot of wave number (\tilde{v}) against $\left(\frac{1}{n^2}\right)$ will be (The Rydberg constant, R_H is in wave number unit):

- (a) Linear with intercept - R_H .
 (b) Non linear.
 (c) Linear with slope R_H .
 (d) Linear with slope - R_H .

8. The isotopes of hydrogen are:

(2019)

- (a) Tritium and protium only.
 (b) Protium and deuterium only.
 (c) Protium, deuterium and tritium.
 (d) Deuterium and tritium only.

9. What is the work function of the metal if the light of wavelength 4000 Å generates photoelectrons of velocity $6 \times 10^5 \text{ ms}^{-1}$ from it?

(2019)

(Mass of electron = $9 \times 10^{-31} \text{ kg}$

Velocity of light = $3 \times 10^8 \text{ ms}^{-1}$

Planck's constant = $6.626 \times 10^{-34} \text{ Js}$

Charge of electron = $1.6 \times 10^{-19} \text{ eV}^{-1}$

- (a) 0.9 eV (b) 3.1 eV
 (c) 2.1 eV (d) 4.0 eV

10. The 71st electron of an element X with an atomic number of 71 enters in to the orbital:

(2019)

- (a) 6 p (b) 4f
 (c) 5d (d) 6s

11. The ground state energy of hydrogen atom is -13.6 eV. The energy of second excited state of He^+ ion eV is:

(2019)

- (a) -54.4 (b) -3.4
 (c) -6.04 (d) -27.2

12. 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:

(2019)

- (a) 0.40 (b) 1.50
 (c) 1.0 (d) 0.75

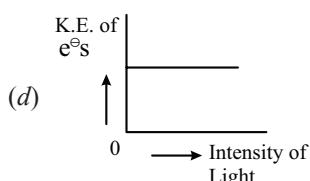
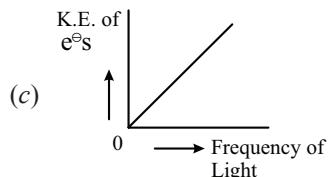
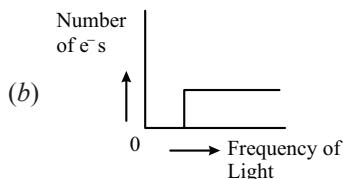
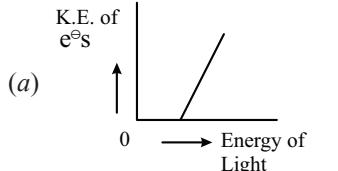
13. The total number of isotopes of hydrogen and number of radioactive isotopes among them, respectively are:

(2019)

- (a) 3 and 1 (b) 3 and 2
 (c) 2 and 1 (d) 2 and 0

14. Which of the graphs shown below does not represent the relationship between incident light and the electron ejected from metal surface?

(2019)



15. The quantum number of four electrons are given below;

(2019)

(I) $n = 4, l = 2, m_l = -2, m_s = -\frac{1}{2}$

(II) $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$

(III) $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$

(IV) $n = 3, l = 1, m_l = 1, m_s = -\frac{1}{2}$

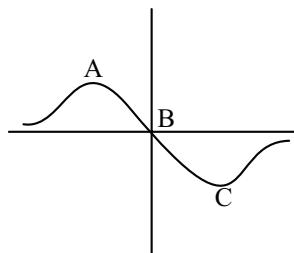
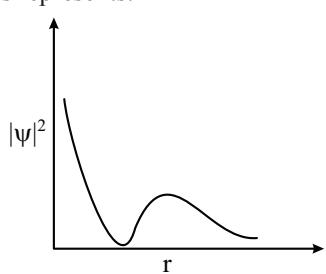
The Correct order of their increasing energies will be:

- (a) IV < III < II < I (b) IV < II < III < I
 (c) I < II < III < IV (d) I < III < II < IV

16. The size of the isoelectronic species Cl^- , Ar and Ca^{2+} is affected by:

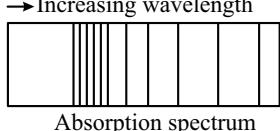
(2019)

- (a) Principal quantum number of valence shell.
 (b) Nuclear charge.
 (c) Azimuthal quantum number of valence shell.
 (d) Electron-electron interaction in the outer orbitals.

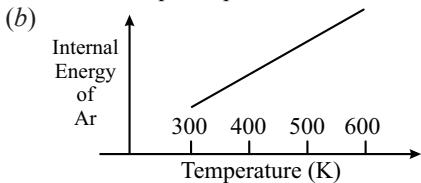
17. The element having greatest difference between its first and second ionization energies, is: (2019)
 (a) Ca (b) K (c) Ba (d) Sc
18. For any given series of spectral lines of atomic hydrogen, let $\Delta\bar{v} = \bar{v}_{\text{max}} - \bar{v}_{\text{min}}$ be the difference in maximum and minimum frequencies in cm^{-1} . The ratio $\Delta\bar{v}_{\text{Lyman}} / \Delta\bar{v}_{\text{Balmer}}$ is: (2019)
 (a) 27 : 5 (b) 4 : 1 (c) 5 : 4 (d) 9 : 4
19. If P is the momentum of the fastest electron ejected from a metal surface after the irradiation of light having wavelength λ , then for 1.5 P momentum of the photoelectron, the wavelength of the light should be:
 (Assume kinetic energy of ejected photoelectron to be very high in comparison to work function). (2019)
- (a) $\frac{1}{2}\lambda$ (b) $\frac{3}{4}\lambda$
 (c) $\frac{2}{3}\lambda$ (d) $\frac{4}{9}\lambda$
20. Which one of the following about an electron occupying the orbital in a hydrogen atom is incorrect? (The Bohr radius is represented by a_0) (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.
21. The electrons are more likely to be found: (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)
22. The isoelectronic set of ions is (2019)
 (a) $\text{N}^{3-}, \text{Li}^+$, Mg^{2+} and O^{2-} (b) $\text{Li}^+, \text{Na}^+, \text{O}^{2-}$ and F^-
 (c) $\text{F}^-, \text{Li}^+, \text{Na}^+$ and Mg^{2+} (d) $\text{N}^{3-}, \text{O}^{2-}, \text{F}^-$ and Na^+
23. The graph between $|\psi|^2$ and r (radial distance) is shown below. This represents: (2019)
- 
- (a) 3s orbital (b) 1s orbital
 (c) 2p orbital (d) 2s orbital
24. The ratio of the shortest wavelength of two spectral series of hydrogen spectrum is found to be about 9. The spectral series are: (2019)
 (a) Paschen and Pfund (b) Lyman and Paschen
 (c) Brackett and Pfund (d) Balmer and Brackett
25. The region in the electromagnetic spectrum where the Balmer series lines appear is: (2020)
 (a) Infrared (b) Microwave
 (c) Ultraviolet (d) Visible
26. The number of orbitals associated with quantum number $n = 5, m_s = +\frac{1}{2}$ is: (2020)
 (a) 11 (b) 25
 (c) 50 (d) 15
27. For the Balmer series in the spectrum of H atom,
 $\bar{v} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$, the correct statement among (I) to (IV) are : (2020)
 (I) As wavelength decreases, the lines in the series converge.
 (II) The integer n_1 is equal to 2.
 (III) The lines of longer wavelength corresponds to $n_2 = 3$.
 (IV) The ionization energy of hydrogen can be calculated from wave number of these lines.
 (a) (I), (III), (IV) (b) (I), (II), (IV)
 (c) (II), (III), (IV) (d) (I), (II), (III)
28. Hydrogen has three isotopes (A), (B) and (C). If the number of neutrons in (A), (B), (C) respectively, are (x), (y) and (z) the sum of (x), (y) and (z) is: (2020)
 (a) 4 (b) 2
 (c) 3 (d) 1
29. The radius of the second Bohr orbit, in terms of the Bohr radius, a_0 , in Li^{2+} is: (2020)
 (a) $\frac{2a_0}{3}$ (b) $\frac{4a_0}{9}$
 (c) $\frac{4a_0}{3}$ (d) $\frac{2a_0}{9}$
30. The de-Broglie wavelength of an electron in the 4th Bohr orbit is: (2020)
 (a) $4\pi a_0$ (b) $2\pi a_0$
 (c) $6\pi a_0$ (d) $8\pi a_0$
31. The work function of sodium metal is $4.41 \times 10^{-19} \text{ J}$. If photons of wavelength 300 nm are incident on the metal, the kinetic energy of the ejected electrons will be: (2020)
 $(h = 6.63 \times 10^{-34} \text{ J s}; c = 3 \times 10^8 \text{ m/s}) \quad \times 10^{-21} \text{ J}$.
32. The metal mainly used in devising photoelectric cells is: (2020)
 (a) Na (b) Rb
 (c) Li (d) Cs
33. The number of subshells associated with $n = 4$ and $m = -2$ quantum numbers is: (2020)
 (a) 2 (b) 8
 (c) 4 (d) 16

34. The figure that is not a direct manifestation of the quantum nature of atoms is: (2020)

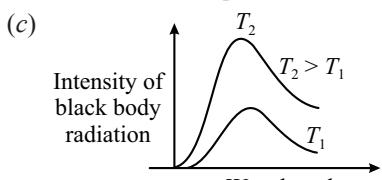
(a) → Increasing wavelength



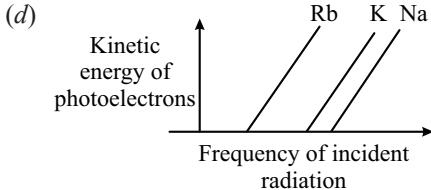
Absorption spectrum



Internal Energy of Ar
Temperature (K)



Intensity of black body radiation
Wavelength



Kinetic energy of photoelectrons
Frequency of incident radiation

35. Consider the hypothetical situation where the azimuthal quantum number, l , takes value $0, 1, 2, \dots n+1$, where n is the principal quantum number. Then, the element with atomic number: (2020)

- (a) 9 is the first alkali metal.
(b) 6 has a 2p-valence subshell.
(c) 8 is the first noble gas.
(d) 13 has a half-filled valence subshell.

36. The photoelectric current from Na (work function, $w_0 = 2.3$ eV) is stopped by the output voltage of the cell Pt(s)|H₂ (g, 1 bar)|HCl(aq., pH = 1)|AgCl(s)|Ag(s).

The pH of aq. HCl required to stop the photoelectric current from K ($w_0 = 2.25$ eV), all other conditions remaining the same, is $\text{_____} \times 10^{-2}$. (to the nearest integer) (2020)

$$\text{Given, } 2.303 \frac{RT}{F} = 0.06 \text{ V; } E_{\text{AgCl}|\text{AgCl}^-}^0 = 0.22 \text{ V}$$

37. The shortest wavelength of H atom in the Lyman series is λ_1 . The longest wavelength in the Balmer series of He⁺ is: (2020)

- (a) $\frac{5\lambda_1}{9}$
(b) $\frac{36\lambda_1}{5}$
(c) $\frac{27\lambda_1}{5}$
(d) $\frac{9\lambda_1}{5}$

38. The correct statement about probability density (except at infinite distance from nucleus) is: (2020)

- (a) It can never be zero for 2s orbital.
(b) It can be zero for 3p orbital.
(c) It can be zero for 1s orbital.
(d) It can be negative for 2p orbital.

39. The difference between radii of 3rd and 4th orbits of Li²⁺ is ΔR_1 . The difference between the radii of 3rd and 4th orbits of He⁺ is ΔR_2 . Ratio $\Delta R_1 : \Delta R_2$ is: (2020)

- (a) 3 : 2
(b) 8 : 3
(c) 2 : 3
(d) 3 : 8

40. The correct electronic configuration and spin only magnetic moment (BM) of Gd³⁺ ($Z = 64$), respectively, are: (2020)

- (a) [Xe] 5f⁷ and 8.9
(b) [Xe] 4f⁷ and 7.9
(c) [Xe] 5f⁷ and 7.9
(d) [Xe] 4f⁷ and 8.9

41. In the sixth period, the orbitals that are filled are: (2020)

- (a) 6s, 4f, 5d, 6p
(b) 6s, 5d, 5f, 6p
(c) 6s, 6p, 6d, 6f
(d) 6s, 5f, 6d, 6p

42. A 50 watt bulb emits monochromatic red light of wavelength of 795nm. The number of photons emitted per second by the bulb is $x \times 10^{20}$. The value of x is _____. (2021)

[Given: $h = 6.63 \times 10^{-34} \text{ Js}$ and $c = 3.0 \times 10^8 \text{ ms}^{-1}$]

43. The value of magnetic quantum number of the outermost electron of Zn⁺ ion is _____. (2021)

44. Ge ($Z = 32$) in its ground state electronic configuration has completely filled orbitals with $m_l = 0$. The value of x is _____. (2021)

45. The number of photons emitted by a monochromatic (single frequency) infrared range finder of power 1mW and wavelength of 1000nm, in 0.1 second is $x \times 10^{13}$. The value of x is _____. (Nearest integer)
($h = 6.63 \times 10^{-34} \text{ Js}$, $c = 3.00 \times 10^8 \text{ ms}^{-1}$) (2021)

46. A proton and a Li³⁺ nucleus are accelerated by the same potential. If λ_{Li} and λ_p denote the de Broglie wavelengths of Li³⁺ and proton respectively, then the value of $\frac{\lambda_{\text{Li}}}{\lambda_p}$ is $x \times 10^{-1}$.

The value of x is _____ (Rounded off to the nearest integer)
[Mass of Li³⁺ = 8.3 mass of proton] (2021)

47. According to Bohr's atomic theory:

- (I) Kinetic energy of electron is $\propto \frac{Z^2}{n^2}$.

- (II) The product of velocity (v) of electron and principal quantum number (n), ' vn ' $\propto Z^2$.

- (III) Frequency of revolution of electron in an orbit is $\propto \frac{Z^3}{n^3}$.

- (IV) Coulombic force of attraction on the electron is $\propto \frac{Z^3}{n^4}$.

Choose the most appropriate answer from the options given below: (2021)

- (a) I, III and IV only
(b) I and IV only
(c) I only
(d) III only

48. Electromagnetic radiation of wavelength 663 nm is just sufficient to ionise the atom of metal A. The ionization energy of metal A in kJ mol is _____. (Rounded-off to the nearest integer)
 $[h = 6.63 \times 10^{-34} \text{ Js}, c = 3.00 \times 10^8 \text{ ms}^{-1}, N_A = 6.02 \times 10^{23} \text{ mol}^{-1}]$ (2021)
49. The orbital having two radial as well as two angular nodes is: (2021)
 (a) 4d (b) 4f (c) 3p (d) 5d
50. Which of the following forms of hydrogen emits low energy β^- particles? (2021)
 (a) Deuterium ${}^2_1\text{H}$ (b) Protium ${}^1_1\text{H}$
 (c) Proton H^+ (d) Tritium ${}^3_1\text{H}$
51. A ball weighing 10 g is moving with a velocity of 90 ms^{-1} . If the uncertainty in its velocity is 5% then the uncertainty in its position is.... $\times 10^{-33} \text{ m}$. (Given $h = 6.63 \times 10^{-34} \text{ Js}$) (2021)
52. When light of wavelength 248 nm falls on a metal of threshold energy 3.0 eV, the de-Broglie wavelength of emitted electrons is... Å.
 [Use: $\sqrt{3} = 1.73$, $h = 6.63 \times 10^{-34} \text{ Js}$, $m_e = 9.1 \times 10^{-31} \text{ kg}$; $c = 3.0 \times 10^8 \text{ ms}^{-1}$; $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$] (2021)
53. The number of orbitals with $n = 5$, $m_l = +2$ is _____. (2021)
54. A certain orbital has $n = 4$ and $m_l = -3$. The number of radial nodes in this orbital is _____. (2021)
55. A certain orbital has no angular nodes and two radial nodes, the orbital is: (2021)
 (a) 2s (b) 3p (c) 3s (d) 2p
56. The Azimuthal quantum number for the valence electrons Ga^+ ion is.....
 (Atomic number of Ga = 31) (2021)
57. The wavelengths of electrons accelerated from rest through a potential difference of 40 kV is $x \times 10^{-12} \text{ m}$. the value of x is _____.
 Given: Mass of electron = $9.1 \times 10^{-31} \text{ kg}$
 Charge on an electron = $1.6 \times 10^{-19} \text{ kg}$
 Planck's constant = $6.63 \times 10^{-34} \text{ Js}$ (2021)
58. Number of electrons that Vandium ($Z = 23$) has in p-orbitals is equal to _____. (2021)
59. A source of monochromatic radiation of wavelength 400 nm provides 1000 J of energy in 10 seconds. When this radiation falls on the surface of sodium, $x \times 10^{20}$ electrons are ejected per second. Assume that wavelength 400 nm is sufficient for ejection of electron from the surface of sodium metal. The value of x is
 $(h = 6.626 \times 10^{-34} \text{ Js})$ (2021)
60. An accelerated electron, has a speed of $5 \times 10^6 \text{ ms}^{-1}$ with an uncertainty of 0.02%. The uncertainty in finding its location while in motion is $x \times 10^{-9} \text{ m}$. The value of x is _____.
 [Use mass of electron = $9.1 \times 10^{-31} \text{ Kg}$. $h = 6.63 \times 10^{-34} \text{ Js}$, $\pi = 3.14$] (2021)
61. Given below are two statements;
Statement-I : Rutherford's gold foil experiment cannot explain the line spectrum of hydrogen atom.
Statement-II: Bohr's model of hydrogen atom contradicts Heisenberg's uncertainty principle.

In the light of the above statements, choose the most appropriate answer from the options given below: (2021)

- (a) Both statement I and statement II are true.
 - (b) Statement I is false but statement II is false.
 - (c) Statement I is true but statement II is false.
 - (d) Both statement I and statement II are false.
62. If the Thompson model of the atom was correct, the then result of Rutherford's gold foil experiment would have been: (2021)
 (a) α -particles pass through the gold foil deflected by small angles and with reduced speed.
 (b) All α -particles get bounced back by 180° .
 (c) All of the α -particles pass through the gold foil without decrease in speed.
 (d) α -particles are deflected over a wide range of angles.
63. Given below are two statements;
Statement-I: According to Bohr's model of an atom, qualitatively the magnitude of velocity of electron increases with decrease in positive charges on the nucleus as there is no strong hold on the electron by the nucleus.
Statement-II: According to Bohr's model of an atom, qualitatively the magnitude of velocity of electron increases with decrease in principal quantum number.
 In the light of the above statements, choose the most appropriate answer from the options given below: (2021)
 - (a) Statement-I is true but Statement-II is false.
 - (b) Statement-I is false but Statement-II is true.
 - (c) Both Statement-I and Statement-II are false.
 - (d) Both Statement-I and Statement-II are true.

64. A metal surface is exposed to 500 nm radiation. The threshold frequency of the metal for photoelectric current is $4.3 \times 10^{14} \text{ Hz}$. The velocity of ejected electron is $x \times 10^5 \text{ ms}^{-1}$.
 [Use : $h = 6.63 \times 10^{-34} \text{ Js}$, $m_e = 9.0 \times 10^{-31} \text{ Kg}$] (2021)

65. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is equal to $\frac{h^2}{xma_0^2}$. The value of $10x$ is ? _____.
 $(a_0$ is radius of Bohr's orbit)
 [Given : $\pi = 3.14$] (2021)

66. The number of f electrons in the ground state electronic configuration of Np ($Z = 93$) is _____. (2021)

67. The number of photons emitted by a monochromatic (single frequency) infrared range finder of power 1mW and wavelength of 1000nm, in 0.1 second is $x \times 10^{13}$. The value of x is _____.
 $(h = 6.63 \times 10^{-34} \text{ Js}, c = 3.00 \times 10^8 \text{ ms}^{-1})$ (2021)

68. The Eu^{2+} ion is a strong reducing agent in spite of its ground state electronic configuration (outermost) : [Atomic number of Eu = 63].
 (a) $4f^8 6s^2$ (b) $4f^7$ (c) $4f^7 6s^2$ (d) $4f^6$ (2021)

69. Identify the element for which electronic configuration in +3 oxidation state is [Ar]3d⁵. (2021)

(a) Ru (b) Co (c) Mn (d) Fe

70. Consider the following pairs of electrons: (2022)

(A) (a) n = 3, l = 1, m_l = 1, m_s = + $\frac{1}{2}$

(b) n = 3, l = 2, m_l = 1, m_s = + $\frac{1}{2}$

(B) (a) n = 3, l = 2, m_l = -2, m_s = - $\frac{1}{2}$

(b) n = 3, l = 2, m_l = -1, m_s = - $\frac{1}{2}$

(C) (a) n = 4, l = 2, m_l = 2, m_s = + $\frac{1}{2}$

(b) n = 3, l = 2, m_l = 2, m_s = + $\frac{1}{2}$

The pairs of electron present in degenerate orbitals is/are:

- (a) Only A (b) Only B
(c) Only C (d) Both (B) and (C)

71. If the radius of the 3rd Bohr's orbit of hydrogen atom is r₃ and the radius of 4th Bohr's orbit is r₄.

Then : (2022)

(a) r₄ = $\frac{9}{16}r_3$ (b) r₄ = $\frac{16}{9}r_3$ (c) r₄ = $\frac{3}{4}r_3$ (d) r₄ = $\frac{4}{3}r_3$

72. Which of the following sets of quantum numbers is not allowed? (2022)

(a) n = 3, l = 2, m_l = 0, s = + $\frac{1}{2}$

(b) n = 3, l = 2, m_l = -2, s = + $\frac{1}{2}$

(c) n = 3, l = 3, m_l = -3, s = - $\frac{1}{2}$

(d) n = 3, l = 0, m_l = 0, s = - $\frac{1}{2}$

73. The wavelength of an electron and a neutron will become equal when the velocity of the electron is x times the velocity of neutron. The value of x is _____. (Nearest Integer)

(Mass of electron is 9.1×10^{-31} kg and mass of neutron is 1.6×10^{-27} kg) (2022)

74. Consider an imaginary ion $^{48}_{22}X^{3-}$. The nucleus contains 'a' % more neutrons than the number of electrons in the ion. the value of 'a' is _____. (2022)

75. Uncertainty in position of a moving particle is 10^{-7} m and uncertainty velocity is 2.4×10^{-24} m/sec, then mass of particle is [X] $\times 10^{-5}$ Kg value of X is [Report your answer to nearest integer] (2022)

76. Which set of quantum number represent degenerate orbital? (2022)

(I) n = 3, l = 2, m = 0, s = $\frac{-1}{2}$ & n = 3, l = 2 m = -1
s = $\frac{+1}{2}$

(II) n = 2, l = 1, m = 1, s = $\frac{-1}{2}$ & n = 3, l = 1 m = 1

s = $\frac{+1}{2}$

(III) n = 4, l = 2, m = -1, s = $\frac{1}{2}$ & n = 3, l = 2 m = -1

s = $\frac{1}{2}$

- (a) I (b) II

- (c) III (d) None of these

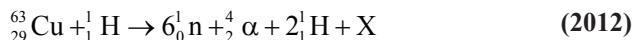
JEE ADVANCED

77. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is [a₀ is Bohr radius]: (2012)

(a) $\frac{h^2}{4\pi^2 ma_0^2}$ (b) $\frac{h^2}{16\pi^2 ma_0^2}$

(c) $\frac{h^2}{32\pi^2 ma_0^2}$ (d) $\frac{h^2}{64\pi^2 ma_0^2}$

78. The periodic table consists of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element X as shown below. To which group, element X belongs in the periodic table?



79. In the nuclear transmutation; (2013)

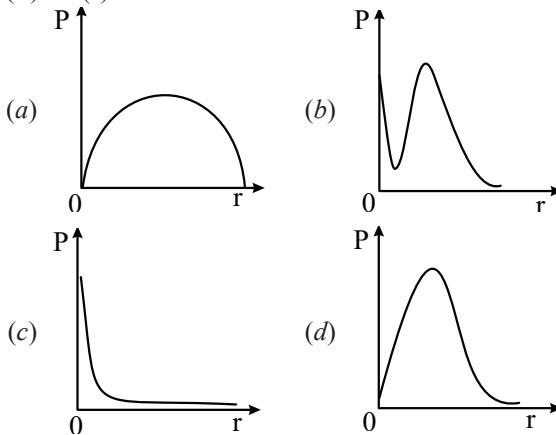


- (a) (γ , n) (b) (p, D) (c) (n, D) (d) (γ , p)

80. In an atom, the total number of electrons having quantum numbers n = 4, |m_l| = 1 and m_s = -1/2 is _____. (2014)

81. 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 _____. (2015)

82. P is the probability of finding 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 (2016)



Comprehension (Q. 83 to 86): Answer 7, 8 and 9 by appropriately matching the information given in the three columns of the following table.

The wave function $\Psi_n l m_l$ 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_l . 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. (2017)

Column 1

- | | |
|-------------------------------|---|
| (I) 1s orbital | (II) 2s orbital |
| (III) 2p _z orbital | (IV) 3d _z ² orbital |

Column 2

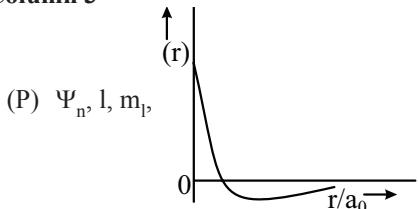
$$(i) \Psi_{n,l,m_l} \propto \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\left(\frac{Zr}{a_0}\right)}$$

(ii) One radial node

$$(iii) \Psi_{n,l,m_l} \propto \left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\left(\frac{Zr}{2a_0}\right)} \cos \theta$$

(iv) xy-plane is a nodal plane

Column 3



(P) Probability density at nucleus $\propto \frac{1}{a_0^3}$.

(R) Probability density is maximum at nucleus.

(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.

83. For He^+ ion, the only **INCORRECT** combination is:

- | | |
|-------------------|-------------------|
| (a) (I) (i) (S) | (b) (II) (ii) (Q) |
| (c) (I) (iii) (R) | (d) (I) (i) (R) |

84. For the given orbital in Column 1, the only **CORRECT** combination for any hydrogen-like species is:

- | | |
|-------------------|---------------------|
| (a) (II) (ii) (P) | (b) (I) (ii) (S) |
| (c) (IV) (iv) (R) | (d) (III) (iii) (P) |

85. For hydrogen atom, the only **CORRECT** combination is:

- | | |
|------------------|------------------|
| (a) (I) (i) (P) | (b) (I) (iv) (R) |
| (c) (II) (i) (Q) | (d) (I) (i) (S) |

86. The ground state energy of hydrogen atom is -13.6 eV . Consider an electronic state ψ 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 ψ ? (2019)

(a) It has 2 angular nodes.

(b) It has 3 radial nodes.

(c) It is a $4d$ state.

(d) The nuclear charge experienced by the electron in this state is less than $2e$, where e is the magnitude of the electronic charge.

Comprehension (Q. 87 to 90): Answer the following by appropriately matching the lists based on the information given in the paragraph

Consider the Bohr's model of a one-electron atom where the electron moves around the nucleus. In the following List-I contains some quantities for the n^{th} orbit of the atom and List-II contains options showing how they depend on n . (2019)

List-I

- | | |
|---|-----------------------|
| (I) Radius of the n^{th} orbit. | (P) $\propto n^{-2}$ |
| (II) Angular momentum of the electron in the n^{th} orbit. | (Q) $\propto n^{-1}$ |
| (III) Kinetic energy of the electron in the n^{th} orbit. | (R) $\propto n^0$ |
| (IV) Potential energy of the electron in the n^{th} orbit. | (S) $\propto n^1$ |
| | (T) $\propto n^2$ |
| | (U) $\propto n^{1/2}$ |

87. Which of the following options has the correct combination considering List-I and List-II?

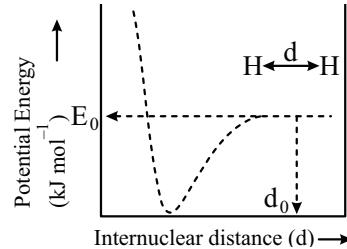
- | | |
|---------------|---------------|
| (a) (II), (R) | (b) (I), (P) |
| (c) (I), (T) | (d) (II), (Q) |

88. Which of the following options has the correct combination considering List-I and List-II?

- | | |
|----------------|----------------|
| (a) (III), (S) | (b) (IV), (Q) |
| (c) (IV), (U) | (d) (III), (P) |

89. The figure below is the plot of potential energy versus internuclear distance (d) of H_2 molecule in the electronic ground state. What is the value of the net potential energy E_0 (as indicated in the figure) in kJ mol^{-1} , for $d=d_0$ at which the electron-electron repulsion and the nucleus-nucleus repulsion energies are absent? As reference, the potential energy of H atom is taken as zero when its electron and the nucleus are infinitely far apart.

Use Avogadro constant as $6.023 \times 10^{-23} \text{ mol}^{-1}$. (2020)



90. Consider a Helium (He) atom that absorbs a photon of wavelength 330 nm . The change in the velocity (in cm s^{-1}) of He atom after the photon absorption is _____.

(Assume: Momentum is conserved when photon is absorbed).

Use: Planck constant = $6.6 \times 10^{-34} \text{ Js}$, Avogadro number = $6 \times 10^{23} \text{ mol}^{-1}$, molar mass of He = 4 g mol^{-1} (2021)

ANSWER KEY

CONCEPT APPLICATION

- | | | | | | | | | | |
|---------|---------|---------|---------|--------------|---------|---------|---------|---------|---------|
| 1. (a) | 2. (d) | 3. (b) | 4. (b) | 5. (c) | 6. (a) | 7. (b) | 8. (c) | 9. (b) | 10. (c) |
| 11. (a) | 12. (b) | 13. (a) | 14. (a) | 15. (c) | 16. (b) | 17. (b) | 18. (a) | 19. (d) | 20. (a) |
| 21. (c) | 22. (d) | 23. (c) | 24. (b) | 25. (b) | 26. (a) | 27. (d) | 28. (a) | 29. (b) | 30. (b) |
| 31. (a) | 32. (c) | 33. (d) | 34. (a) | 35. (0.423Å) | | 36. (c) | | | |

EXERCISE-1 (TOPICWISE)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (a) | 2. (c) | 3. (b) | 4. (d) | 5. (c) | 6. (d) | 7. (c) | 8. (d) | 9. (a) | 10. (d) |
| 11. (d) | 12. (c) | 13. (a) | 14. (a) | 15. (d) | 16. (c) | 17. (c) | 18. (c) | 19. (d) | 20. (c) |
| 21. (a) | 22. (b) | 23. (a) | 24. (a) | 25. (b) | 26. (a) | 27. (b) | 28. (b) | 29. (a) | 30. (b) |
| 31. (b) | 32. (a) | 33. (d) | 34. (c) | 35. (c) | 36. (c) | 37. (b) | 38. (c) | 39. (d) | 40. (d) |
| 41. (c) | 42. (c) | 43. (c) | 44. (a) | 45. (b) | 46. (c) | 47. (d) | 48. (d) | 49. (b) | 50. (b) |
| 51. (c) | 52. (d) | 53. (a) | 54. (d) | 55. (b) | 56. (b) | 57. (a) | 58. (b) | 59. (b) | 60. (b) |
| 61. (d) | 62. (c) | 63. (a) | 64. (c) | 65. (c) | 66. (c) | 67. (c) | 68. (d) | 69. (d) | 70. (b) |

EXERCISE-2 (LEARNING PLUS)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (a) | 2. (c) | 3. (d) | 4. (c) | 5. (a) | 6. (b) | 7. (a) | 8. (b) | 9. (b) | 10. (d) |
| 11. (c) | 12. (b) | 13. (d) | 14. (d) | 15. (a) | 16. (c) | 17. (c) | 18. (b) | 19. (b) | 20. (c) |
| 21. (d) | 22. (b) | 23. (d) | 24. (b) | 25. (d) | 26. (a) | 27. (b) | 28. (c) | 29. (c) | 30. (c) |
| 31. (b) | 32. (d) | 33. (c) | 34. (b) | 35. (b) | 36. (a) | 37. (b) | 38. (c) | 39. (b) | 40. (c) |

EXERCISE-3 (JEE ADVANCED LEVEL)

- | | | | | | | | | | |
|------------------|------------|-------------------------------------|-------------|---|---------------|------------|-------------|-------------|--------------------|
| 1. (a,c) | 2. (a,b,c) | 3. (a,b,c,d) | 4. (b,c) | 5. (a,b,c,d) | 6. (a,c,d) | 7. (b,c,d) | 8. (a,b,c) | 9. (a,b,c) | 10. (a) |
| 11. (b) | 12. (c) | 13. (d) | 14. (a) | 15. (c) | 16. (a) | 17. (b) | 18. (c) | 19. (d) | 20. (a,c) |
| 21. (b,c,d) | 22. (c,d) | 23. (a,c) | 24. (a,b,c) | 25. (b,c) | 26. (b) | 27. (c,d) | 28. (a,b,c) | 29. (a,b,c) | 30. [14] |
| 31. [6] | 32. [6] | 33. [5] | 34. [26] | 35. [4] | 36. [5] | 37. [20] | 38. [3] | 39. [4] | 40. $\frac{5R}{9}$ |
| 41. 1240 kJ/mol. | 42. [31] | 43. [12] | 44. [5] | 45. [12] | 46. -435.2 eV | | 47. [90 nm] | 48. [91 nm] | |
| 49. 973.5 Å | | 50. $[5 \times 10^{-26} \text{ m}]$ | | 51. $[3.63 \times 10^6 \text{ m}^{-1}]$ | 52. [300303] | | | | |

EXERCISE-4 (PAST YEAR QUESTIONS)

JEE Main

- | | | | | | | | | | |
|------------|---------|------------|---------|------------|-----------|----------|-----------|---------|----------|
| 1. (d) | 2. (d) | 3. (d) | 4. (a) | 5. (d) | 6. (a) | 7. (d) | 8. (c) | 9. (c) | 10. (c) |
| 11. (c) | 12. (d) | 13. (a) | 14. (c) | 15. (b) | 16. (b) | 17. (b) | 18. (d) | 19. (d) | 20. (d) |
| 21. (b) | 22. (d) | 23. (d) | 24. (b) | 25. (d) | 26. (b) | 27. (d) | 28. (c) | 29. (c) | 30. (d) |
| 31. [222] | 32. (d) | 33. (a) | 34. (b) | 35. (d) | 36. [142] | 37. (d) | 38. (b) | 39. (c) | 40. (b) |
| 41. (a) | 42. [2] | 43. [0] | 44. [7] | 45. [50] | 46. [2] | 47. (b) | 48. [180] | 49. (d) | 50. (d) |
| 51. [1.17] | 52. [9] | 53. [3] | 54. [0] | 55. (c) | 56. [0] | 57. [6] | 58. [12] | 59. [2] | 60. [58] |
| 61. (a) | 62. (a) | 63. (b) | 64. [5] | 65. [3155] | 66. [4] | 67. [50] | 68. (b) | 69. (d) | 70. (b) |
| 71. (b) | 72. (c) | 73. [1758] | 74. [4] | 75. [22] | 76. [1] | | | | |

JEE Advanced

- | | | | | | | | | | |
|---------|---------|----------------|---------|----------|---------|---------|---------|---------|-----------|
| 77. (c) | 78. [8] | 79. (a,b) | 80. [6] | 81. [3] | 82. (d) | 83. (c) | 84. (a) | 85. (d) | 86. (a,c) |
| 87. (c) | 88. (d) | 89. [-5246.49] | | 90. [30] | . | | | | |

CHAPTER

3

States of Matter

INTRODUCTION

Matter as we know broadly exists in three states.

There are always two opposite tendencies between particles of matter which determine the state of matter.

- ❖ Inter molecular attractive forces.
- ❖ The molecular motion / random motion.

Properties	Solid state	Liquid state	Gaseous state
Attractive force	• Large	• Smaller	• Almost zero
Thermal motion	• Almost zero	• Greater	• Random motion
Volume	• Fixed volume	• Fixed volume	• Varies with container
Geometry	• Definite	• Not definite	• Not definite

In this chapter the properties and behaviour of the gases will be analysed and discussed in detail. These properties are measured with the help of the gas laws as proposed by Boyle, Charles, Gay Lussac etc.

GASEOUS LAW

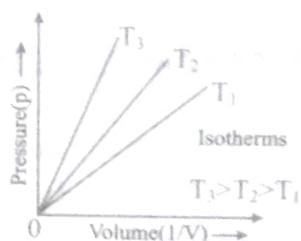
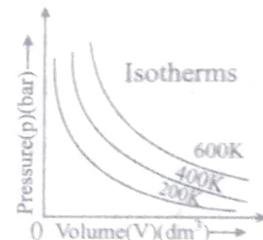
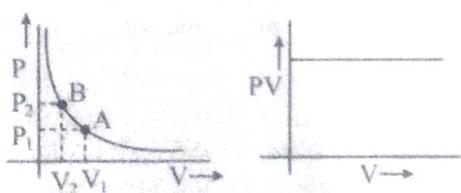
Boyle's Law and Measurement

For a fixed amount of gas at constant temperature, the volume occupied by the gas is inversely proportional to the pressure applied on the gas or pressure of the gas.

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

Hence $PV = \text{constant}$

This constant will be dependent on the amount of the gas and temperature of the gas.



Application of Boyle's Law : For the two points 'A' and 'B'
 $P_1 V_1 = K$ & $P_2 V_2 = K$

hence it follows that $P_1 V_1 = P_2 V_2$.

Atmospheric pressure: The pressure exerted by atmosphere on earth's surface at sea level is called 1 atm.

$$1 \text{ atm} = 1.013 \times 10^5 \text{ N/m}^2 = 1.013 \text{ bar} = 760 \text{ torr}$$



Train Your Brain

Example 1: A gas is initially at 1 atm pressure. To compress it to $\frac{1}{4}$ th of initial volume, what will be the pressure required?

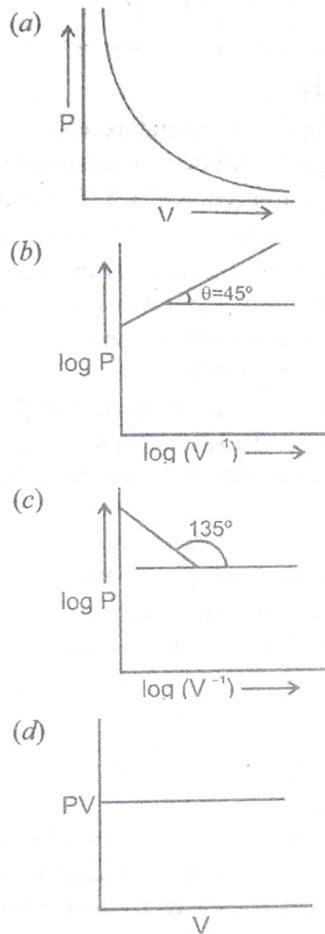
Sol. $P_1 = 1 \text{ atm}$ $V_1 = V$

$$P_2 = ? \quad V_2 = \frac{V}{4}$$

$$P_1 V_1 = P_2 V_2 \quad \text{at const. } T \& n$$

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{1 \text{ atm} \times V}{\frac{V}{4}} = 4 \text{ atm}$$

Example 2: Which of the following curve does not represent Boyle's law?



Sol. (c)

$$PV = K$$

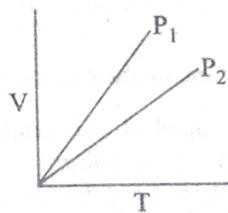
$$P = \frac{K}{V} = KV^{-1}$$

$$\log P = \log K + \log V^{-1}$$

It follows equation of line
then option c is incorrect



Concept Application



- (a) $P_1 > P_2$ (b) $P_1 < P_2$
 (c) $P_1 = P_2$ (d) All of these

Charle's Law

For a fixed amount of gas at constant pressure, volume occupied by the gas is directly proportional to temperature of the gas on absolute scale of temperature.

$$V \propto T \text{ or } V = kT$$

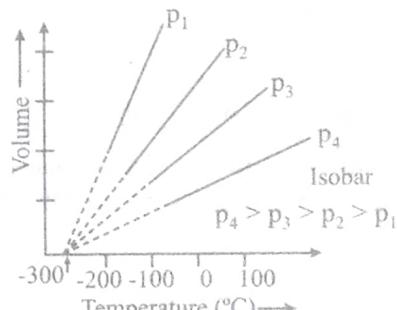
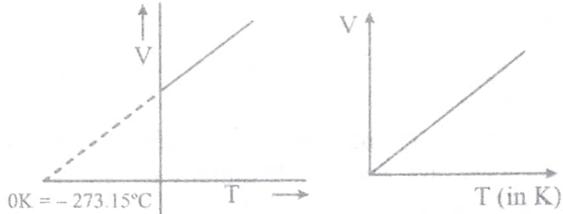
$\frac{V}{T} = \text{constant}$ where 'k' is a proportionality constant and is dependent on amount of gas and pressure.

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

Temperature on absolute scale, kelvin scale or ideal gas scale.

$$V = a + bt$$

Temperature on centigrade scale.



Relation : $T = t + 273$

- Since volume is proportional to absolute temperature. The volume of a gas should be theoretically zero at absolute zero temperature.
- Infact no substance exists as gas at a temperature near absolute zero, though the straight line plots can be extra plotted to zero volume. Absolute zero can never be attained practically though it can be approached only.
- By considering -273.15°C as the lowest approachable limit, Kelvin developed temperature scale which is known as absolute scale.

Gay-lussac's Law

For a fixed amount of gas at constant volume, pressure of the gas is directly proportional to temperature of the gas on absolute scale of temperature.

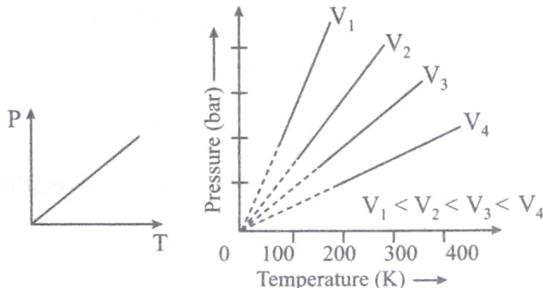
$$P \propto T$$

$$\frac{P}{T} = \text{constant} \text{ (dependent on amount and volume of gas)}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ (temperature on absolute scale originally)}$$

The law was developed on the centigrade scale, where it was found that pressure is a linear function of temperature $P = P_0 + bt$ where 'b' is a constant and P_0 is pressure at zero degree centigrade.

Isochore:



Train Your Brain

Example 3: If the temperature of a particular amount of gas is increased from 27°C to 57°C . Find final volume of the gas, if initial volume = 1L and assume pressure is constant.

$$\text{Sol. } \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{1}{(273 + 27)} = \frac{V_2}{(273 + 57)} \text{ So } V_2 = 1.1\text{L}$$

Example 4: The temperature of a certain mass of a gas in a rigid container is doubled. If initially the gas is at 1 atm pressure. Find the % increase in pressure?

$$\text{Sol. } \frac{P_1}{T_1} = \frac{P_2}{T_2}; \frac{1}{T} = \frac{P_2}{2T}$$

$$\% \text{ increase} = \frac{2-1}{1} \times 100 = 100\%$$

Example 5: The temperature of a certain mass of a gas was increased from 27°C to 37°C at constant volume. What will be the pressure of the gas.

$$\text{Sol. } \frac{P_1}{T_1} = \frac{P_2}{T_2}; \frac{P}{300} = \frac{P_2}{310}; P_2 = \frac{31}{30} P$$

Concept Application

- 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
- Equal weights of ethane & hydrogen are mixed in an empty container at 25°C , the fraction of the total pressure exerted by hydrogen is :

(a) 1: 2	(b) 1: 1
(c) 1: 16	(d) 15: 16
- A mixture of hydrogen and oxygen at one bar pressure contains 20% by weight of hydrogen. Partial pressure of hydrogen will be

(a) 0.2 bar	(b) 0.4 bar
(c) 0.6 bar	(d) 0.8 bar

Avogadro's Hypothesis

For similar values of pressure & temperature equal number of molecules of different gases will occupy equal volume.

$$N_1 \longrightarrow V \text{ (volume of } N_1 \text{ molecules at } P \text{ & } T \text{ of one gas)}$$

$$N_2 \longrightarrow V \text{ (volume of } N_2 \text{ molecules at } P \text{ & } T \text{ of second gas)}$$

\Rightarrow Molar volume & volume occupied by one mole of each and every gas under similar conditions will be equal.

One mole of any gas or a combination of gases occupies 22.413996 L of volume at STP.

The previous standard is still often used, and applies to all chemistry data more than decade old, in this definition **Standard Temperature and Pressure STP** denotes the same temperature of 0°C (273.15K), but a slightly higher pressure of 1 atm (101.325 kPa).

Standard Ambient Temperature and Pressure (SATP), Conditions are also used in some scientific works. SATP conditions means 298.15 K and 1 bar (i.e. exactly 10^5 Pa) At SATP (1 bar and 298.15 K), the molar volume of an ideal gas is 24.789 L mol⁻¹

EQUATION OF STATE

Combining all the gas relations in a single expression which describes relationship between pressure, volume and temperature, of a given mass of gas we get an expression known as equation of state.

$$\frac{PV}{T} = \text{constant} \text{ (dependent on amount of the gas (n)).}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Ideal gas Equation:

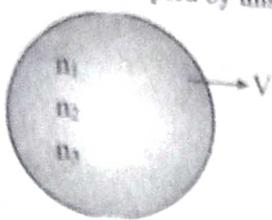
$$\frac{PV}{nT} = R \text{ (universal gas constant)}$$

$$R = 8.314 \text{ J/Kmole} \approx 25/3 = 1.987 \text{ cal/k.mole} \approx 2 \\ = 0.0821 \text{ Latm/K/mole} \approx 1/12$$



DALTON'S LAW OF PARTIAL PRESSURE

In a mixture of non reacting gases partial pressure of any component of gas is defined as pressure exerted by this component if whole of volume of mixture had been occupied by this component.



partial pressure of first component gas

$$P_1 = \frac{n_1 RT}{V}; P_2 = \frac{n_2 RT}{V}; P_3 = \frac{n_3 RT}{V}$$

Total pressure = $P_1 + P_2 + P_3$.

Dalton's law: For a non reacting gaseous mixture total pressure of the mixture is the summation of partial pressure of the different component gases.

$$P_{\text{total}} = P_1 + P_2 + P_3 = \frac{(n_1 + n_2 + n_3)RT}{V}$$

$$\frac{P_1}{P_T} = \frac{n_1}{n_T} = X_1 \quad (\text{mole fraction of first component of gas})$$

$$\frac{P_2}{P_T} = \frac{n_2}{n_T} = X_2 \quad (\text{mole fraction of second component of gas})$$

$$\frac{P_3}{P_T} = \frac{n_3}{n_T} = X_3 \quad (\text{mole fraction of third component of gas})$$



Train Your Brain

Example 6: The partial pressure of hydrogen in a flask containing two grams of hydrogen and 32 gm of sulphur dioxide is

- (a) 1/16th of the total pressure
- (b) 1/9th of the total pressure
- (c) 2/3 of the total pressure
- (d) 1/8th of the total pressure

$$\text{Sol. } n_{H_2} = \frac{2g}{2\text{ g/mol}} = 1\text{ mol. } n_{SO_2} = \frac{32\text{ g}}{64\text{ g/mol}} = 0.5\text{ mol}$$

$$\therefore P_{H_2} = \frac{n_{H_2}}{(n_{H_2} + n_{SO_2})} \times P_T = \frac{1}{(1+0.5)} \times P_T = \frac{2}{3} P_T.$$

Example 7: Equal volume of two gases which do not react together are enclosed in separate vessels. Their pressures are 10 mm and 400 mm respectively. If the two vessels are joined together, then what will be the pressure of the resulting mixture (temperature remaining constant):

- (a) 120 mm
- (b) 500 mm
- (c) 1000 mm
- (d) 205 mm

Sol. Let, vol of containers be V & temperature be T

$$P_1 = 10 \text{ mm} \quad P_2 = 400 \text{ mm}$$

$$\therefore n_1 = \frac{P_1 V}{RT} \quad \& \quad n_2 = \frac{P_2 V}{RT}$$

$$\therefore n_1 + n_2 = \frac{(P_1 + P_2) \times V}{RT} \quad \dots (i)$$

After joining two containers final volume = $(V + V) = 2V$ (for gases)

$$\therefore P_{\text{final}} = \frac{(n_1 + n_2)RT}{V_{\text{final}}} = \frac{(P_1 + P_2) \times V}{RT} \times \frac{RT}{2V}$$

$$= \frac{(P_1 + P_2)}{2} = \frac{(10 + 400)}{2} = 205 \text{ mm.}$$

Concept Application

6. Which of the following gas mixture is not applicable for Dalton's law of partial pressure?

- (a) SO₂ and Cl₂
- (b) CO₂ and N₂
- (c) CO and CO₂
- (d) CO and N₂

7. A 2.5L flask contains 0.25 mol each of SO₂ and CO₂ gas at 27°C. Calculate the partial pressure exerted by SO₂, CO₂ and total pressure respectively.

- (a) 2.46, 2.46, 4.92
- (b) 1.23, 2.46, 2.46
- (c) 2.46, 1.23, 1.23
- (d) None of these

8. 56 g of nitrogen and 96 g of oxygen are mixed isothermally and at a total pressure of 10 atm. The partial pressures of oxygen and nitrogen (in atm) are respectively:

- (a) 4, 6
- (b) 5, 5
- (c) 2, 8
- (d) 6, 4

9. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is:

- (a) $\frac{2}{3}$
- (b) $\frac{1}{3} \times \frac{273}{298}$
- (c) $\frac{1}{3}$
- (d) $\frac{1}{2}$

ANALYSIS OF GASEOUS MIXTURE

Vapour density: Vapour density of any gas is defined as the density of any gas with respect to density of the H₂ gas under identical conditions of temperature T and pressure P.

$$\text{vapour density} = \frac{\text{density of gas at T \& P}}{\text{density of H}_2 \text{ under same P \& T}}$$

$$P = \frac{m}{V} \cdot \frac{RT}{M} \Rightarrow P = \rho \frac{RT}{M} \Rightarrow \rho = \frac{PM}{RT}$$

$$\text{Vapour density} = \frac{PM_{\text{gas}} RT}{RT PM_{H_2}} = \frac{M_{\text{gas}}}{M_{H_2}} = \frac{M_{\text{gas}}}{2}$$

$$M_{\text{gas}} (\text{molar mass of gas}) = 2 \times \text{vapour density}$$

Average molecular mass of gaseous mixture : Total mass of the mixture divided by total no. of moles in the mixture

$$M_{\text{mix}} = \frac{\text{Total mass of mixture}}{\text{Total no. of moles in mixture}}$$

If we have

'n₁', 'n₂' and 'n₃' are moles of three different gases having molar mass 'M₁', 'M₂' and 'M₃' respectively.

$$M_{\text{mix}} = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3}{n_1 + n_2 + n_3}$$



Train Your Brain

Example 8: Calculate the mean molar mass of a mixture of gases having 7 g of Nitrogen, 22 g of CO₂, and 5.6 litres of CO at STP.

$$\text{Sol. Moles of N}_2 = 7/28 = 1/4$$

$$\text{Moles of CO}_2 = 22/44 = 1/2$$

$$\text{Moles of CO} = 5.6/22.4 = 1/4$$

$$\begin{aligned} \text{Mean molar mass } M_{\text{mix}} &= \frac{n_1 M_1 + n_2 M_2 + n_3 M_3}{n_1 + n_2 + n_3} \\ &= \frac{\frac{1}{4} \times 28 + \frac{1}{2} \times 44 + \frac{1}{4} \times 28}{\frac{1}{4} + \frac{1}{2} + \frac{1}{4}} \\ &= (7 + 7 + 22)/1 = 36 \end{aligned}$$

Example 9: A gaseous mixture of H₂ and CO₂ gas contains 66 mass % of CO₂. The vapour density of the mixture is:

$$(a) 6.1$$

$$(b) 5.4$$

$$(c) 2.7$$

$$(d) 10.8$$

$$\text{Sol. (c) Average molar mass} = \frac{\text{Total mass}}{\text{Total moles}}$$

$$= \frac{100}{\frac{66}{44} + \frac{34}{2}} = \frac{100}{18.5}$$

$$\text{Vapour density} = \frac{\text{molar mass}}{2} = 2.7$$



Concept Application

10. A and B are two identical vessels. A contains 15 g of ethane at 1 atm and 298 K. The vessel B contains 75 g of a gas X₂ at same temperature and pressure. The vapour density of X₂ is:

- (a) 75 (b) 150
(c) 37.5 (d) 45

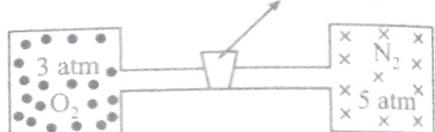
11. The vapour density of a mixture containing NO₂ and N₂O₄ is 27.6. The mole fraction of N₂O₄ in the mixture is:

- (a) 0.1 (b) 0.2
(c) 0.5 (d) 0.8

GRAHAM'S LAW OF DIFFUSION/EFFUSION

Diffusion : Net spontaneous flow of gaseous molecules from region of high concentration (higher partial pressure) to the region of lower concentration or lower partial pressure. Flow will be from both sides, both gas will try to equalise its partial pressure in both the vessels, and so will O₂.

when removed



$$\begin{array}{ll} P_{N_2} = 2.5 \text{ atm} & P_{N_2} = 2.5 \text{ atm} \\ P_{O_2} = 1.5 \text{ atm} & P_{O_2} = 1.5 \text{ atm} \end{array}$$

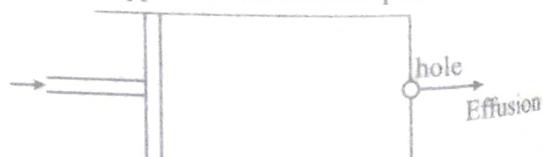
Graham's Law

"Under similar conditions of pressure (partial pressure) the rate of diffusion of different gases is inversely proportional to square root of the density of different gases."

$$\text{Rate of diffusion } r \propto \frac{1}{\sqrt{d}} \quad \{d = \text{density of gas}\}$$

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} = \frac{\sqrt{V \cdot D_2}}{\sqrt{V \cdot D_1}} \quad V.D \text{ is vapour density}$$

Effusion: (forced diffusion) a gas is made to diffuse through a hole by the application of external pressure.



Diffusion: Flow of gas to occupy available volume is called Diffusion.

Selective diffusion: If one or more than one components of a mixture are allowed to diffuse and others are not allowed to, it is selective diffusion of those components.

KINETIC ENERGY AND MOLECULAR SPEEDS

Molecules of gases remain in continuous motion. While moving they collide with each other and with the walls of the container. This results in change of their speed and redistribution of energy. So the speed and energy of all the molecules of the gas at any instant are not the same. Thus, we can obtain only average value of speed of molecules. If there are n number of molecules in a sample and their individual speeds are u_1, u_2, \dots, u_n , then average speed of molecules u_{av} can be calculated as follows:

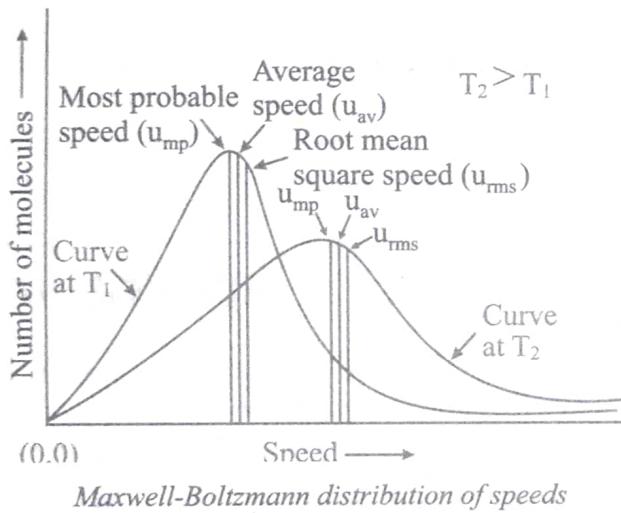
$$u_{av} = \frac{u_1 + u_2 + \dots + u_n}{n} = \sqrt{\frac{8RT}{\pi M}}$$

R = universal gas constant

T = absolute temperature

M = Molar mass of the gas

Maxwell and Boltzmann have shown that actual distribution of molecular speeds depends on temperature and molecular mass of a gas. Maxwell derived a formula for calculating the number of molecules possessing a particular speed. shows schematic plot of number of molecules v/s. molecular speed at two different temperatures T_1 and T_2 (T_2 is higher than T_1). The distribution of speeds shown in the plot is called Maxwell-Boltzmann distribution of speeds.



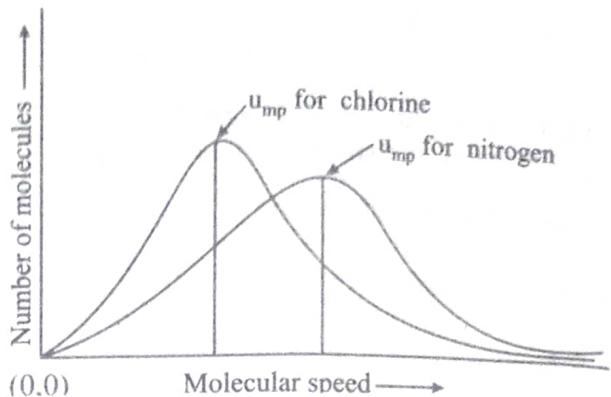
Maxwell-Boltzmann distribution of speeds

The graph shows that number of molecules possessing very high and very low speed is very small. The maximum in the curve represents speed possessed by maximum number of molecules. This speed is called **most probable speed**, u_{mp} .

$$u_{mp} = \sqrt{\frac{2RT}{M}}$$

This is very close to the average speed of the molecules. On increasing the temperature most probable speed increases. Also, speed distribution curve broadens at higher temperature. Broadening of the curve shows that number of molecules moving at higher speed increases. Speed distribution also depends upon mass of molecules. At the same temperature, gas molecules with heavier mass have slower speed than lighter gas molecules. For example, at the same temperature lighter nitrogen molecules

move faster than heavier chlorine molecules. Hence, at a given temperature, nitrogen molecules have higher value of most probable speed than the chlorine molecules. Look at the molecular speed distribution curve of chlorine and nitrogen given in. Though at a particular temperature the individual speed of molecules keep changing, the distribution of speeds remains same.



Distribution of molecular speeds for chlorine and nitrogen at 300 K

We know that kinetic energy of a particle is given by the expression:

$$\text{Kinetic Energy} = \frac{1}{2}mu^2$$

Therefore, if we want to know average translational kinetic energy, $\frac{1}{2}mu^2$, for the movement of a gas particle in a straight line, we require the value of mean of square of speeds, mu^2 , of all molecules. This is represented as follows:

$$\overline{u^2} = \frac{u_1^2 + u_2^2 + \dots + u_n^2}{n}$$

The mean square speed is the direct measure of the average kinetic energy of gas molecules. If we take the square root of the mean of the square of speeds then we get a value of speed which is different from most probable speed and average speed. This speed is called **root mean square speed** and is given by the expression as follows:

$$u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3PV}{M}}$$

Root mean square speed, average speed and the most probable speed have following relationship:

$$u_{rms} > u_{av} > u_{mp}$$

The ratio between the three speeds is given below:

$$u_{mp} : u_{av} : u_{rms} = 1 : 1.128 : 1.224$$

KINETIC MOLECULAR THEORY OF GASES

So far we have learnt the laws (e.g., Boyle's law, Charles' law etc.) which are concise statements of experimental facts observed in the laboratory by the scientists. Conducting careful experiments is an important aspect of scientific method and it tells us how the particular system is behaving under different conditions. However,

Once the experimental facts are established, a scientist is curious to know why the system is behaving in that way. For example, gas laws help us to predict that pressure increases when we compress gases but we would like to know what happens at molecular level when a gas is compressed? A theory is constructed to answer such questions. A theory is a model (i.e., a mental picture) that enables us to better understand our observations. The theory that attempts to elucidate the behaviour of gases is known as kinetic molecular theory. Assumptions or postulates of the kinetic molecular theory of gases are given below. These postulates are related to atoms and molecules which cannot be seen, hence it is said to provide a microscopic model of gases.

- ❖ Gases consist of large number of identical particles (atoms or molecules) that are so small and so far apart on the average that the actual volume of the molecules is negligible in comparison to the empty space between them. They are considered as point masses. This assumption explains the great compressibility of gases.
- ❖ There is no force of attraction between the particles of a gas at ordinary temperature and pressure. The support for this assumption comes from the fact that gases expand and occupy all the space available to them.
- ❖ Particles of a gas are always in constant and random motion. If the particles were at rest and occupied fixed positions, then a gas would have had a fixed shape which is not observed.
- ❖ Particles of a gas move in all possible directions in straight lines. During their random motion, they collide with each other and with the walls of the container. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.
- ❖ Collisions of gas molecules are perfectly elastic. This means that total energy of molecules before and after the collision remains same. There may be exchange of energy between colliding molecules, their individual energies may change, but the sum of their energies remains constant. If there were loss of kinetic energy, the motion of molecules will stop and gases will settle down. This is contrary to what is actually observed.
- ❖ At any particular time, different particles in the gas have different speeds and hence different kinetic energies. This assumption is reasonable because as the particles collide, we expect their speed to change. Even if initial speed of all the particles was same, the molecular collisions will disrupt this uniformity. Consequently, the particles must have different speeds, which go on changing constantly. It is possible to show that though the individual speeds are changing, the distribution of speeds remains constant at a particular temperature.
- ❖ If a molecule has variable speed, then it must have a variable kinetic energy. Under these circumstances, we can talk only about average kinetic energy. In kinetic theory, it is assumed that average kinetic energy of the gas molecules is directly proportional to the absolute temperature. It is seen that on heating a gas at constant volume, the pressure increases. On

heating the gas, kinetic energy of the particles increases and these strike the walls of the container more frequently, thus, exerting more pressure.

Kinetic theory of gases allows us to derive theoretically, all the gas laws studied in the previous sections. Calculations and predictions based on kinetic theory of gases agree very well with the experimental observations and thus establish the correctness of this model.



Train Your Brain

Example 12: Find the temperature at which methane and ethane will have the same rms speed as carbon dioxide at 400°C.

$$\text{Sol. } v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

$$\Rightarrow \frac{T_1}{M_1} = \frac{T_2}{M_2}$$

$$(a) T_{\text{CH}_4} = \frac{673}{44} \times 16 = 244.73\text{K}$$

$$(b) T_{\text{C}_2\text{H}_6} = \frac{673}{44} \times 30 = 458.86\text{K}$$

Example 13: Two gases A and B have the same value of most probable speed at 298 K for A and 150 K for B. Calculate the ratio of their molar masses.

$$\text{Sol. Most Probable} = \left(\sqrt{\frac{2RT}{M}} \right)$$

$$\frac{T_A}{M_A} = \frac{T_B}{M_B}$$

$$\therefore \frac{M_A}{M_B} = \frac{T_A}{T_B} = \frac{298}{150} \approx 2$$

$$\therefore M_A : M_B = 2 : 1$$

Example 14: Calculate the ratio of kinetic energy per mole of nitrogen at 27°C and hydrogen at 127°C.

$$\text{Sol. Kinetic energy (K.E)} = \frac{3}{2} RT$$

$$KE_{\text{N}_2} = \frac{3}{2} RT_{\text{N}_2}$$

$$KE_{\text{H}_2} = \frac{3}{2} RT_{\text{H}_2}$$

$$\frac{KE_{\text{N}_2}}{KE_{\text{H}_2}} = \frac{T_{\text{N}_2}}{T_{\text{H}_2}} = \frac{300}{400} = \frac{3}{4}$$



Concept Application

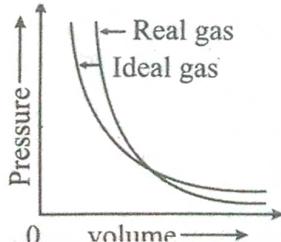
15. The R.M.S. speed of the molecules of a gas of density 4 kg m^{-3} and pressure $1.2 \times 10^5 \text{ N m}^{-2}$ is:
 (a) 120 ms^{-1} (b) 300 ms^{-1}
 (c) 600 ms^{-1} (d) 900 ms^{-1}
16. The temperature of an ideal gas is increased from 120 K to 480 K . If at 120 K the root-mean-square velocity of the gas molecules is v , at 480 K it becomes :
 (a) $4v$ (b) $2v$
 (c) $v/2$ (d) $v/4$
17. 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
18. Initially, the root mean square (rms) velocity of N_2 molecules at certain temperature is u . If this temperature is doubled and all the nitrogen molecules dissociate into nitrogen atoms, then the new rms velocity will be:
 (a) $2u$ (b) $14u$
 (c) $u/2$ (d) $4u$

REAL GASES

- ❖ Real gases do not obey the ideal gas laws exactly under all conditions of temperature and pressure.
- ❖ Real gases deviates from ideal behaviour because Real gas molecules have a finite volume {since on liquefaction real gases occupy a finite volume}.
- ❖ Inter molecular attractive forces between real gas molecules is not zero {Real gases can be converted into liquid where as ideal gases can't be}.
- ❖ Deviation of real gases from ideal behaviour can be measured by using compressibility factor : (Z)

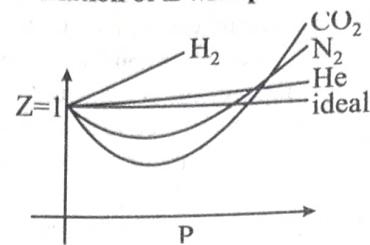
$$Z = \frac{(PV)_{\text{real}}}{(PV)_{\text{ideal}}} ; (PV)_{\text{ideal}} = nRT$$

$Z = \frac{PV}{nRT} = \frac{PV_m}{RT}$, V_m is volume of one mole of gas or molar volume.

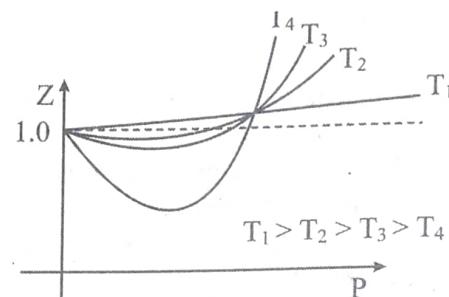


$$Z = \frac{V_m}{V_{m \text{ ideal}}}$$

Variation of Z with pressure at constant temperature:



Variation of Z with pressure at different temperature (for a gas):



Conclusions:

$Z = 1$ for ideal gas ;

$Z > 1$ at all pressures for He/H_2

$Z < 1$ at low pressure (for all other gases) ; $Z > 1$ at high pressure (for all other gases)

Vander Waal's Equation of Real Gases

The ideal gas equation does not consider the effect of attractive forces and molecular volume. Vander Waal's corrected the ideal gas equation by taking the effect of

(a) Molecular volume (b) Molecular attraction

❖ Volume correction:

Ideal gas equation:

$P_i V_i = nRT$; In the equation ' V_i ' stands for the volume which is available for free movement of the molecules.

V_{ideal} = volume available for free movement of gaseous molecule

hence, $V_i = V - \{\text{volume not available for free movement}\}$
For an ideal gas

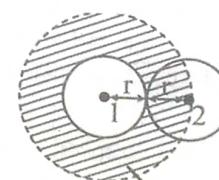
$V_i = V$ { V = volume of container}

but for a real gas

$V_i \neq V$, as all the volume is not available for free movement

Molecules have finite volume : The volume that is not available for free movement is called excluded volume.

let us see, how this excluded volume is calculated.



Excluded volume
(not available for free movement)

For above example, the entire shaded region is excluded, as its centre of mass cannot enter this region.

If both molecules were ideal, then they would not have experienced any excluded volume but not in the case of real gas as the centre of mass of '2' cannot go further.
Hence for this pair of real gas molecules,

$$\text{Excluded volume per molecule} = \frac{1}{2} \left\{ \frac{4}{3} \pi (2r)^3 \right\}$$

$$= 4 \left\{ \frac{4}{3} \pi r^3 \right\}$$

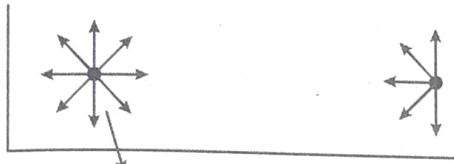
$$= \text{excluded volume per mole of gas (b)} = N_A 4 \left\{ \frac{4}{3} \pi r^3 \right\}$$

$$= 4 \times N_A \times \text{Volume of individual molecule}$$

for n moles, excluded volume = nb

$$V_i = V - nb \text{ volume correction}$$

❖ Pressure correction or effect of molecular attraction forces:



Molecule in the middle of container

Due to these attraction, speed during collisions will be reduced
Momentum will be less

Force applied will be less

Pressure will be less.

$$P_{\text{ideal}} = P + \{\text{correction term}\}$$

Correction term \propto no. of molecules attracting the colliding molecule $\propto (n/V)$.

Correction term \propto density of molecules $\propto (n/V)$.

$$\text{no. of collision} \propto \text{density of molecules} \propto \left(\frac{n}{V} \right)$$

$$\text{net correction term} \propto \left(\frac{n}{V} \right) \left(\frac{n}{V} \right) = \frac{an^2}{V^2}$$

'a' is constant of proportionality

and this is dependent on force of attraction

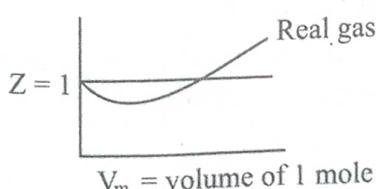
Stronger the force of attraction greater will be 'a' (Constant)

$$P_i = P + \frac{an^2}{V^2}$$

$$\text{Vander waal's equation is } \left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

VERIFICATION OF VANDER WAAL'S EQUATIONS

Variation of Z with P for vander waals' equation at any temp.



Vander waal equation for 1mole:

$$\left(P + \frac{a}{V_m^2} \right) (V_m - b) = RT$$

❖ AT LOW PRESSURE (at separate temp.)

At low pressure V_m will be high.

Hence b can be neglected in comparision to V_m . but $\frac{a}{V_m^2}$ can't be neglected as pressure is low

$$\text{Thus equation would be } \left(P + \frac{a}{V_m^2} \right) V_m = RT$$

$$PV_m + \frac{a}{V_m} = RT$$

$$\frac{PV_m}{RT} + \frac{a}{V_m RT} = 1$$

$$Z = 1 - \frac{a}{V_m RT} \quad Z < 1$$

Real gas is easily compressible as compared to an ideal gas.

❖ AT HIGH PRESSURE (moderate temperature)

V_m will be low so b can't be neglected in comparision to V_m but $\frac{a}{V_m^2}$ can be neglected as compared to much higher values of P.

Then vander Waals' equation will be

$$P(V_m - b) = RT$$

$$PV_m - Pb = RT$$

$$\frac{PV_m}{RT} = \frac{Pb}{RT} + 1$$

$$Z = \frac{Pb}{RT} + 1 \quad (Z > 1)$$

If $Z > 1$, then gas is more difficult to compress as compared to an ideal gas.

❖ At low pressure and very high temperature.

V_m will be very large hence 'b' can be neglected and $\frac{a}{V_m^2}$ can also be neglected as V_m is very large

$$PV_m = RT \text{ (ideal gas condition)}$$

❖ For H₂ or He a ≈ 0 because molecules are smaller in size or vander Waal's forces will be very weak, these are non polar so no dipole-dipole interactions are present in the actions.

$$P(V_m - b) = RT$$

$$\text{So } Z = 1 + \frac{Pb}{RT}$$

❖ 'a' factor depends on inter molecular attractive forces.

❖ 'a' factor for polar molecule > 'a' factor for non polar molecule.



Train Your Brain

Example 15: Arrange following in decreasing 'a' factor (H_2O , CO_2 , Ar)

$$\text{Sol. } \text{H}_2\text{O} > \text{CO}_2 > \text{Ar}$$

For non polar molecules: Greater the size or surface area, greater will be vander waal's forces, so greater will be 'a' constant.

Example 16: Arrange following gases according to 'a' He, Ar, Ne, Kr.

$$\text{Ans. } a_{\text{Kr}} > a_{\text{Ar}} > a_{\text{Ne}} > a_{\text{He}}$$

- ❖ More 'a' factor means higher will be boiling point.
- ❖ **Liquification pressure:** Is the pressure required to convert gas into liquid.

for easy liquefaction $a \uparrow$ and $P \downarrow$

When $Z < 1$, $V_m < V_{m, \text{ideal}}$ \Rightarrow easily liquifiable

$Z > 1$, $V_m > V_{m, \text{ideal}}$ \Rightarrow more difficult to compress.

Example 17: Arrange the following according to liquification pressure: n-pentane ; iso-pentane , neo pentane.

$$a_{\text{n-pentane}} > a_{\text{iso-pentane}} > a_{\text{neo-pentane}}$$

liquification pressure = LP

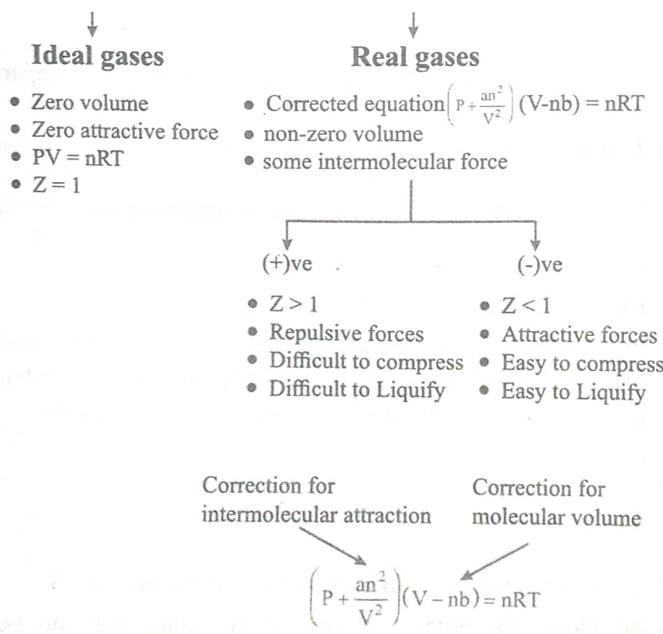
$$\text{Sol. } L_{P_{\text{n-pentane}}} < L_{P_{\text{iso pentane}}} < L_{P_{\text{neo pentane}}}$$

- ❖ b is roughly related with size of the molecule.

$$b = N_A 4 \left\{ \frac{4}{3} \pi r^3 \right\}$$

Example 18: Two vander waals gases have same value of b but different a values. Which of these would occupy greater volume under identical conditions?

Sol. If two gases have same value of 'b' but different values of 'a', then the gas having a larger value of 'a' will occupy lesser volume. This is because the gas with a larger value of 'a' will have larger force of attraction and hence lesser distance between its molecules.



Concept Application

19. A gas behaves like an ideal gas at:

- high pressure and low temperature
- low pressure and high temperature
- high pressure and high temperature
- low pressure and low temperature

20. Vander Waals constant b of helium is 24 mL mol^{-1} . Find molecular diameter of helium.

- $1.335 \times 10^{-10} \text{ cm}$
- $1.335 \times 10^{-8} \text{ cm}$
- $2.67 \times 10^{-8} \text{ cm}$
- $4.34 \times 10^{-8} \text{ cm}$

21. For a gas deviation from ideal behaviour is maximum at:

- 0°C and 1.0 atm
- 100°C and 2.0 atm
- -13°C and 1.0 atm
- -13°C and 2.0 atm

22. Consider the equation $Z = \frac{PV}{RT}$. Which of the following statements is correct?

- When $Z > 1$, real gases are easier to compress than the ideal gas
- When $Z = 1$, real gases get compressed easily
- When $Z > 1$, real gases are difficult to compress
- When $Z = 1$, real gases are difficult to compress

CRITICAL CONSTANTS

- ❖ Critical temperature of a gas is the temperature at or above which vapor of the gas cannot be liquefied, no matter how much pressure is applied.
- ❖ At critical temperature liquid phase passes into gaseous state imperceptibly and continuously.
- ❖ A gas below the critical temperature can be liquefied by applying pressure and is called vapour of the substance.
- ❖ At critical temperature, density of vapour phase equal to density of liquid phase.
- ❖ Pressure required to liquefy a gas at its critical temperature is called **critical pressure (P_C)**.
- ❖ The volume occupied by 1 mole of the gas at critical temperature and critical pressure is **critical volume (V_C)**.
- ❖ **Relationship between critical constants and Van der Waals constants**

$$P_C = \frac{a}{27b^2}; V_C = 3b; T_C = \frac{8a}{27Rb}$$

Boyle's Temperature (T_B)

- ❖ It is that temperature at which a real gas behaves ideally over a large pressure range as shown:

$$T_B = \frac{a}{Rb}$$

The numerical value of $\frac{RT_c}{P_c V_{m,c}} = \frac{8}{3}$ (on substituting T_c , P_c , $V_{m,c}$). Thus one can write that the value of RT/PV at critical conditions is $8/3$ of normal conditions.

$$\text{i.e., } \frac{RT_c}{P_c V_{m,c}} = \frac{8}{3} = \frac{8 RT}{3 PV} \left(\because \frac{RT}{PV} = 1 \right)$$

$$\Rightarrow \text{At critical conditions, } Z = \frac{P_c V_{m,c}}{RT_c} = \frac{3}{8}$$

Note : Boyle's temperature of a gas is always higher than its critical temperature (T_c).

- ❖ Reduced pressure is P/P_c
- ❖ Reduced volume is V/V_c
- ❖ Reduced temperature T/T_c

COLLISION FREQUENCY AND MEAN FREE PATH

The collision rate (i.e., the number of collisions taking place in unit time per unit volume) is called collision frequency (z) and is given by

$$z = \frac{\pi n^2 \sigma^2 u_{avg}}{\sqrt{2}}$$

The average of distances travelled by a molecule between successive collisions is called mean free path (λ).

$$\lambda = \frac{1}{\sqrt{2} \pi n \sigma^2}$$

where n is the number of molecules per unit molar volume.

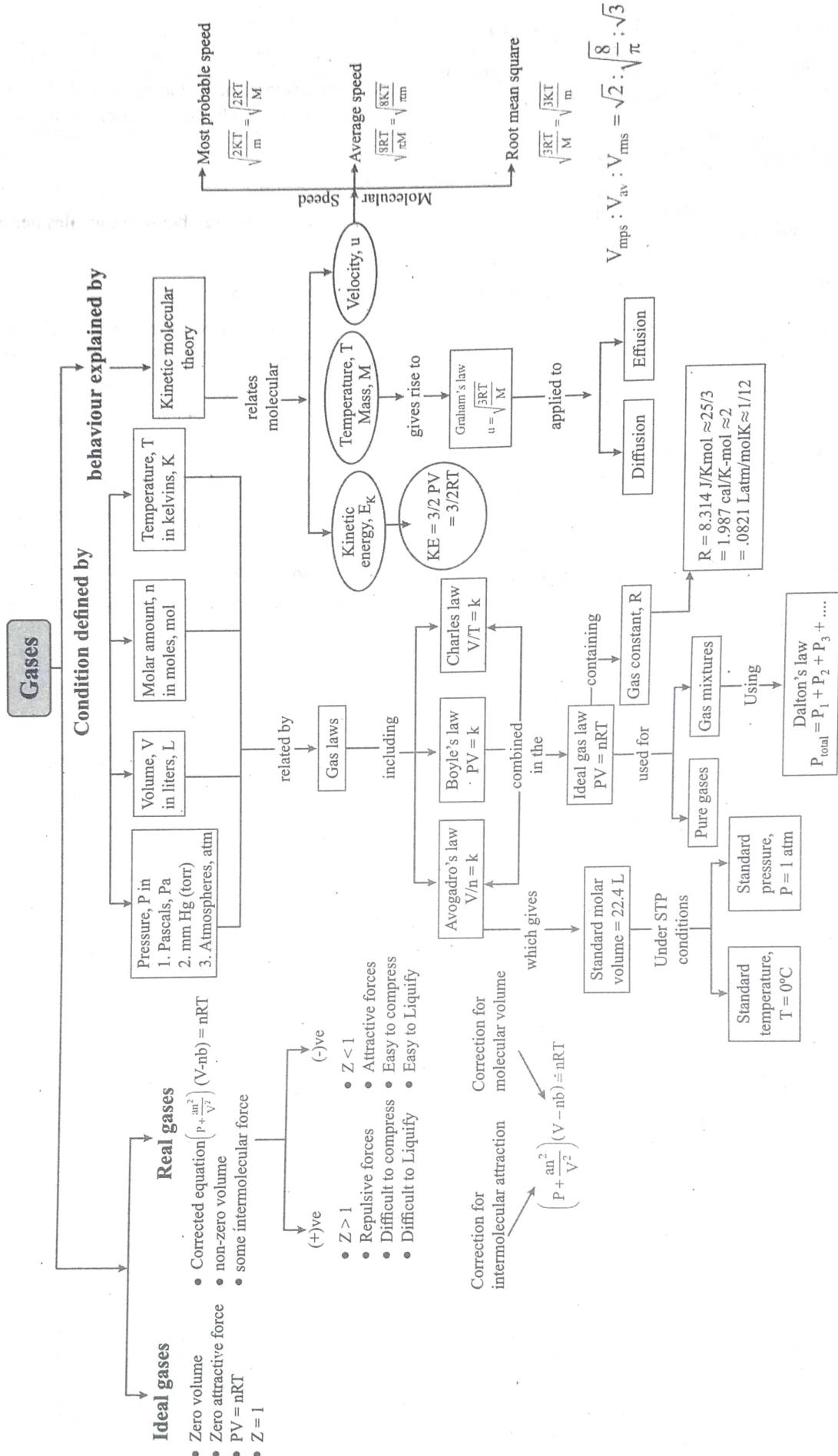
$$n = \frac{6.02 \times 10^{23}}{0.0224} \text{ m}^{-3}$$

u_{avg} = average velocity, σ = collision diameter i.e., the minimum distance between the centres of two molecules when at the point of collision.

Also based on kinetic theory of gases, mean free path $\lambda \propto \frac{T}{P}$.

Thus,

- ❖ Larger the size of the molecules, smaller the mean free path.
- ❖ Greater the number of molecules per unit volume, smaller the mean free path.
- ❖ Larger the temperature, larger the mean free path.
- ❖ Larger the pressure, smaller the mean free path.



Short Notes

Gas's Law

Boyle's law:

$$V \propto \frac{1}{P} (n, T = \text{const}) [P_1 V_1 = P_2 V_2]$$

Charle's law:

$$V \propto T (n, P = \text{const}) \frac{V_2}{V_1} = \frac{T_2}{T_1}$$

Gay lussac's law:

$$P \propto T (n, V = \text{const}) \frac{P_2}{P_1} = \frac{T_2}{T_1}$$

Avogadro's law:

$V \propto$ moles \propto number of molecules ($P, T = \text{const}$)

Ideal gas equation $PV = nRT$

$R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \text{ or } 8.314 \text{ N} \times \text{m K}^{-1} \text{ mol}^{-1}$$

$$R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}, R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

Graham's Diffusion Law

It is applicable for non reacting gases

$$r \propto \frac{1}{\sqrt{d}}; r \propto \frac{1}{\sqrt{VD}}; r \propto \frac{1}{\sqrt{M_w}} (P, T = \text{constant})$$

$$VD = \frac{d_{\text{gas}}}{d_{H_2}} = \frac{M_w}{2}$$

Rate of diffusion

$$r = \frac{l_{\text{diffused gas}}}{t_{\text{time taken}}} ; r = \frac{V_{\text{diffused gas}}}{t_{\text{time taken}}} ; r = \frac{n_{\text{diffused gas}}}{t_{\text{time taken}}}$$

(When, l = distance traveled by diffused gas)

Kinetic Gas Equation : $PV = \frac{1}{3} mN V_{\text{rms}}^2$

Dalton's Law of Partial Pressure

$$P_{\text{mixture}} = \underbrace{P_1 + P_2 + P_3 \dots}_{\text{Partial pressure}} (T \& V \text{ const.})$$

Partial pressure

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

It is applicable for non reacting gases.

Methods of determination of partial pressure

(P_A & P_B are partial pressure)

From ideal gas equation

$$P_A V = n_A RT \& P_B V = n_B RT$$

In the form of mole fraction.

$$P_A = X_A P_T = \frac{n_A}{n_T} P_T;$$

$$P_B = X_B P_T = \frac{n_B}{n_T} P_T$$

$$[X_A + X_B = 1]$$

P_T = sum of partial pressure of all gases

In the form of volume fraction.

$$P_A = \frac{V_A}{V} P_T \& P_B = \frac{V_B}{V} P_T$$

If individual pressure and individual volume are given

$$P_A = \frac{V_A}{V} P_1 \text{ and } P_B = \frac{V_B}{V} P_2$$

P_1, P_2 = pressure of gases before mixing

P_A, P_B = pressure of gases after mixing

Average Kinetic Energy (KE_{av})

$$K.E_{\text{av}} = \frac{3}{2} nRT \text{ (n moles)}$$

$$K.E_{\text{av}} = \frac{3}{2} RT \text{ (1 mol or } N_A \text{ molecules)}$$

$$K.E_{\text{av}} = \frac{3}{2} KT \text{ (1 molecule)}$$

$$K_B = 1.38 \times 10^{-23} \text{ JK}^{-1} \text{ molecule}^{-1}$$

K_B is called Boltzman's constant

$$u_{\text{rms}} = \sqrt{\frac{v_1^2 + v_2^2 + \dots v_n^2}{N}}$$

$$u_{\text{av}} = \frac{v_1 + v_2 + v_3 \dots v_n}{N}$$

$$u_{\text{rms}} = \sqrt{\frac{3RT}{Mw}}; u_{\text{av}} = \sqrt{\frac{8}{\pi} \frac{RT}{Mw}}; u_{\text{mp}} = \sqrt{\frac{2RT}{Mw}}$$

$$u_{\text{rms}} = \sqrt{\frac{3PV}{Mw}}; u_{\text{av}} = \sqrt{\frac{8}{\pi} \frac{PV}{Mw}}; u_{\text{mp}} = \sqrt{\frac{2PV}{Mw}}$$

$$u_{\text{rms}} = \sqrt{\frac{3P}{d}}; u_{\text{av}} = \sqrt{\frac{8P}{\pi d}}; u_{\text{mp}} = \sqrt{\frac{2P}{d}}$$

$$\begin{aligned} u_{\text{rms}} : u_{\text{av}} : u_{\text{mp}} &= \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} \\ &= 1 : 0.92 : 0.82 \end{aligned}$$

$$\begin{aligned} u_{\text{mp}} : u_{\text{av}} : u_{\text{rms}} &= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} \\ &= 1 : 1.128 : 1.224 \end{aligned}$$

Compressibility factor

$$(z) = \frac{(V_m)_{\text{obs}}}{V_1} = \frac{P(V_m)_{\text{obs}}}{RT}$$

If $z = 1$, the gas show ideal gas behaviour.

If $z > 1$, the gas show positive deviation.

If $z < 1$, the gas show negative deviation.

Vanderwaal's Equation

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

$$P_i = P_R + \frac{an^2}{V^2} \Rightarrow P_i > P_R$$

a increases force of attraction increases
liquification increases;
b increases effective size of molecule increases,
incompressible volume increases,
compressible vol. decreases

Vanderwaal's Equation

❖ At high pressure, Vanderwaal's eqⁿ is

$$PV_m - Pb = RT$$

❖ At low pressure or Moderate pressure vanderwaal's eqⁿ is

$$PV_m + \frac{a}{V_m} = RT$$

❖ At very low pressure, high temp. Vanderwaal's Equation is

$$VP = nRT$$

Ideal gas behaviour.

❖ Gases having higher value of a; will have higher T_c; higher rate of liquefaction.



Solved Examples

1. A rubber balloon contains some solid marbles each of volume 10 ml. A gas is filled in the balloon at a pressure of 2 atm and the total volume of the balloon is 1 litre in this condition. If the external pressure is increased to 4 atm the volume of Balloon becomes 625 ml. Find the number of marbles present in the balloon.

Sol. Let the no. of marbles be = n.

Volume of marble = 10 n ml.

Volume of balloon earlier = 1000 ml.

Later = 625 ml.

Now for the gas inside the balloon temperature and amount of the gas is constant, hence boyles law can be applied

$$P_1 V_1 = P_2 V_2$$

$$4 \times (625 - 10n) = 2 \times (1000 - 10n)$$

$$625 \times 4 = 2000 - 20n + 40n$$

$$625 \times 4 - 2000 = 20n$$

$$\frac{625 \times 4 - 2000}{20} = n. \frac{125}{5} = n; n = 25$$

2. If water is used in place of mercury then what should be minimum length of Barometer tube to measure normal atmospheric pressure.

Sol. P_{Hg} = P_{H₂O} = P_{atm}.

Pressure = ρgh

$$0.76 \text{ m} \times 13.6 \times g = h_{H_2O} \times 1 \times g$$

$$h_{H_2O} = 0.76 \times 13.6 = 10.336 \text{ m}$$

3. An open container of volume V contains air at temperature 27°C or 300 K. The container is heated to such a temperature so that amount of gas coming out is 2/3 of

(a) amount of gas initially present in the container.

(b) amount of gas finally remaining in the container.
Find the temperature to which the container should be heated.

Sol. (a) Here, P & V are constant, n & T are changing. Let, initially the amount of gas present be n & temp is 27°C or

300 K. Finally amount of gas present in container = n - $\frac{2}{3}n$ & final temp. be T.

Then using $n_1 T_1 = n_2 T_2$, we have,

$$n \times 300 = \frac{n_2}{3} \times T_2 \Rightarrow T_2 = 900 \text{ K}$$

i.e., final temp = 900 K

(b) Let there be x moles of gas remaining in the container, $\frac{2}{3}$ of x come out

$$\therefore (x + \frac{2}{3}x) = n \Rightarrow \frac{5x}{3} = n \therefore x = \frac{3n}{5}$$

$$\therefore \text{Using } n_1 T_1 = n_2 T_2 \text{ } n \times 300 \text{ K} = \frac{3n}{5} \times T_2$$

$$\therefore T_2 = 500 \text{ K}$$

Final temperature = 500 K

4. Find the lifting power of a 100 litre balloon filled with He at 730 mm and 25°C (Density of air = 1.25 g/L).

Sol. Since, PV = nRT PV = $\frac{W}{M} RT$

$$\therefore W = \frac{PVM}{RT} = \frac{730}{760} \times \frac{100 \times 4}{0.082 \times 298} \text{ g}$$

i.e., Wt. of He = 15.72 g

Wt. of air displaced = $100 \times 1.25 \text{ g/L} = 125\text{g}$

∴ Lifting power of the balloon = $125\text{g} - 15.72 \text{ g} = 109.28 \text{ g}$

5. Some spherical balloons each of volume 2 litre are to be filled with hydrogen gas at one atm & 27°C from a cylinder of volume 4 litres. The pressure of the H₂ gas inside the cylinder is 20 atm at 127°C. Find number of balloons which can be filled using this cylinder. Assume that temperature of the cylinder is 27°C.

Sol. No. of moles of gas taken initially $n = \frac{PV}{RT} = \frac{20 \times 4}{R \times 400} = 2.43$

No. of moles of gas left in cylinder $= \frac{1 \times 4}{R \times 300} = 0.162$

No. of moles of gas to be filled in balloons
 $= 2.43 - 0.162 = 2.268$

Let we have 'n' balloons that we can fill

No. of moles of gas that can be filled in 1 balloon

$$= \frac{1 \times 2}{0.082 \times 300} = 0.081$$

$\therefore 0.081 \times n = 2.268$

$n = 28$ balloons.

6. Four one litre flasks are separately filled with the gases O₂, F₂, CH₄ and CO₂ under the same conditions. The ratio of number of molecules in these gases:

- (a) 2 : 2 : 4 : 3 (b) 1 : 1 : 1 : 1
 (c) 1 : 2 : 3 : 4 (d) 2 : 2 : 3 : 4

Sol. (b) According to avogadro's hypothesis.

All the flasks contains same no. of molecules

\therefore Ratio of no. of molecules of O₂, F₂, CH₄ & CO₂
 $= 1 : 1 : 1 : 1$

7. A sample of water gas has a composition by volume of 50% H₂, 45% CO and 5% CO₂. Calculate the volume in litres at STP at which water gas which on treatment with excess of steam will produce 5 litre of H₂. The equation for the reaction is:



Sol. If x L CO is needed then

Volume of H₂ in water gas $= \left(\frac{x}{0.45} \times 50\% \right) \text{L}$

$$= \left(\frac{x}{0.45} \times \frac{1}{2} \right) \text{L} = \frac{x}{0.9} \text{L}$$

But, from equation : CO + H₂O \rightarrow CO₂ + H₂
 & Gay-Lussac's law, we get, that the volume of H₂ produced = volume of CO taken.

\therefore Volume of H₂ due to reaction = x L

\therefore Total volume of H₂ $= \left(\frac{x}{0.9} + x \right) \text{L} = 5 \text{ L}$

$$\Rightarrow \frac{1.9x}{0.9} = 5 \text{ L}$$

$$\therefore x = \frac{0.9 \times 5}{1.9} \Rightarrow 2.37$$

\therefore Volume of water gas

$$= \frac{x}{0.45} \text{L} = \frac{2.37}{0.45} \text{L} = 5.263 \text{ L Ans.}$$

8. The stop cock connecting the two bulbs of volume 5 litre and 10 litre containing as ideal gas at 9 atm and 6 atm respectively, is opened. What is the final pressure if the temperature remains same.

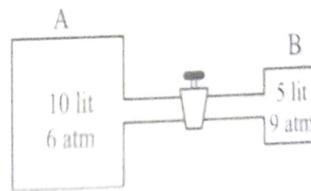
Sol. After the opening of the stop cock the pressure of the each bulb will remain same.

$$n = \frac{PV}{RT}$$

At the beginning, the no. of moles of gas in A $= \frac{10 \times 6}{RT}$

At the beginning, the no. of moles of gas in B $= \frac{5 \times 9}{RT}$

\therefore Total no. of moles at the beginning $= \frac{105}{RT}$



Total no. of moles of gas before opening the stop cock

$=$ total no. of moles of gas after opening stopcock $= \frac{105}{RT}$

\therefore Pressure after the opening of the stop cock

$$P = \frac{105}{RT} \times \frac{RT}{V_{\text{total}}} = \frac{105}{10 + 5} = 7 \text{ atm}$$

9. A mixture of NO₂ & CO having total volume of 100 ml contains 70 ml of NO₂ at 1 atm, mixture is left for some time and same NO₂ get dimerised to N₂O₄ such that final volume of the mixture become 80 ml at 1 atm, calculate the mole fraction of NO₂ in final equilibrium mixture.

Sol. Initial volume of NO₂ = 70 ml

Initial volume of CO = 100 - 70 = 30 ml

Final volume of mixture = 80 ml

Let the volume of NO₂ in final mixture be x

Let 'v' ml NO₂ be converted to N₂O₄



$$V \quad V/2$$

Hence final volume

= volume of CO + volume of NO₂ left + volume of N₂O₄ formed

$$30 + 70 - V + V/2 = 80$$

$$V = 40 \text{ ml}$$

Hence volume of NO₂ left = 70 - V = 30 ml

Now as volume \propto moles

$$\therefore \text{mole fraction} = \text{volume fraction} = \frac{30}{80} = \frac{3}{8}$$

10. 5 ml of H₂ gas diffuses out in 1 sec from a hole. Find the volume of O₂ that will diffuse out from the same hole under identical conditions in 2 sec.



Let both the gases meet in time t

$$\sqrt{17}t + \sqrt{36.5}t = 200$$

$$t = \frac{200}{\sqrt{17} + \sqrt{36.5}}$$

$$= \frac{200}{4.12 + 6.04}$$

$$= \frac{200}{10.16}$$

$$= 19.68 \text{ sec}$$

Distance from x will be

$$= 19.68 \times \sqrt{17}$$

$$= 81.14 \text{ cm}$$

17. A teacher enters a classroom from front door while a student enter from back door. There are 13 equidistant rows of benches in the classroom. The teacher releases N_2O , the laughing gas, from the first bench while the student releases the weeping gas ($\text{C}_6\text{H}_{11}\text{OBr}$) from the last bench. At which row will the students starts laughing and weeping simultaneously.

Sol. Let distance between two bench is x.

$$\text{Total distance covered} = 12x$$

$$\frac{r_{\text{N}_2\text{O}}}{r_{\text{tear gas}}} = \sqrt{\frac{179}{44}}$$

Let in time 't' both the gases meet

$$\sqrt{179}t + \sqrt{144}t = 12x$$

$$t = \frac{12x}{\sqrt{179} + \sqrt{144}}$$

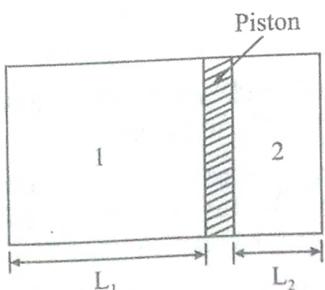
$$= \frac{12x}{20}$$

distance at which both gases will meet

$$= \sqrt{179} \times \frac{12x}{20}$$

$$= 8x \Rightarrow 9^{\text{th}} \text{ bench}$$

18. The closed cylinder shown in figure has a freely moving piston separating chambers 1 and 2. Chamber 1 contains 280 mg of N_2 gas, and chamber 2 contains 200 mg of helium gas. When equilibrium is established, what will be the ratio α_2/α_1 ? (Molecular weights of N_2 and He are 28 and 4).



$$\text{Sol. } n_{\text{N}_2} = \frac{280 \times 10^{-3}}{28} = 10^{-2}$$

$$n_{\text{He}} = \frac{200 \times 10^{-3}}{4} = 5 \times 10^{-2}$$

$$\alpha_1$$

$$\alpha_2$$

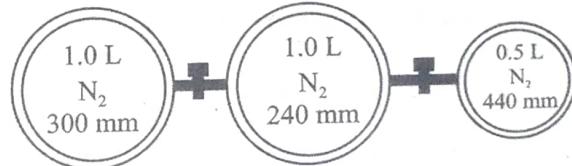
At equilibrium pressure in both the chamber will be same i.e.

$$P_1 = P_2$$

$$\frac{10^{-2} RT}{\alpha_1 A} = \frac{5 \times 10^{-2} RT}{\alpha_2 A}$$

$$\frac{\alpha_2}{\alpha_1} = 5$$

19. Consider the arrangement of bulbs shown below.



If the pressure of the system when all the stopcocks are opened is x (in atm) then find 100 x?

$$(760 \text{ mm Hg} = 1 \text{ atm})$$

Sol. Initial mole = final mole

$$\frac{300 \times 1}{RT} + \frac{240 \times 1}{RT} + \frac{440 \times 0.5}{RT} = \frac{P2.5}{RT}$$

$$760 = P \times 2.5$$

$$P = \frac{760}{2.5} \text{ mm}$$

$$P = \frac{2}{5} \text{ atm} = x$$

$$100x = 100 \times \frac{2}{5} = 40 \text{ atm}$$

20. A closed container of volume 30 litre contains a mixture of nitrogen and oxygen gases, at a temperature of 27°C and pressure of 4 atm. The total mass of the mixture is 148 gm. The moles of individual gases in the container are (Take $R = 0.08 \text{ litre atm/moleK}$)

$$\text{Sol. } V = 30 \text{ L}$$

$$T = 300 \text{ K}$$

$$P = 4 \text{ atm}$$

$$PV = nRT$$

$$4 \times 30 = n \times 0.08 \times 300$$

$$n = 5 \text{ moles}$$

$$\text{Let moles of } \text{N}_2 = n_1$$

$$\text{moles of } \text{O}_2 = 5 - n_1 = n_2$$

$$28n_1 + 32(5 - n_1) = 148$$

$$160 - 4n_1 = 148$$

$$4n_1 = 12$$

$$n_1 = 3 \text{ & } n_2 = 2$$

Exercise-1 (Topicwise)

IDEAL GAS EQUATION OF GAS LAWS

1. If P, V, T represent pressure, volume and temperature of the gas, the correct representation of Boyle's law is

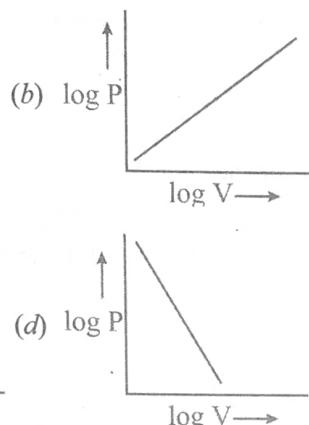
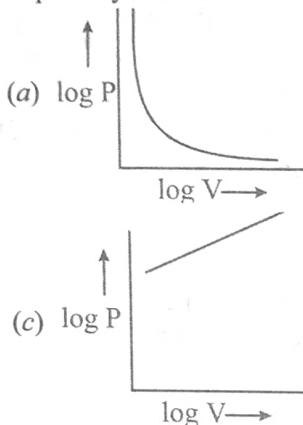
(a) $V \propto \frac{1}{T}$ (at constant P)

(b) $PV = RT$

(c) $V \propto 1/P$ (at constant T)

(d) $PV = nRT$

2. Which of the following represent log P vs log V variation as per Boyle's law?



3. If 20cm^3 gas at 1 atm is expanded to 50 cm^3 at constant T, then what is the final pressure of gas?

(a) $20 \times \frac{1}{50}$

(b) $50 \times \frac{1}{20}$

(c) $1 \times \frac{1}{20} \times 50$

(d) None of these

4. At the definite temperature, the volume of a definite mass of gas is 10 L at 5 atm pressure. At the same temperature, if the pressure of the gas is decreased to 1 atm , the volume of same gas becomes:

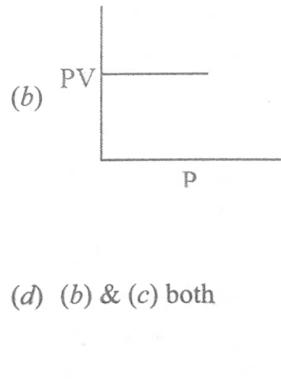
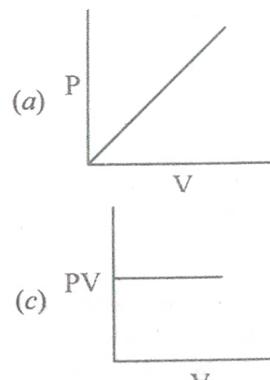
(a) 50 L

(b) 2 L

(c) 5 L

(d) 0.5 L

5. Which of the following graphs represent Boyle's law?



(d) (b) & (c) both

6. Which of the following expression at constant pressure represents Charle's law?

(a) $V \propto \frac{1}{T}$

(b) $V \propto \frac{1}{T^2}$

(c) $V \propto T$

(d) $V \propto d$

7. If two moles of an ideal gas at 546K occupy a volume of 44.8 litres , the pressure must be

(a) 2 atm

(b) 3 atm

(c) 4 atm

(d) 1 atm

8. Correct gas equation is

(a) $\frac{V_1 T_2}{P_1} = \frac{V_2 T_1}{P_2}$

(b) $\frac{P_1 V_1}{P_2 V_2} = \frac{T_1}{T_2}$

(c) $\frac{P_1 T_2}{V_1} = \frac{P_2 V_2}{T_2}$

(d) $\frac{V_1 V_2}{T_1 T_2} = P_1 P_2$

9. The vapour density of a gas is 11.2 . The volume occupied by 11.2 g of this gas at N.T.P. is

(a) 1 L

(b) 11.2 L

(c) 22.4 L

(d) 20 L

10. A pre-weighed vessel was filled with oxygen at N.T.P. and weighed. It was then evacuated, filled with SO_2 at the same temperature and pressure, and again weighed. The weight of oxygen will be

(a) The same as that of SO_2

(b) Half of that of SO_2

(c) Twice that of SO_2

(d) One fourth that of SO_2

11. In the gas equation $PV = nRT$, the value of universal gas constant would depend only on -

(a) The nature of the gas

(b) The pressure of the gas

(c) The temperature of the gas

(d) The units of measurement

12. When the pressure of 5L of N_2 is doubled and its temperature is raised from 300K to 600K , the final volume of the gas would be-

(a) 10 L

(b) 5 L

(c) 15 L

(d) 20 L

13. One litre of a gas collected at NTP when kept at 2 atmospheric pressure and 27°C will occupy

(a) $\frac{300}{2 \times 273}\text{ litre}$

(b) $\frac{2 \times 300}{273}\text{ litre}$

(c) $\frac{273}{2 \times 300}\text{ litre}$

(d) $\frac{2 \times 273}{300}\text{ litre}$

DALTON'S LAW OF PARTIAL PRESSURES

19. Dalton's law of partial pressures are applicable to

 - (a) Non reacting gases
 - (b) Ideal gases
 - (c) Temperature of the component gases in the mixture remain same
 - (d) All of these

20. 1000 ml of a gas A at 600 torr and 500 ml of gas B at 800 torr are placed in a 2L flask. The final pressure will be

(a) 2000 torr	(b) 1000 torr
(c) 500 torr	(d) 1400 torr

MIXING OF GASES

GRAHAM'S LAW OF DIFFUSION

23. If three unreactive gases having partial pressures P_A , P_B and P_C and their moles are 1, 2 and 3 respectively, then their total pressure will be

(a) $P = P_A + P_B + P_C$ (b) $P = \frac{P_A + P_B + P_C}{6}$
 (c) $P = \frac{\sqrt{P_A + P_B + P_C}}{3}$ (d) None of these

24. Rate of diffusion of a gas is

(a) Directly proportional to its density
 (b) Directly proportional to its molecular mass
 (c) Directly proportional to the square root of its molecular mass
 (d) Inversely proportional to the square root of its molecular mass

25. The densities of two gases are in the ratio of 1 : 16. The ratio of their rates of diffusion is

(a) 16 : 1 (b) 4 : 1
 (c) 1 : 4 (d) 1 : 16

26. A bottle of ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends, the white ammonium chloride ring first formed will be

(a) At the centre of the tube
 (b) Near the hydrogen chloride bottle
 (c) Near the ammonia bottle
 (d) Throughout the length of the tube

27. In an effusion experiment, it required 40 s for a certain number of moles of a gas of unknown molar mass to pass through a small orifice into a vacuum. Under the same conditions, 16 s were required for the same number of moles of O_2 to effuse. What is the molar mass of the unknown gas?

(a) 5.1 g/mol (b) 12.8 g/mol
 (c) 80 g/mol (d) 200 g/mol

28. 50 ml of a gas A diffuse through a membrane in the same time as for the diffusion of 40 ml of gas B under identical conditions of pressure and temperature. If the molecular mass of A is 64, molar mass of B would be

(a) 100 (b) 250
 (c) 200 (d) 80

KINETIC THEORY OF GASES

- 31.** The density of a gas A is three times that of a gas B at same temperature. If the molecular mass of A is M, the molecular mass of B is
- $3M$
 - $\sqrt{3}M$
 - $M/3$
 - $M\sqrt{3}$
- 32.** The ratio of root mean square velocity to average velocity of gas molecules at a particular temperature is
- $1.086 : 1$
 - $1 : 1.086$
 - $2 : 1.086$
 - $1.086 : 2$
- 33.** The ratio among most probable velocity, mean velocity and root mean square velocity is given by
- $1 : 2 : 3$
 - $1 : \sqrt{2} : \sqrt{3}$
 - $\sqrt{2} : \sqrt{3} : \sqrt{8/\pi}$
 - $\sqrt{2} : \sqrt{8/\pi} : \sqrt{3}$
- 34.** At constant volume, for a fixed number of moles of a gas, the pressure of the gas increases with increase in temperature due to
- Increase in the average molecular speed
 - Increased rate of collision amongst molecules
 - Increase in molecular attraction
 - Decrease in mean free path
- 35.** Molecular velocities of the two gases at the same temperature are u_1 and u_2 . Their masses are m_1 and m_2 respectively. Which of the following expressions is correct?
- $\frac{m_1}{u_1^2} = \frac{m_2}{u_2^2}$
 - $m_1 u_1 = m_2 u_2$
 - $\frac{m_1}{u_1} = \frac{m_2}{u_2}$
 - $m_1 u_1^2 = m_2 u_2^2$
- 36.** If a gas is allowed to expand at constant temperature, then
- number of molecules of the gas decreases
 - the kinetic energy of the gas molecules decreases
 - the kinetic energy of the gas molecules increases
 - the kinetic energy of the gas molecules remains the same
- 37.** At constant volume, for a fixed number of mole of a gas, the pressure of the gas increases with rise of temperature due to
- increase in average molecular speed
 - increased rate of collisions amongst molecules
 - increase in molecular attraction
 - decrease in mean free path
- 38.** In a closed flask of 5 litre, 1.0 g of H_2 is heated from 300-600 K. Which statement is not correct?
- The rate of collision increases.
 - The energy of gaseous molecules increases.
 - The number of mole of the gas increases.
 - Pressure of the gas increases.
- 39.** The molecules of which of the following gas have highest speed?
- Hydrogen at $-50^\circ C$
 - Methane at $298K$
 - Nitrogen at $1000^\circ C$
 - Oxygen at $0^\circ C$

REAL GAS

Vander Waal Equation and Virial Equation of State

- 40.** Which of the following satisfies the greater compressibility of real gas?
- $Z < 1$
 - At the higher pressure
 - Above the Boyle's temperature
 - Lesser the value of "a" but higher value of "b"
- 41.** Gases deviate from the ideal gas behaviour because their molecules
- Possess negligible volume
 - Have forces of attraction between them
 - Are polyatomic
 - Are not attracted to one another
- 42.** The compressibility factor of a gas is defined as $Z = PV/RT$. The compressibility factor of an ideal gas is
- 0
 - Infinity
 - 1
 - 1
- 43.** Vander Waal's equation of state is obeyed by real gases. For n moles of a real gas, the expression will be
- $\left(\frac{P}{n} + \frac{na}{V^2} \right) \left(\frac{V}{n-b} \right) = RT$
 - $(P + \frac{a}{V^2})(V - b) = nRT$
 - $(P + \frac{na}{V^2})(nV - b) = nRT$
 - $(P + \frac{n^2a}{V^2})(V - nb) = nRT$
- 44.** When is deviation more in the behaviour of a gas from the ideal gas equation $PV = nRT$?
- At high temperature and low pressure
 - At low temperature and high pressure
 - At high temperature and high pressure
 - At low temperature and low high pressure
- 45.** The Vander Waal's constant 'a' for the gases O_2 , N_2 , NH_3 and CH_4 are 1.3, 1.390, 4.170 and $2.253 \text{ L}^2 \text{ atm mol}^{-2}$ respectively. The gas which can be most easily liquefied is
- O_2
 - N_2
 - NH_3
 - CH_4
- 46.** The compressibility factor of a gas is less than 1 at STP. Its molar volume V_m will be
- $V_m > 22.42$
 - $V_m < 22.42$
 - $V_m = 22.42$
 - None of these



47. The critical temperature of a gas is that temperature

 - (a) above which it can no longer remain in the gaseous state.
 - (b) above which it cannot be liquefied by pressure.
 - (c) at which it solidifies.
 - (d) at which the volume of the gas becomes zero.

48. In van der Waals' equation of state for a non-ideal gas, the term that accounts for intermolecular force is

$$(a) \left(P + \frac{a}{V^2} \right) \quad (b) (V - b)$$

Exercise-2 (Learning Plus)

8. 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 = 3.0 gm dm^{-3} and that of B = 1.5 gm dm^{-3} and the molar mass of A = $1/2$ of B, then the ratio of pressure exerted by gases is
 (a) $P_A/P_B = 2$ (b) $P_A/P_B = 1$
 (c) $P_A/P_B = 4$ (d) $P_A/P_B = 3.$

9. The density of neon will be highest at
 (a) STP (b) $0^\circ\text{C}, 2 \text{ atm}$
 (c) $273^\circ\text{C}, 1 \text{ atm}$ (d) $273^\circ\text{C}, 2 \text{ atm}$

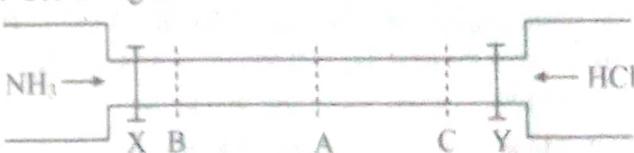
10. Equal weights of ethane & hydrogen are mixed in an empty container at 25°C , the fraction of the total pressure exerted by hydrogen is :
 (a) 1:2 (b) 1:1
 (c) 1:16 (d) 15:16

11. A mixture of hydrogen and oxygen at one bar pressure contains 20% by weight of hydrogen. Partial pressure of hydrogen will be
 (a) 0.2 bar (b) 0.4 bar
 (c) 0.6 bar (d) 0.8 bar

12. The rates of diffusion of SO_2 , CO_2 , PCl_3 , and SO_3 are in the following order -
 (a) $\text{PCl}_3 > \text{SO}_3 > \text{SO}_2 > \text{CO}_2$
 (b) $\text{CO}_2 > \text{SO}_2 > \text{PCl}_3 > \text{SO}_3$
 (c) $\text{SO}_3 > \text{SO}_2 > \text{PCl}_3 > \text{CO}_2$
 (d) $\text{CO}_2 > \text{SO}_2 > \text{SO}_3 > \text{PCl}_3$

13. 20L of SO_2 diffuses through a porous partition in 60 seconds. Volume of O_2 diffuse under similar conditions in 30 seconds, will be
 (a) 12.14L (b) 14.14L
 (c) 18.14L (d) 28.14L

14. See the figure:-



The valves 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
15. X ml of H_2 gas effuses through a hole in a container in 5 sec. The time taken for the effusion of the same volume of the gas specified below under identical conditions is:
- (a) 10 sec, He
 - (b) 20 sec, O_2
 - (c) 25 sec, CO_2
 - (d) 55 sec, CO_2
16. The rate of diffusion of 2 gases 'A' and 'B' are in the ratio 16: 3. If the ratio of their masses present in the mixture is 2 : 3, then
- (a) The ratio of their molar masses is 16 : 1.
 - (b) The ratio of their molar masses is 1 : 4.
 - (c) The ratio of their moles present inside the container is 8 : 3.
 - (d) (b) & (c) both
17. Three footballs are respectively filled with nitrogen, hydrogen and helium. If the leaking of the gas occurs with time from the same area of hole, then the ratio of the rate of leaking of gases ($r_{\text{N}_2} : r_{\text{H}_2} : r_{\text{He}}$) from three footballs (in equal time interval) is:
- (a) $(1 : \sqrt{14} : \sqrt{7})$
 - (b) $(\sqrt{14} : \sqrt{7} : 1)$
 - (c) $(\sqrt{7} : 1 : \sqrt{14})$
 - (d) $(1 : \sqrt{7} : \sqrt{14})$
18. The volume of CO_2 produced by the combustion of 40 ml of gaseous acetone in excess of oxygen, is
- (a) 40 ml
 - (b) 80 ml
 - (c) 60 ml
 - (d) 120 ml
19. Temperature at which r.m.s. speed of O_2 is equal to that of neon at 300K, is :
- (a) 280 K
 - (b) 480 K
 - (c) 680 K
 - (d) 180 K
20. The temperature of an ideal gas is increased from 120 K to 480K. If at 120K the root-mean-square velocity of the gas molecules is v, then at 480K, it becomes :
- (a) $4v$
 - (b) $2v$
 - (c) $v/2$
 - (d) $v/4$
21. The ratio between the r.m.s. velocity of H_2 at 50 K and that of O_2 at 800K is:
- (a) 4
 - (b) 2
 - (c) 1
 - (d) $1/4$
22. 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

23. By how many folds the temp of a gas would increase when the r.m.s. velocity of gas molecules in a closed container of fixed volume is increased from $5 \times 10^4 \text{ cm s}^{-1}$ to $10 \times 10^4 \text{ cm s}^{-1}$?
- (a) 0.5 times
 - (b) 2 times
 - (c) 4 times
 - (d) 16 times.

24. The correct relationship between T_c , T_b and T_i is
- (a) $T_c < T_b < T_i$
 - (b) $T_c > T_b > T_i$
 - (c) $T_c < T_i < T_b$
 - (d) $T_i < T_b < T_c$

25. In vander Waal's equation of state for a non ideal gas, the term that accounts for intermolecular forces is:
- (a) nb
 - (b) nRT
 - (c) $n^2 a/V^2$
 - (d) $(nRT)^{-1}$

26. The correct order of normal boiling points of O_2 , N_2 , NH_3 and CH_4 , for whom the values of vander Waal's constant 'a' are 1.360, 1.390, 4.170 and 2.253 $\text{L}^2 \text{ atm mol}^{-2}$ respectively, is:
- (a) $\text{O}_2 < \text{N}_2 < \text{NH}_3 < \text{CH}_4$
 - (b) $\text{O}_2 < \text{N}_2 < \text{CH}_4 < \text{NH}_3$
 - (c) $\text{NH}_3 < \text{CH}_4 < \text{N}_2 < \text{O}_2$
 - (d) $\text{NH}_3 < \text{CH}_4 < \text{O}_2 < \text{N}_2$

27. A real gas obeying Vander Waal's 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

28. For the non-zero values of force of attraction between gas molecules, gas equation will be:

$$(a) PV = nRT - \frac{n^2 a}{V} \quad (b) PV = nRT + nbP$$

$$(c) PV = nRT \quad (d) P = \frac{nRT}{V - b}$$

29. Compressibility factor for H_2 behaving as real gas is:

$$(a) 1 \quad (b) \left(1 - \frac{a}{RTV}\right)$$

$$(c) \left(1 + \frac{Pb}{RT}\right) \quad (d) \frac{RTV}{(1-a)}$$

30. At low pressures (For 1 mole), the Vander Waal's equation is written as

$$\left[P + \frac{a}{V^2} \right] V = RT$$

The compressibility factor is then equal to:

$$(a) \left(1 - \frac{a}{RTV}\right) \quad (b) \left(1 - \frac{RTV}{a}\right)$$

$$(c) \left(1 + \frac{a}{RTV}\right) \quad (d) \left(1 + \frac{RTV}{a}\right)$$

31. Calculate the radius of He atoms if its Vander Waal's constant 'b' is 24 ml mol^{-1} .

(Note 1ml = 1 cubic centimeter)

$$(a) 1.355 \text{ \AA} \quad (b) 1.314 \text{ \AA}$$

$$(c) 1.255 \text{ \AA} \quad (d) 0.355 \text{ \AA}$$

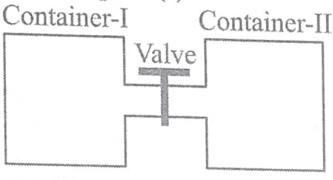
32. Which of the following gas has higher value of the van der waals constant 'b'?
- N_2
 - O_2
 - O_3
 - F_2
33. A certain saturated hydrocarbon effuses 0.525 times fast as methane. The molecular formula of the hydrocarbon (a compound made up of only carbon and hydrogen) is
- C_4H_8
 - C_4H_{10}
 - C_3H_6
 - C_3H_8
34. Consider the gaseous reaction, $N_2 + 3H_2 \rightarrow 2NH_3$, 1 mol N_2 and 4 mole H_2 are taken in 15 L flask at 27°C. After the completion of the reaction, 5L of H_2O is added to the reaction vessel, pressure setup in the flask would be (assume conversion to be 100%)
- $\frac{3 \times 0.0821 \times 300}{15} \text{ atm}$
 - $\frac{2 \times 0.0821 \times 300}{10} \text{ atm}$
 - $\frac{1 \times 0.0821 \times 300}{15} \text{ atm}$
 - $\frac{1 \times 0.0821 \times 300}{10} \text{ atm}$
35. 20 ml of O_2 contracts to 17 ml when subjected to silent electric discharge in an ozoniser. What further contraction would be observed if the partially ozonised oxygen is treated with oil of cinnamon (which absorbs ozone). All volumes are reported at the same temperature and pressure.
- 2 ml
 - 8 ml
 - 6 ml
 - 4 ml
36. NH_3 is liquefied more easily than N_2 , hence
- $a_{NH_3} > a_{N_2}$ and $b_{NH_3} > b_{N_2}$
 - $a_{NH_3} > a_{N_2}$ but $b_{NH_3} < b_{N_2}$
 - $a_{NH_3} < a_{N_2}$ but $b_{NH_3} > b_{N_2}$
 - None
37. The temperature of an ideal gas is reduced from 927°C to 27°C. The r.m.s. velocity of the molecules becomes
- Double the initial value
 - Half of the initial value
 - Four times the initial value
 - Ten times the initial value
38. An open vessel containing air is heated from 300 K to 400 K. The fraction of air, which goes out with respect to originally present is
- 3/4
 - 1/4
 - 2/3
 - 1/8
39. 4.0 g of argon has pressure 'P' at temperature 'T' K in a vessel. On keeping the sample at 50° higher temperature, 0.8 g gas was given out to maintain the pressure 'P'. The original temperature was
- 73 K
 - 100 K
 - 200 K
 - 510 K
40. The pressure of the atmosphere 100 miles above the surface of earth is about 7.6×10^{-6} mm of Hg and its temperature is -23°C. How many molecules are there in 1 ml of a gas at this altitude?
- 2.93×10^{11}
 - 7.58×10^{10}
 - 0.05×10^{11}
 - 2.07×10^{10}
41. The density of phosphorus vapour at 310°C and 775 torr is 2.64 g/l. What is the molecular formula of phosphorus?
- P
 - P_2
 - P_4
 - P_5
42. A gas cylinder containing cooking gas can withstand a pressure of 14.9 atm. The pressure gauge of cylinder indicates 12 atm at 27°C. Due to sudden fire in building the temperature starts rising. The temperature at which the cylinder explodes is
- 42.5°C
 - 67.8°C
 - 99.5°C
 - 25.7°C
43. At constant pressure what would be the percentage decrease in the density of an ideal gas for a 10% increase in the temperature.
- 10%
 - 9.1%
 - 11%
 - 12.09%
44. The diameter of a balloon filled by 8 moles of He gas is 10 cm. If 7 moles of He gas escape out in the night, then what should be the diameter of balloon in the next morning? Assume constant pressure and temperature for the gas.
- 5 cm
 - $\left(\frac{7}{8}\right)^{1/3} \times 5 \text{ cm}$
 - $\left(\frac{8}{7}\right)^{1/3} \times 5 \text{ cm}$
 - 20 cm
45. A volume of 50 L of dry N_2 is passed through 36 g of water at 300 K. After the passage of gas, there is a loss of 1.20 g in water. The vapour pressure of water at 300 K is
- 0.033 mm Hg
 - 24.96 mm Hg
 - 16.05 mm Hg
 - 38.73 mm Hg
46. Which of the following graph is correct for hydrogen gas at 0°C?
-

47. The equation of state for a gas is $P(V - nb) = nRT$, where b and R are constants. If the pressure and temperature are such that $V_m = 10b$, then what is the compressibility factor of gas in this condition?
- 10/9
 - 9/11
 - 11/10
 - 10
48. Under what pressure will carbon dioxide have the density of 2.2 g/litre at 300 K? For CO_2 , $a = 3.6 \text{ atm L}^2 \text{mol}^{-2}$ and $b = 0.05 \text{ mol}^{-1} \text{L}$.
- 1.23 atm
 - 1.28 atm
 - 2.46 atm
 - 0.64 atm
49. At moderate pressure, the compressibility factor for a gas is given as, where P is in bar and T is in Kelvin. What is the Boyle's temperature of the gas?
- 168 K
 - 480 K
 - 58.8 K
 - 575 K

Exercise-3 (JEE Advanced Level)

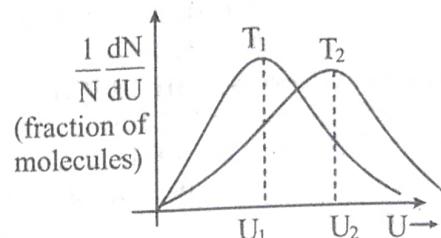
MULTIPLE CORRECT TYPE QUESTIONS

1. A gas cylinder containing cooking gas can withstand a pressure of 14.9 atmosphere. The pressure guaze of cylinder indicates 12 atmosphere at 27 °C. Due to sudden fire in the building temperature starts rising. The temperature at which cylinder will explode is :
 - (a) 372.5 K
 - (b) 99.5 °C
 - (c) 199 °C
 - (d) 472.5 K
2. Select the correct observation for a 8.21L container, filled with 2 moles of He at 300 K.,
 - (a) It has pressure 6 atm.
 - (b) If it is an open rigid container, its pressure increases to 8 atm on heating to 400 K.
 - (c) If it is closed non-rigid (like thin skin balloon), its volume increases to 16.42 lit. on heating to 600 K.
 - (d) When connected with another similar empty container maintained at 150 K while maintaining original container at 300 K, pressure reduces to $\frac{2}{3}$ atm.
3. Select the correct option(s):

Container-I  <p>300K 2 mol H₂ 16.42 lit</p>	Container-II  <p>400K 1 mol H₂ 8.21 lit</p>
--	--

 - (a) Pressure in container-I is 3 atm before opening the valve.
 - (b) Pressure after opening the valve is 3.57 atm.
 - (c) Moles in each compartment are same after opening the valve.
 - (d) Pressure in each compartment are same after opening the valve.
4. Which of the following statements are correct ?
 - (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 CO₂ does.
 - (d) Helium escapes at a rate 4 times as fast as SO₂ does.
5. The rate of diffusion of 2 gases 'A' and 'B' are in the ratio of 16 : 3. If the ratio of their masses present in the mixture is 2 : 3, then
 - (a) The ratio of their molar masses is 16 : 1.
 - (b) The ratio of their molar masses is 1 : 4.
 - (c) The ratio of their moles present inside the container is 1 : 24.
 - (d) The ratio of their moles present inside the container is 8 : 3.

6.



In the above maxwellian plot at two different temperatures, which of the following statements may be true?

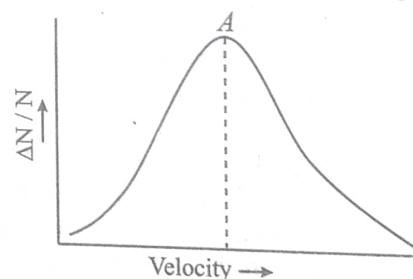
- (a) Area under the two plots is the same.
- (b) Fraction of molecules with speed u₁ at T₁ > fraction of molecules having speed u₂ at T₂.
- (c) U₂ > U₁ and T₂ > T₁
- (d) U_{MPS} at T₁ < U_{MPS} at T₂; U_{RMS} at T₁ < U_{RMS} at T₂

7. If a closed container of volume 200L of O₂ gas (ideal gas) at 1 atm & 200 K is taken to another planet. Find the pressure of oxygen gas at the planet at 821 K in same container

- (a) $\frac{10}{e^{100}}$
- (b) $\frac{20}{e^{50}}$
- (c) 1 atm
- (d) 4.1 atm

8. Which of the following are correct statements?
 - (a) van der Waals' constant 'a' is a measure of attractive force.
 - (b) van der Waals' constant 'b' is also called co-volume or excluded volume.
 - (c) b is expressed in L mol⁻¹.
 - (d) b is one-third of critical volume.

9. Point A in the given curve shifts to higher value of velocity if



- (a) T is increased
- (b) P is decreased
- (c) V is decreased
- (d) molecular weight M is decreased

10. According to the kinetic theory of gases
 - (a) pressure of a gas is due to collisions of molecules with each other.
 - (b) kinetic energy is proportional to square root of the temperature.
 - (c) pressure of a gas is due to collisions of molecules against the sides of the container.
 - (d) there is no force of attraction between gas molecules.



11. For two gases, A and B with molecular weights M_A and M_B , it is observed that at a certain temperature T , the mean velocity of A is equal to the V_{rms} of B. Thus the mean velocity of A can be made equal to the mean velocity of B, if

- (a) A is at temperature T and B at T' such that $T > T'$.
- (b) Temperature of A is lowered to T_2 while B is at T such that $T_2 < T$.
- (c) Both A and B are raised to a higher temperature.
- (d) Heat energy is supplied to A.

12. If for two gases of molecular weights M_A and M_B at temperature T_A and T_B , it is observed that $T_A M_B = T_B M_A$, then which property has the same magnitude for both the gases.

- (a) PV if mass of gases taken are same
- (b) Pressure
- (c) KE per mol
- (d) V_{rms}

13. Molecular attraction and size of the molecules in a gas are not negligible at

- (a) Critical point
- (b) High pressure
- (c) High temperature and low pressure
- (d) low temperature and high pressure

14. Select correct statements

- (a) Vapour may be condensed to liquid by the application of pressure.
- (b) To liquefy a gas one must lower the temperature below T_c and apply pressure.
- (c) At T_c there is no distinction between liquid and vapour state.
- (d) At T_c , density of liquid is very high as compared to its gaseous state.

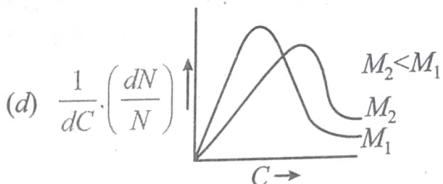
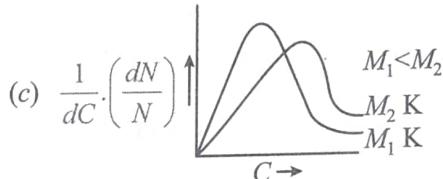
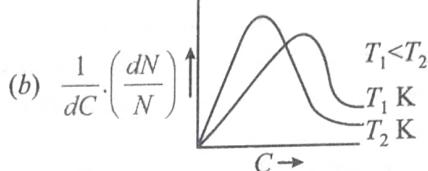
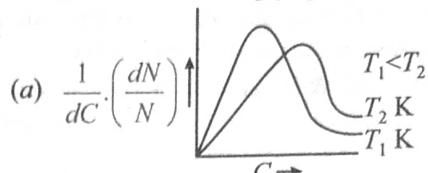
15. Which of the following statement is/are correct?

- (a) All real gases are less compressible than ideal gas at high pressure.
- (b) Hydrogen and helium are more compressible than ideal gas for all values of pressure.
- (c) Except H_2 and He , the compressibility factor $Z = \left(\frac{PV}{nRT} \right) < 1$ for all gases at low pressure.
- (d) The compressibility factor of real gases is independent of temperature.

16. Precisely 1 mole of helium and 1 mole of neon are placed in a container. Indicate the correct statements about the system

- (a) Molecules of the two gases strike the wall of the container with same frequency.
- (b) Molecules of helium strike the wall more frequently.
- (c) Molecules of helium has greater average molecular speed.
- (d) Helium exerts larger pressure.

17. Which of the following graphs are correct for ideal gases?



18. The critical temperature and pressure of a gas are 340 K and 42 atm, respectively. The gas can be liquefied at

- (a) 340 K and 45 atm
- (b) 340 K and 40 atm
- (c) 350 K and 100 atm
- (d) 320 K and 42 atm.

19. Which of the following statement(s) is/are correct?

- (a) The physical state of the system at critical condition cannot be defined.
- (b) All the physical properties of liquid and gaseous state of a substance become identical at critical condition.
- (c) For a gas, there is no distinction between liquid and vapour state at critical condition.
- (d) Easily liquefiable gases have higher Boyle's temperature while the gases difficult to liquefy has lower Boyle's temperature.

20. For a real gas (van der Waals gas), behaving ideally, the pressure may be

- | | |
|-----------------------------|-----------------------------|
| (a) $a \cdot b \cdot V_m$ | (b) $\frac{V_m}{a \cdot b}$ |
| (c) $\frac{a}{V_m \cdot b}$ | (d) $\frac{b}{V_m \cdot a}$ |

21. Van der Waals constant 'a' can be expressed as

- | | |
|---|---|
| (a) $\frac{9RT_C V_C}{8}$ | (b) $3P_C V_C^2$ |
| (c) $\frac{3}{8} \cdot \frac{P_C V_C}{T_C}$ | (d) $\frac{27}{64} \cdot \frac{R^2 T_C^2}{P_C}$ |

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 22 to 24): Two containers X & Y are present with container X consisting of some mass of He at some temperature while container Y having double the volume as that

of container X & kept at same temperature containing same mass of H_2 gas as the mass of Helium gas. Based on this data & the following conditions, answer the question that follows:

Assume sizes of H_2 molecule & He atom to be same & size of H-atom to be half to that of He-atom & only bimolecular collisions to be occurring.

Condition I: All except one atom of He are stationary in container X & all molecules of H₂ are moving in container Y.

Condition II: Both containers contain all moving molecules.

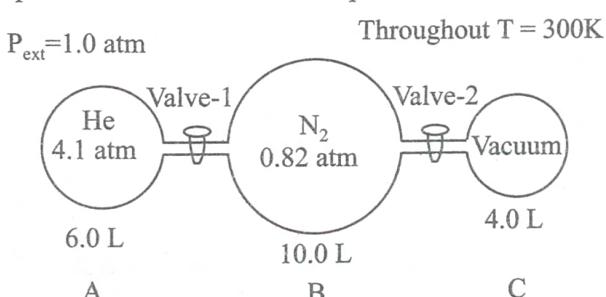
22. Assuming **condition I** to be applicable & if no. of *total collisions* occurring per unit time is 'A' in container X, then no. of total collisions made by any one molecule in container Y will be:

23. Assuming **condition II** then ratio of ‘total no. of collisions per unit volume per unit time’ in container X & container Y is (container X : container Y)

24. Assuming condition II to be applicable, if temperature only of container Y is doubled to that of original (causing dissociation of all H_2 gas into H gaseous atoms) then, if no. of total collisions per unit volume per unit time in container X is A then, no. of 'total collisions made by all molecules per unit volume in container Y would be

- (a) $2\sqrt{2}A$ (b) $\sqrt{2}A$
 (c) $8\sqrt{2}A$ (d) None of these

Comprehension (Q. 25 to 28): The figure given below shows three glass chambers that are connected by valves of negligible volume. At the outset of an experiment, the valves are closed and the chambers contain the gases as detailed in the diagram. All the chambers are at the temperature of 300K and external pressure of 1.0 atm.

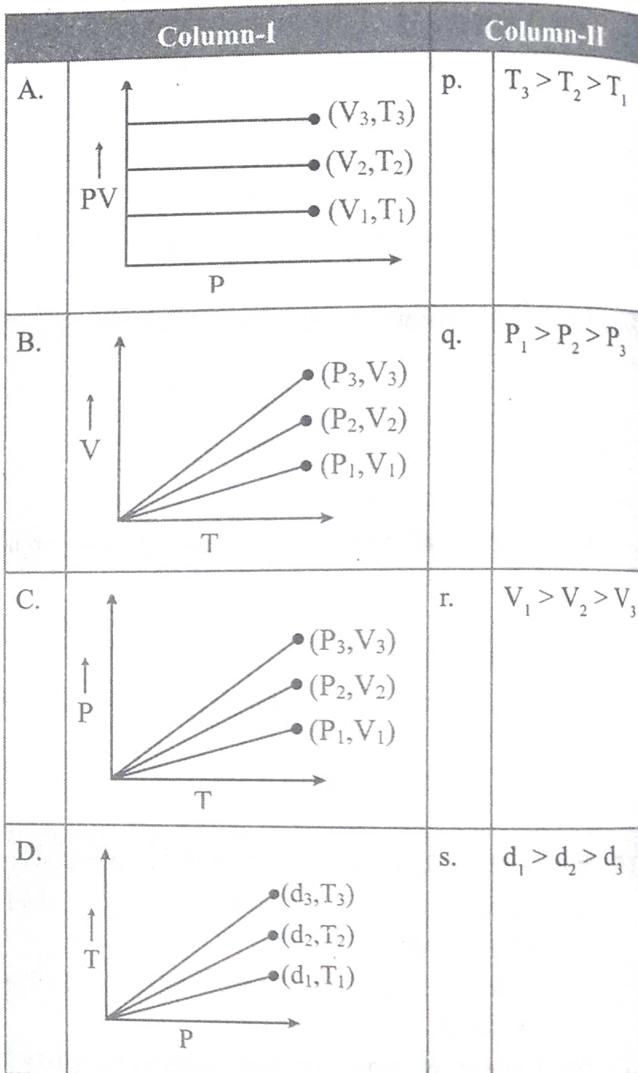


25. What will be the work done by N_2 gas when the valve-2 is opened and valve-1 remaining closed?

26. Which of the following represents the total kinetic energy of all the gas molecules after both valves are opened? ($R = 0.082 \text{ atm L K}^{-1} \text{ mol}^{-1} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

MATCH THE COLUMN TYPE QUESTIONS

29. For a fixed amount of the gas, match the two columns:



- (a) $A \rightarrow s; B \rightarrow q,s; C \rightarrow r; D \rightarrow p,r$
 (b) $A \rightarrow q,s; B \rightarrow s; C \rightarrow r; D \rightarrow p,r$
 (c) $A \rightarrow s; B \rightarrow r; C \rightarrow q,s; D \rightarrow p,r$
 (d) $A \rightarrow s; B \rightarrow q,s; C \rightarrow p,r; D \rightarrow r$

30. The vander waal gas constant 'a' is given by

- $$(a) \quad \frac{1}{3} V_C \quad (b) \quad 3P_C V_C^2$$

- $$(c) \frac{1}{8} \frac{RT_C}{P_C} \quad (d) \frac{27}{64} \frac{R^2 T_C^2}{P_C}$$

31. For gaseous state, which of the following is incorrect?

- (a) Thermal energy = Molecular attraction
- (b) Thermal energy \gg Molecular attraction
- (c) Thermal energy \ll Molecular attraction
- (d) Molecular force \gg attraction in liquid

32. Select the incorrect statement(s):

- (a) At Boyle's temperature, a real gas behaves like an ideal gas irrespective of pressure.
- (b) At critical condition, a real gas behaves like an ideal gas.
- (c) On increasing the temperature four times, collision frequency (Z_{11}) becomes double at constant volume.
- (d) At high pressure, Vander Waal's constant 'b' dominates over 'a'.

33. Match the column & choose the correct option among the options given.

(Note: Each statement in column-I has one or more matches in column-II.)

Column-I		Column-II	
A.	Critical temperature	p.	Gas can be liquefied.
B.	Boyle's temperature	q.	Deviate from ideal gas equation.
C.	Compressibility factor (Z) < 1	r.	Gas follows the ideal gas equation.
D.	High temperature and low pressure	s.	Assumption of no intermolecular force of attraction is valid.

(a) A \rightarrow p, q; B \rightarrow r, s; C \rightarrow p, q; D \rightarrow r, s

(b) A \rightarrow p, r; B \rightarrow r, s; C \rightarrow p, r; D \rightarrow r, s

(c) A \rightarrow r, s; B \rightarrow p, q; C \rightarrow r, s; D \rightarrow p, q

(d) A \rightarrow p, q; B \rightarrow p, q; C \rightarrow r, s; D \rightarrow r, s

34. Match the column & choose the correct option among the options given.

(Note: Each statement in column-I has one or more matches in column-II.)

Column-I		Column-II	
A.	Diffusion of gas	p.	High when molecular mass is low
B.	Compressibility of gas (Z) < 1	q.	$V_{\text{real}} < V_{\text{ideal}}$
C.	V_{rms}	r.	Increases with increase in temperature
D.	Liquefaction of gas	s.	Attractive force dominates

(a) A \rightarrow p, r; B \rightarrow p, r, s; C \rightarrow p, r; D \rightarrow p, q, s

(b) A \rightarrow p, r; B \rightarrow q, r, s; C \rightarrow p, r; D \rightarrow q, s

(c) A \rightarrow p, r; B \rightarrow q, r, s; C \rightarrow p, q, r; D \rightarrow p, q, s

(d) A \rightarrow p, r; B \rightarrow p, q; C \rightarrow p, q, s; D \rightarrow p, q, s

35. Match the column & choose the correct option among the options given.

(Note: Each statement in column-I has only one match in column-II.)

Column-I		Column-II	
A.	Compressibility factor (Z) for ideal gas	p.	$\frac{3}{8}$
B.	Z for real gas at low P	q.	$(1 + Pb/RT)$
C.	Z for real gas at high P	r.	1
D.	Z for critical state	s.	$(1 - a/RTV)$

(a) A \rightarrow p; B \rightarrow s; C \rightarrow q; D \rightarrow r

(b) A \rightarrow r; B \rightarrow q; C \rightarrow s; D \rightarrow p

(c) A \rightarrow r; B \rightarrow s; C \rightarrow q; D \rightarrow p

(d) A \rightarrow p; B \rightarrow q; C \rightarrow s; D \rightarrow r

36. Match the columns & choose the correct option among the options given.

(Note: Each statement in column-I has one or more matches in column-II.)

Column-I		Column-II	
A.	H_2 gas at 300 K	p.	Maximum translational K.E. per mol.
B.	CH_4 gas at 400 K	q.	Maximum translational K.E. per gram.
C.	O_2 gas at 900 K	r.	Minimum translational K.E. per mol.
D.	He gas at 600 K	s.	Minimum translational K.E. per gram.

(a) A \rightarrow q, r; B \rightarrow p; C \rightarrow s; D \rightarrow q

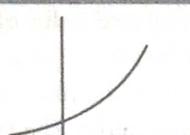
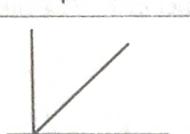
(b) A \rightarrow q, r; B \rightarrow q; C \rightarrow p; D \rightarrow s

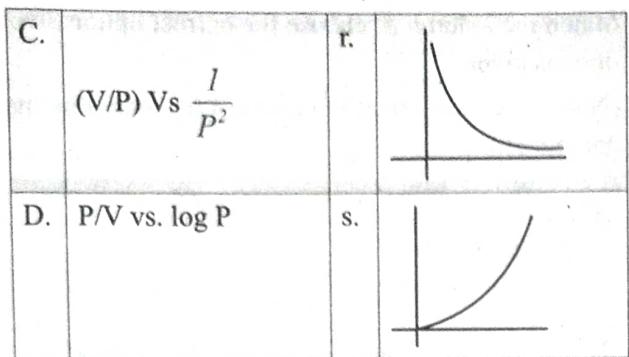
(c) A \rightarrow q, r; B \rightarrow p; C \rightarrow q; D \rightarrow s

(d) A \rightarrow q, r; B \rightarrow s; C \rightarrow p; D \rightarrow q

37. Match the description in Column-I with graph in Column-II for 'n' moles of an ideal gas at constant temperature & choose the correct option among the options given.

(Note: Each statement in column-I has only one match in column-II.)

Column-I		Column-II	
A.	P/V vs. P	p.	
B.	P/V vs. V	q.	



- (a) A \rightarrow r; B \rightarrow r; C \rightarrow q; D \rightarrow p
 (b) A \rightarrow s; B \rightarrow r; C \rightarrow p; D \rightarrow q
 (c) A \rightarrow s; B \rightarrow r; C \rightarrow q; D \rightarrow p
 (d) A \rightarrow r; B \rightarrow q; C \rightarrow p; D \rightarrow s

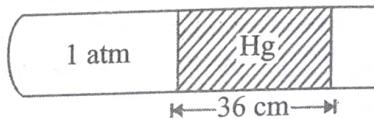
NUMERICAL TYPE QUESTIONS

38. A vertical cylinder containing some ideal gas is closed at both ends. A frictionless piston is fitted in the cylinder such that it divides the cylinder into two equal parts at 300K. Moles of gas in one part is double than that in other part. To what temperature (in Kelvin) the cylinder should be heated or cooled such that the volume of upper part becomes three times that of lower part?
39. 500 ml of a vessel contains an ideal gas saturated with water vapours at 3.2 atm and 47°C. Now the entire mass is transferred into vessel of 1800 ml capacity maintained at 87°C. The final pressure (in atm) becomes (vapour pressure of water at 47°C and 87°C are 0.2 atm and 0.6 atm, respectively) _____.
40. At 400 K, the root mean square (rms) speed of gas X (molecular mass = 40) is equal to the most probable speed of gas Y at 60K. The molecular mass of the gas Y is _____.
41. The molecular weight of a gas which diffuse through a porous plug at 1/6th of the speed of hydrogen under identical conditions, is

42. A gaseous mixture containing equal moles of H₂, O₂ and He is subjected to series of effusion steps. The composition (by moles) of effused mixture after 4 effusion steps is x : 1 : y respectively. Then, find the value of $\left(\frac{x}{y}\right)$.

43. Air is trapped in a horizontal glass tube by 40cm mercury column as shown below:

If the tube is held vertical keeping the open end up, length of air column shrink to 19cm. Length in cm by which the mercury column shifts down is _____.

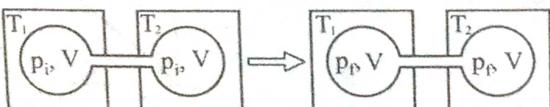


44. An iron meteorite was analysed for its isotopic argon content. The amount of Ar³⁶ was 1.911 mm³ (STP) per kg of meteorite. If each Ar³⁶ atom had been formed by a single cosmic event, then how many such events must there have been per kg of meteorite? If the answer is X, then the value of X/10¹⁶ is (R = 8.4 J/K-mol, N_A = 6.0 × 10²³)
45. A vessel of volume 3.0 L contains ideal gas at the temperature 0°C. After a portion of the gas has been let out, the pressure in the vessel decreases by 0.8 atm (the temperature remaining constant). The gas density under the normal condition (0°C and 1 atm) is 1.25 g/L. The mass of released gas in (g) is
46. Two identical vessels are connected by a tube with a valve letting the gas to pass from one vessel into the other if the pressure difference $\Delta P \geq 2.0$ atm. Initially, there was a vacuum in one vessel while the other contained ideal gas at a temperature 300 K and pressure 4.0 atm. Then both vessels were heated to a temperature 600 K. Up to what value will be the pressure (in atm) in the first vessel (which had a vacuum initially) increase?

Exercise-4 (Past Years Questions)

JEE MAIN

1. Two closed bulbs of equal volume (V) containing an ideal gas initially at pressure p_i and temperature T₁ 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 T₂. The final pressure p_f is: (2016)



- (a) $p_i \left(\frac{T_1 T_2}{T_1 + T_2} \right)$ (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) $2p_i \left(\frac{T_1 T_2}{T_1 + T_2} \right)$

2. The volume of gas A is twice that of gas B. The compressibility factor of gas A is thrice that of gas B at same temperature. The pressure of gases for equal moles are (2019)
 (a) $3P_A = 2P_B$ (b) $2P_A = 3P_B$
 (c) $P_A = 3P_B$ (d) $P_A = 2P_B$

3. 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 1000K. Given: R is the gas constant in $\text{JK}^{-1} \text{ mol}^{-1}$, x is

$$(a) \frac{2R}{4+R} \quad (b) \frac{2R}{4-R}$$

$$(c) \frac{4+R}{2R} \quad (d) \frac{4-R}{2R}$$

4. Consider the van der Waals constants, a and b, for the following gases:

Gas	Ar	Ne	Kr	Xe
a/(atm $\text{dm}^6 \text{ mol}^{-2}$)	1.3	0.2	5.1	4.1
b/($10^{-2} \text{ dm}^3 \text{ mol}^{-1}$)	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

5. 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

$$P = \frac{RT}{V-b} \text{ at } T.$$

Here, b is the van der Waals constant, which gas will exhibit steepest increase in the plot of Z(compression factor) vs p?

- (a) Ne (b) Ar
(c) Xe (d) Kr

6. Consider the following table:

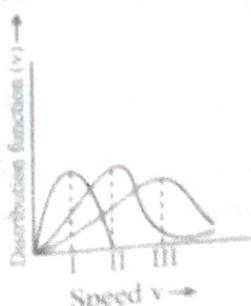
Gas	a/(k pa $\text{dm}^6 \text{ mol}^{-10}$)	b/($\text{dm}^3 \text{ mol}^{-1}$)
A	642.32	0.05192
B	155.21	0.04136
C	431.91	0.05196
D	155.21	0.4382

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.

7. Points I, II and III in the following plot respectively correspond to

(V_{mp} : most probable velocity)



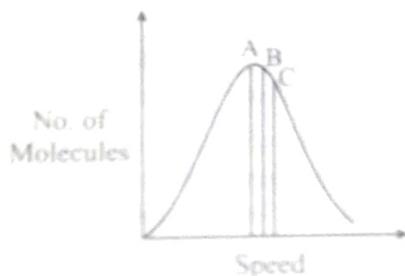
- (a) V_{mp} of N₂ (300K); V_{mp} of H₂ (300K); V_{mp} of O₂ (400K)
(b) V_{mp} of H₂ (300K); V_{mp} of N₂ (300K); V_{mp} of O₂ (400K)
(c) V_{mp} of O₂ (400K); V_{mp} of N₂ (300K); V_{mp} of H₂ (300K)
(d) V_{mp} of N₂ (300K); V_{mp} of O₂ (400K); V_{mp} of H₂ (300K)

8. The noble gas that does NOT occur in the atmosphere is:

- (a) He (b) Rn
(c) Ne (d) Kr

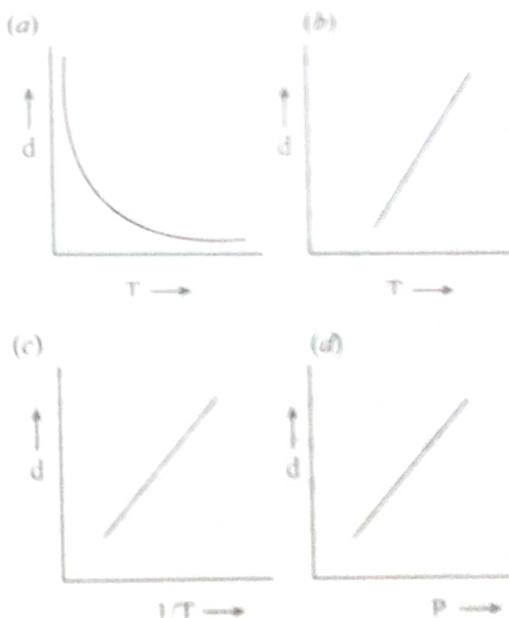
9. Identify the correct of A, B and C in the following graph from the options below:

Root mean square speed (V_{rms}); most probable speed (V_{mp}); Average speed (V_{av})



- (a) A - V_{mp} , B - V_{rms} , C - V_{av}
(b) A - V_{rms} , B - V_{mp} , C - V_{av}
(c) A - V_{av} , B - V_{rms} , C - V_{mp}
(d) A - V_{mp} , B - V_{av} , C - V_{rms}

10. Which one of the following graphs is not correct for ideal gas?



d = Density, P = Pressure, T = Temperature

11. A mixture of one mole each of H₂, He and O₂ each are enclosed in a cylinder of volume V at temperature T. If the partial pressure of H₂ is 2 atm, the total pressure of the gases in the cylinder is

- (a) 14 atm (b) 38 atm
(c) 22 atm (d) 6 atm

12. A spherical balloon of radius 3 cm containing helium gas has a pressure of 48×10^{-3} bar. At the same temperature, the pressure, of a spherical balloon of radius 12 cm containing the same amount of gas will be _____ $\times 10^{-6}$ bar. (2020)

13. An empty LPG cylinder weighs 14.8kg. When full, it weighs 29.0kg and shows a pressure of 3.47 atm. In the course of use at ambient temperature, the mass of the cylinder is reduced to 23.0kg. The final pressure inside the cylinder is _____ atm (Nearest integer)
(Assume LPG to be an ideal gas) (2021)

14. When 5.1g of solid NH_4HS is introduced into a two litre evacuated flask at 27°C , 20% of the solid decomposes into gaseous ammonia and hydrogen sulphide. The K_p for the reaction at 27°C is $x \times 10^{-2}$.
The value of x is _____ (Integer answer)
[Given: $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$] (2021)

15. An LPG cylinder contains gas at a pressure of 300kPa at 27°C . The cylinder can withstand the pressure of 1.2×10^6 Pa. The room in which the cylinder is kept catches fire. The minimum temperature at which the bursting of cylinder will take place is _____ $^\circ\text{C}$. (Nearest integer) (2021)

16. A home owner uses $4.00 \times 10^3 \text{ m}^3$ of methane (CH_4) gas, (assume CH_4 is an ideal gas) in a year to heat his home. Under the pressure of 1.0 atm and 300 K, mass of gas used is $x \times 10^5$ g. The value of x is _____ (Nearest integer)
(Given: $R = 0.083 \text{ L atm K}^{-1} \text{ mol}^{-1}$) (2021)

17. At 300 K, a sample of 3.0 g of gas A occupies the same volume as 0.2 g of hydrogen at 200 K at the same pressure. The molar mass of gas A is _____ g mol^{-1} (nearest integer). Assume that the behaviour of gases as ideal. (Given: The molar mass of hydrogen (H_2) gas is 2.0 g mol^{-1}) (2021)

18. A rigid nitrogen tank stored inside a laboratory has a pressure of 30 atm at 06:00 am when the temperature is 27°C . At 03:00 pm, when the temperature is 45°C , the pressure in the tank will be _____ atm. [nearest integer] (2022)

19. A sealed flask with a capacity of 2 dm³ contains 11 g of propane gas. The flask is so weak that it will burst if the pressure becomes 2 MPa. The minimum temperature at which the flask will burst is _____ $^\circ\text{C}$. [Nearest integer]
(Given: $R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$. Atomic masses of C and H are 12u and lu respectively.) (Assume that propane behaves as an ideal gas.) (2022)

20. A mixture of hydrogen and oxygen contains 40% hydrogen by mass when the pressure is 2.2 bar. The partial pressure of hydrogen is _____ bar. (Nearest Integer) (2022)

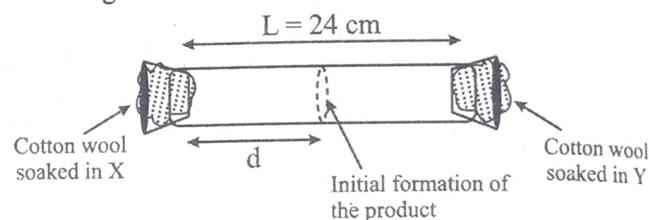
21. For a real gas at 25°C temperature and high pressure (99 bar), the value of compressibility factor is 2, so the value of Vander Waal's constant 'b' should be _____ $\times 10^{-2} \text{ L mol}^{-1}$ (Nearest integer)
(Given: $R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$) (2022)

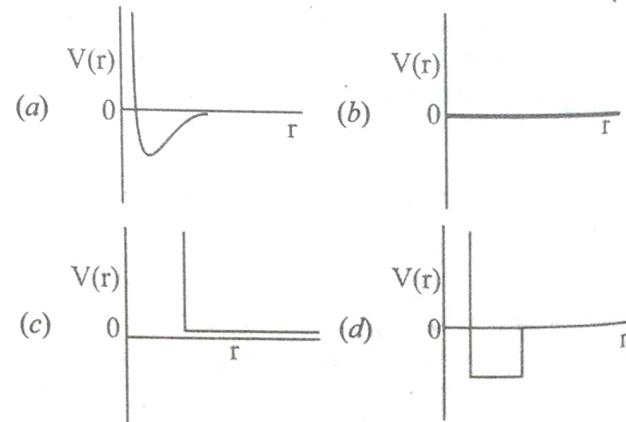
JEE ADVANCED

22. The atomic masses of He and Ne are 4 and 20 a.m.u., respectively. The value of the de Broglie wavelength of He gas at -73°C is "M" times that of the de Broglie wavelength of Ne at 727°C . M is _____. (2013)

Paragraph for questions 23 and 24

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 simultaneously placed at the ends of a tube of length $L = 24 \text{ cm}$, as shown in the figure. The tube is filled with an inert gas at 1 atmosphere pressure and a temperature of 300 K . Vapours of X and Y react to form a product which is first observed at a distance $d \text{ cm}$ from the plug soaked in X. Take X and Y to have equal molecular diameters and assume ideal behaviour for the inert gas and the two vapours.





27. 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 (2016)

28. 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 _____. (2018)

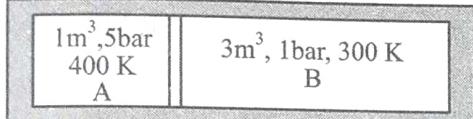


Figure 1

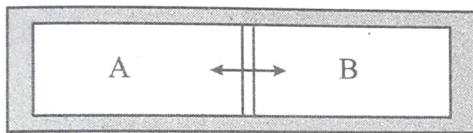
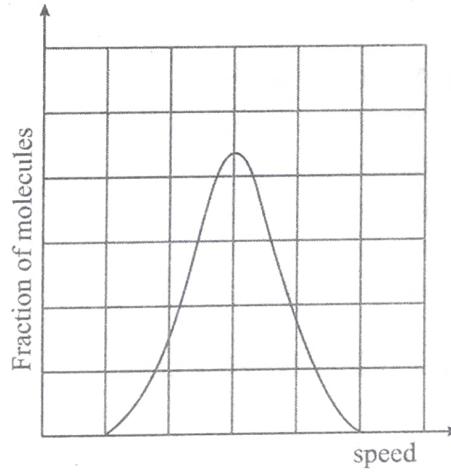


Figure 2

29. Which of the following statement(s) is (are) correct regarding the root mean square speed (U_{rms}) and average translational kinetic energy (ε_{av}) of a molecule in a gas at equilibrium? (2019)

- (a) U_{rms} is doubled when its temperature is increased four times.
- (b) ε_{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) ε_{av} is doubled when its temperature is increased four times.

30. If the distribution of molecular speeds of a gas is as per the figure shown below, then the ratio of the most probable, the average and the roots mean square speeds, respectively, is _____ (2020)



- (a) 1:1:1
- (b) 1:1:1.224
- (c) 1:1.128:1.224
- (d) 1:1.128:1

ANSWER KEY

CONCEPT APPLICATION

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (a) | 2. (b) | 3. (a) | 4. (d) | 5. (d) | 6. (a) | 7. (a) | 8. (d) | 9. (c) | 10. (a) |
| 11. (a) | 12. (b) | 13. (b) | 14. (d) | 15. (b) | 16. (b) | 17. (b) | 18. (a) | 19. (b) | 20. (c) |
| 21. (d) | 22. (c) | | | | | | | | |

EXERCISE-1 (TOPICWISE)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c) | 2. (d) | 3. (a) | 4. (a) | 5. (d) | 6. (c) | 7. (a) | 8. (b) | 9. (b) | 10. (b) |
| 11. (d) | 12. (b) | 13. (a) | 14. (c) | 15. (d) | 16. (b) | 17. (c) | 18. (c) | 19. (d) | 20. (c) |
| 21. (c) | 22. (a) | 23. (a) | 24. (d) | 25. (b) | 26. (b) | 27. (d) | 28. (a) | 29. (a) | 30. (d) |
| 31. (c) | 32. (a) | 33. (d) | 34. (a) | 35. (d) | 36. (d) | 37. (a) | 38. (c) | 39. (a) | 40. (a) |
| 41. (b) | 42. (c) | 43. (d) | 44. (b) | 45. (c) | 46. (b) | 47. (b) | 48. (a) | | |

EXERCISE-2 (LEARNING PLUS)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c) | 2. (d) | 3. (d) | 4. (b) | 5. (b) | 6. (c) | 7. (c) | 8. (c) | 9. (b) | 10. (d) |
| 11. (d) | 12. (d) | 13. (b) | 14. (c) | 15. (b) | 16. (d) | 17. (a) | 18. (d) | 19. (b) | 20. (b) |
| 21. (c) | 22. (a) | 23. (c) | 24. (a) | 25. (c) | 26. (b) | 27. (a) | 28. (a) | 29. (c) | 30. (a) |
| 31. (a) | 32. (c) | 33. (b) | 34. (d) | 35. (c) | 36. (b) | 37. (b) | 38. (b) | 39. (c) | 40. (a) |
| 41. (c) | 42. (c) | 43. (b) | 44. (a) | 45. (b) | 46. (a) | 47. (a) | 48. (a) | 49. (b) | |

EXERCISE-3 (JEE ADVANCED LEVEL)

- | | | | | | | | | | |
|-------------|-----------|-------------|-------------|-----------|--------------|-----------|--------------|---------------|-----------|
| 1. (a,b) | 2. (a,c) | 3. (a,d) | 4. (b,d) | 5. (b,d) | 6. (a,b,c,d) | 7. (d) | 8. (a,b,c,d) | 9. (a,d) | 10. (c,d) |
| 11. (a,d) | 12. (a,d) | 13. (a,b,d) | 14. (a,b,c) | 15. (a,c) | 16. (b,c) | 17. (a,d) | 18. (a,d) | 19. (a,b,c,d) | 20. (c) |
| 21. (a,b,d) | 22. (d) | 23. (c) | 24. (b) | 25. (c) | 26. (d) | 27. (d) | 28. (b) | 29. (a) | 30. (b,d) |
| 31. (a,c,d) | 32. (a,b) | 33. (a) | 34. (b) | 35. (c) | 36. (d) | 37. (c) | 38. [90] | 39. [0001] | 40. [4] |
| 41. [72] | 42. [4] | 43. [10] | 44. [5] | 45. [3] | 46. [3] | | | | |

EXERCISE-4 (PAST YEAR QUESTIONS)

JEE Main

- | | | | | | | | | | |
|----------|-----------|---------|---------|-----------|----------|----------|----------|------------|---------|
| 1. (c) | 2. (b) | 3. (d) | 4. (a) | 5. (c) | 6. (c) | 7. (d) | 8. (b) | 9. (d) | 10. (b) |
| 11. (d) | 12. [750] | 13. [2] | 14. (6) | 15. [927] | 16. [26] | 17. [45] | 18. [32] | 19. [1655] | 20. [2] |
| 21. [25] | | | | | | | | | |

JEE Advanced

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|------------|-------------|---------|--|
| 22. [5] | 23. (c) | 24. (d) | 25. [9] | 26. (c) | 27. [4] | 28. [2.22] | 29. (a,b,c) | 30. (b) | |
|---------|---------|---------|---------|---------|---------|------------|-------------|---------|--|

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