

# Engineering Materials

## Mechanical Engineering



Comprehensive Theory *with* Solved Examples

# Civil Services Examination



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**Engineering Materials**

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# Chemical Bonding

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## 2.1 Basic Laws of Chemistry

### Atomic mass unit

- It is defined as a mass exactly equal to one-twelfth the mass of one carbon - 12 atom.

$$1 \text{ amu} = 1.66056 \times 10^{-24} \text{g}$$

### Mole

- The mole is unit of measurement for mass of substance in the International System of Units (SI).
- "One mole is the amount of a substance that contains as many particles or entities as there are atoms in exactly 12 g (or 0.012 kg) of the  $^{12}\text{C}$  isotope".

$$1 \text{ mole} = 6.023 \times 10^{23} \text{ atoms}$$

- The mass of one mole of a substance in grams is called molar mass.

### Avogadro number

- In 1811, Avogadro proposed that equal volumes of gases at the same temperature and pressure should contain equal number of molecules. The number of entities or atoms in a mole is termed as Avogadro number, denoted by  $N_A$ .

$$N_A = 6.023 \times 10^{23} \text{ atoms/mol}$$

### Law of conservation of mass

Antoine Lavoisier in 1789 stated that:

- "Matter can neither be created nor be destroyed by any chemical reactions or physical transformations."
- He performed careful experimental studies for chemical reactions for reaching to the above conclusion.
- According to this in a closed system for chemical reaction, the mass of the products must be equal to the mass of the reactants.

### Law of Definite Proportions

A French chemist, Joseph Proust stated that:

- "A given compound always consist exactly the fixed and same proportion of elements by mass." It is sometimes also referred as Law of definite composition.

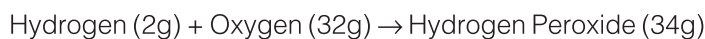
- An example is  $\text{CO}_2$ . This gas is produced from a variety of reactions, often by the burning of materials, wood or fossil fuels. The structure of the gas always consists of one atom of carbon and two atoms of oxygen.

### Law of Multiple Proportions

John Dalton proposed this law in 1803, he states that:

- When two elements combine to form more than one compound, the mass of one element that combines with a fixed mass of the other element, will always be in a ratio of whole numbers.

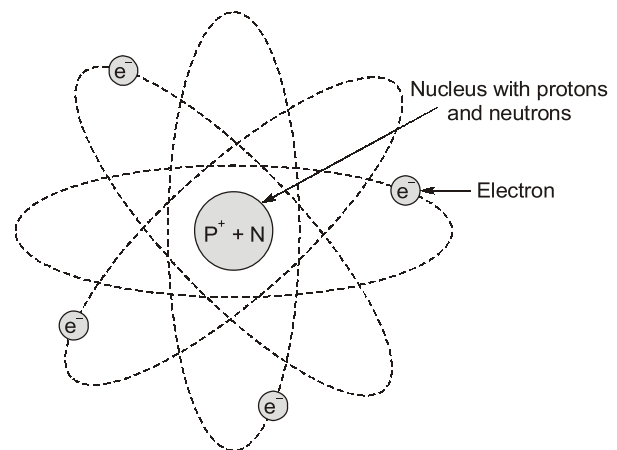
**Example:** Hydrogen combines with oxygen to form two compounds, named as water and hydrogen peroxide.



Here, the masses of oxygen (16 g and 32 g) which combine with a fixed mass of hydrogen (2g) bear a simple ratio, i.e. 16:32 or 1:2.

## 2.2 Fundamental Concepts

- A substance which can not be decomposed into other substances is known as element. The smaller particle of an element which takes part in chemical reaction is known as an atom.
- An atom consists of a very small nucleus at its centre which is composed of protons and neutrons. The nucleus is encircled by moving electrons.
- The electron is a negatively charged particle and it has mass of about  $1/1836$  times that of the neutron. Proton has positive charge while a neutron is an uncharged particle having approximately mass equal to the proton.
- Each chemical element is characterized by the number of protons in the nucleus or the **atomic number (Z)**. For an electrically neutral or complete atom, the atomic number also equals the number of electrons.
- The **atomic mass (A)** of a specific atom may be expressed as the sum of the masses of protons and neutrons within the nucleus.
- The atomic weight of an element corresponds to the weighted average of the atomic masses of the atom's naturally occurring isotopes. The **atomic mass unit (amu)** may be used for computations of atomic weight.



**Fig. Concept of an atom**

#### NOTE



A scale has been established whereby 1 amu is defined as  $1/12$  of the atomic mass of the most common isotope of carbon, (carbon -12,  $A = 12.00000$ ). Within this scheme, the masses of protons and neutrons are slightly greater than unity and

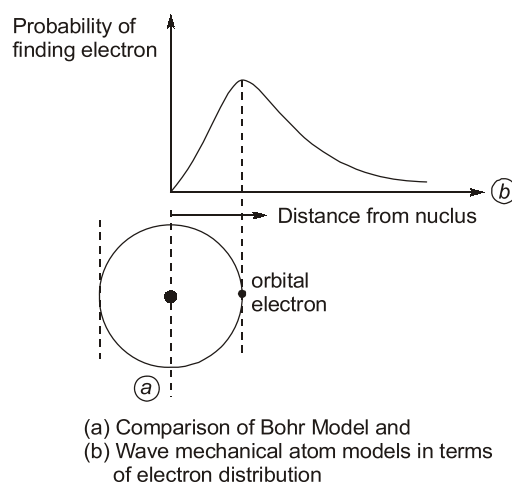
$$A \cong Z + N$$

where N = Number of neutrons.

- **Isotopes:** Isotopes have different atomic weights but they have same atomic number. Isotopes are chemically inseparable as they possess identical chemical properties. Isotopes of the same element have the same atomic number and the same charge on the nucleus.  ${}_1\text{H}^1$ ,  ${}_1\text{H}^2$  and  ${}_1\text{H}^3$  are isotopes of hydrogen while  ${}_{17}\text{Cl}^{37}$  and  ${}_{17}\text{Cl}^{35}$  are isotopes of chlorine.
- **Isobars:** Atoms which have same mass number (atomic weight or number of protons and neutrons) but they differ in atomic number are called isobars. Isobars are atoms of different chemical elements but they have same atomic mass number.  $\text{Ar}^{40}$  and  $\text{Ca}^{40}$  are isobars having same atomic mass number of 40 but they have varying number of protons (atomic number) and neutrons.
- **Isotones:** Atoms whose nuclei have the same number of neutrons but different number of protons. Thus, chlorine-37 and potassium-39 are isotones as their nuclei contain 17 and 19 protons respectively but same 20 neutrons. Isotones have different atomic number and different chemical properties.

## 2.3 Electrons in Atoms

- The electrons, protons and neutrons in atoms of various elements are identical. Thus, it follows that electrons, protons and neutrons are the fundamental particles of the universe. If it is so, then why do various elements behave differently? This is because of the difference in the number and arrangement of the electrons, protons and neutrons of which each atom is composed
- All the electrons of an atom do not move in the same orbit. The electrons in an atom are arranged in different orbits or shells.



### Remember



In general a shell (or orbit) can contain a maximum of  $2n^2$  electrons, where  $n$  is the number of shell (or orbit). But according to this rule, there is an exception, the outermost orbit in an atom can not accommodate more than eight electrons. The electrons present in the outermost shell (or orbit) are called valence electrons. These valence electrons participate in bonding.

- All the elements have been arranged in a periodic table according to the electronic arrangements in their atoms. The element placed in one vertical column have very similar properties.

## 2.4 The Periodic Table

- All the elements have been classified according to electron configuration in the **periodic table**. Here, the elements are situated, with increasing atomic number, in seven horizontal rows called periods.
- The arrangement is such that all elements arrayed in a given column or group have similar valence electron structures, as well as chemical and physical properties. These properties change gradually, moving horizontally across each period and vertically down each column.
- The elements positioned in Group 0, the rightmost group, are the inert gases, which have filled electron shells and stable electron configurations. Group VIIA and VIA elements are one and two electrons deficient, respectively, from having stable structures.
- The Group VIIA elements (F, Cl, Br, I and At) are sometimes termed the halogens. The alkali and the alkaline earth metals (Li, Na, K, Be, Mg, Ca etc.) are labeled as Groups IA and IIA, having, respectively, one and two electrons in excess of stable structures.



- The elements in the three long periods, Groups IIIB through IIB, are termed as the transition metals, which have partially filled *d* electron states and in some cases one or two electrons in the next higher energy shell.
- Groups IIIA, IVA and VA (B, Si, Ge, As etc.) display characteristics that are intermediate between the metals and nonmetals by virtue of their valence electron structures.
- As may be noted from the periodic table, most of the elements really come under the metal classification. These are sometimes termed **electropositive** elements, indicating that they are capable of giving up their few valence electrons to become positively charged ions.
- Furthermore, the elements situated on the right-hand side of the table are **electronegative**; that is, they readily accept electrons to form negatively charged ions or sometimes they share electrons with other atoms.
- Atoms are more likely to accept electrons if their outer shells are almost full and if they are less “shielded” from (i.e., closer to) the nucleus.

IA		Key																0	
1 H 1.0080																	2 He 4.0026		
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180		
11 Na 22.990	12 Mg 24.305	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.054	17 Cl 35.453	18 Ar 39.948		
19 K 39.099	20 Ca 40.08	21 Sc 44.956	22 Ti 47.87	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.69	29 Cu 63.54	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.922	34 Se 75.96	35 Br 79.904	36 Kr 83.80		
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 105.4	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.30		
55 Cs 132.91	56 Ba 137.34	Rare earth series	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.2	76 Os 190.23	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.19	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)		
87 Fr (223)	88 Ra (225)	Actinide series	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hd (227)	109 Mt (268)	110 Ds (281)										
Rare earth series		57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97			
Actinide series		89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)			

**Fig.** *The periodic table of the elements. The numbers in parentheses are the atomic weights of the most stable or common isotopes.*

## 2.5 Comparison of Alpha ( $\alpha$ ), Beta ( $\beta$ ) and Gamma ( $\gamma$ ) Rays

### 2.5.1 Alpha Rays

- Alpha rays or alpha particles are the positively charged particles.
- These particles have highly active & energetic helium nucleus which contains two protons and two neutrons.
- Alpha particles have the least penetration power but the greatest ionization power.
- They cannot penetrate the skin but this does not mean that they are not dangerous. Since they have a great ionization power, so if they get into the body they can cause serious damage.

### 2.5.2 Beta Rays

- Beta particles are extremely energetic electrons that are liberated from the inner nucleus.

- They are negatively charged and have a negligible mass. On the emission of a beta particle, a neutron in the nucleus splits into a proton and an electron.
- Hence, it is the electron that is emitted by the nucleus at a rapid pace.
- Beta particles have a higher penetration power and lower ionization power when compared to alpha particles and can travel through the skin with ease.

### 2.5.3 Gamma Rays

- The waves arising from the high-frequency end of the electromagnetic spectrum that has no mass are known as gamma rays.
- They hold the highest power of penetration. They are the most penetrating but least ionizing and very difficult to resist them from entering the body.
- The Gamma rays carry a large amount of energy and can also travel via thick concrete and thin lead.

### 2.5.4 Properties of Alpha, Beta and Gamma rays

**Table (a): Characteristics of Alpha, Beta and Gamma Rays**

Characteristic	Alpha ( $\alpha$ )	Beta ( $\beta$ )	Gamma ( $\gamma$ )
Emission of	$2P + 2N$	1 electron – High K.E.	Photon - very high frequency electromagnetic radiation
Changes from	Uranium to Plutonium	Radium to Polonium	No change
Charge (C)	+2	-1	0
Mass (amu)	4	1/1850	0
Speed km/s	15000	300000	300000
% of speed of light	5%	Close to 100%	100%
K.E.	3-6 MeV	5 MeV to 1 MeV	100 keV less than 10 MeV
Penetration Power	Low - Large mass & charge -can be stopped by a thin sheet of paper	Moderate - Medium mass and charge- can be stopped by a few mm thick metal	Very high - no mass, no charge, can be stopped only by a very thick cement or steel block
Ionization power	Very high - Large charge	Moderate - Low charge	Low - No charge

## 2.6 Quantum Number

Quantum numbers are used to find the electron configuration of an atom and the probable location, energy level, other characteristics like ionization and atomic radius of an electron in the atom. Quantum numbers are also applied to check the movement and orbit of each and every electron within an atom. Quantum numbers are of four types:

### 2.6.1 The principal quantum number ( $n$ )

- Principal quantum number of any electron in an atom stands for the main energy level or shell to which an electron belongs. Energy of an electron and its average distance from nucleus depends upon principal quantum number. Increasing the value of 'n' results the distance of electron from its nucleus and its energy also start increasing and stability decreases.
- Shells are specified by a principal quantum number  $n$ , which may require an integral value beginning with unity; sometimes these shells are designated by the letters  $K, L, M, N, O$  and so on, which correspond, respectively to  $n = 1, 2, 3, 4, 5, \dots$ , shown in Table (b).

Table (b): Electron states in some of electron shells &amp; subshells

Principal quantum Number (n)	Shell Designation	Subshells	No. of States	Number of Electrons	
				Per Subshell	Per Shell
1	K	s	1	2	2
2	L	s	1	2	8
		p	3	6	
3	M	s	1	2	18
		p	3	6	
		d	5	10	
4	N	s	1	2	32
		p	3	6	
		d	5	10	
		f	7	14	

### 2.6.2 The orbital angular momentum/ azimuthal quantum number ( $l$ ):

$l$  is the second quantum number which represents the sub-shell, denoted by letters  $s, p, d$  or  $f$ ; it is related to the shape of the sub-shell of electron. The number of these sub-shells is defined by the magnitude of  $n$ . It specifies the number of units of angular momentum connected with an electron in a given orbit and finds the shape of the orbit and the energy of the sublevel.

**Note:** For any value of  $n$  quantum number  $l$  can have any integral value from 0 to  $n - 1$ . Hence we can have  $4d, 5f, 2p$  and  $2s$  electrons whereas  $1p, 2d, 3f$  subshell electrons do not exist.

**Example:** For

$$n = 1, \quad l = 0$$

$$n = 2, \quad l = 0, 1$$

$$n = 3, \quad l = 0, 1, 2$$

We have observed that  $n$  is the principal quantum number that defines principal shell.  $l$  provides the possible orbital sub-shells. The sub-shells in the main shell are  $s, p, d, f, g$  and  $h$  with quantum number  $l = 0, 1, 2, 3, 4$  and  $5$  respectively. We can demonstrate it as follows:

For  $n = 1, l = 0$ , the electron is said to be in  $1s$  sub-shell

$n = 2, l = 1$ , the electron is said to be in  $2p$  sub-shell

$n = 2, l = 0$ , the electron is said to be in  $2s$  sub-shell

### 2.6.3 The magnetic quantum number ( $m_l$ )

The third quantum number  $m_l$  is used to determine the number of orbitals for each subshell. For an 's' subshell, there is a single energy state, whereas for  $p, d$  and  $f$  subshells three, five and seven states exist, respectively (Table (b)).

- The value of  $m_l$  varies between  $+l$  to  $-l$  with zero and as we know that  $m_l$  have  $(2l + 1)$  values for a given  $l$ . For any specific value of  $l$ , an electron may have integral values of its inner quantum number  $m_l$  from  $+l$  through 0 to  $-l$ . Thus for  $l = 2$ ,  $m_l$  can take on the values  $+2, +1, 0, -1$  and  $-2$ . Thus we get

$$\text{For } l = 0, \quad m_l = 0$$

$$l = 1, \quad m_l = -1, 0, 1$$

$$l = 2, \quad m_l = -2, -1, 0, +1, +2$$

### 2.6.4 The Magnetic Spin Quantum Number ( $m_s$ )

- The electron can spin either in the clockwise or anticlockwise direction and values of spin can be  $+\frac{1}{2}$  and  $-\frac{1}{2}$ , depending upon the direction of spin.  $m_s$  is used to represent the spin of an electron.
- We need to remember that the three quantum numbers  $n$ ,  $l$  and  $m_l$  can have the same values for two electrons in an atom and that these two electrons will have their spins oriented in opposite directions.

#### Example 2.1

Write the four quantum numbers for each of the electrons in the outermost shell of a boron atom?

**Solution:**

For boron,  $Z = 5$ , obviously, it has 5 electrons in it. Out of these 2 are in  $K$  shell and remaining 3 in the  $L$ -shell of the 3 electrons in the  $L$  shell 2 are  $s$  electrons and 1 is a  $p$  electron. Hence the quantum numbers of the electrons in the  $L$ -shell are as follows:

$n$	$l$	$m_l$	$m_s$
2	0	0	$+\frac{1}{2}$
2	0	0	$-\frac{1}{2}$
2	1	0	$\pm\frac{1}{2}$

## 2.7 Electron Affinity

- This is the amount of energy released, when an electron is added by a neutral atom.
- The energy required to transfer an electron from one atom to another atom is the difference between the ionization energy  $I_1$  and the electronic affinity  $E_{12}$  of the respective atoms,  $I_1 - E_{12}$ .
- Chlorine has the highest electron affinity.

#### NOTE



1. Electron affinity decreases with increase in atomic radius.
2. Sign given to electron affinity is negative because energy is released.
3. When force of attraction decreases electron affinity decreases.

## 2.8 Electronegativity

- Electronegativity is a chemical property that defines the tendency of an atom to attract a bonding pair of electrons towards itself. When an element strongly attracts electrons then it means that element has high electronegativity.
- Electronegativity is a measure of the ability of an atom in a chemical compound to attract shared electrons to it.
- The higher the associated electronegativity number, the more an element or compound attracts electrons towards it.
- Caesium is the least electronegative element in the periodic table ( $= 0.79$ ), while fluorine is most electronegative ( $= 3.98$ ). Electro-positivity is opposite of electronegativity that is a measure of an element's ability to donate electrons.

## 2.9 Pauli's Exclusion Principle:

He stated that, "No two electrons within the same atom can have the same numerical values for their set of four quantum numbers." This principle states that each electron state can hold no more than two electrons, which must have opposite spins. Thus,  $s$ ,  $p$ ,  $d$  and  $f$  sub-shells may each accommodate a total of 2, 6, 10 and 14 electrons respectively.

- Two electrons in an atom cannot be in the same quantum state i.e., all the four quantum numbers can't be same.
- Of the four quantum numbers at least one must be different for the two electrons. For example  $n$ ,  $l$ ,  $m_l$  may be the same for the two electrons in an atom but the fourth quantum number  $m_s$  must be different for the two electrons. If  $m_s$  have  $+\frac{1}{2}$  for one electron then it must have  $-\frac{1}{2}$  for the other.
- Maximum number of electrons for a shell will be  $= 2n^2$  where  $n$  is the principal quantum number.

## 2.10 Auf-bau Principle

It is used to predict which electron shells will be filled first in an atom. According to this

- Electron fill up the lowest available energy level first before beginning to fill the next shell or this states "Electrons are filled in the orbit of atoms in increasing energy order." That means lower energy level orbits will be filled first then electrons enters into higher energy order or level.
- For an atom to be in ground state the orbital of higher energy can be filled only when all the lower energy orbital are completely filled up. Order of increasing energy in orbital:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s \dots\dots$$

**Note:** Electrons follow  $(n + l)$  rule to fill the orbital. The orbital having smaller  $(n + l)$  value will be filled first.

### Example 2.2

Electron will be filled first in which of these two orbits: 5f or 6d?

**Solution:**

$$\text{For } 5f: (n + l) = 5 + 3 = 8$$

$$\text{For } 6d: (n + l) = 6 + 2 = 8$$

So in this case when  $(n + l)$  have same values then the electron will be filled first in the orbit which has smaller principle quantum number so 5f will be filled first.

## 2.11 Hund's Rule

Hund's Rule tells us about how the electrons in an atom should be placed into degenerate orbits.

- It demonstrates that, electrons should be placed into separate orbits before going into the same orbital twice.
- For filling up oxygen atom electrons in three p orbital, we first distribute them one in each orbit of p then we double the first orbit.

Every orbital in a sublevel is singly occupied before any orbital is doubly occupied. All of the electrons in singly occupied orbits have the same spin to maximize total spin.

### Example 2.3

How many unpaired electrons are there in a chromium atom?

**Solution:**

Chromium (24) =  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$  (Normal case)

Actual configuration =  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$  (for Better stability),

There are 6 unpaired electrons.

## 2.12 Heisenberg Uncertainty Principle

Heisenberg in 1927 remarked that

- The wave representation of the particle implies some uncertainty  $\Delta x$  of the position  $x$  of the particle and a corresponding uncertainty  $\Delta p$  in specifying its momentum  $p$  simultaneously.
- He proposed the following relationship between uncertainties  $\Delta x$  and  $\Delta p$ :

$$\Delta x \cdot \Delta p \geq \left( \frac{h}{4\pi} \right)$$

Here  $\Delta x$  is uncertainty in position,  $\Delta p$  is uncertainty in momentum and Planck's constant

$$h = 6.6256 \times 10^{-34} \text{ J s.}$$

This is known as Heisenberg's uncertainty relation. This principle asserts that it is impossible to determine precisely both the position and momentum of a body in motion simultaneously.

## 2.13 Gay Lussac's Law of Gaseous Volumes

Gay Lussac in 1808 has observed that, when gases have chemical reactions, they do so in a simple ratio by volume. Provided all gases are at identical temperature and pressure.

**Example:**



2 vols.    1 vol.            2 vols.

2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of water.

## 2.14 Dalton's Atomic Theory

In 1808, Dalton published 'A New System of Chemical Philosophy' in which he stated that:

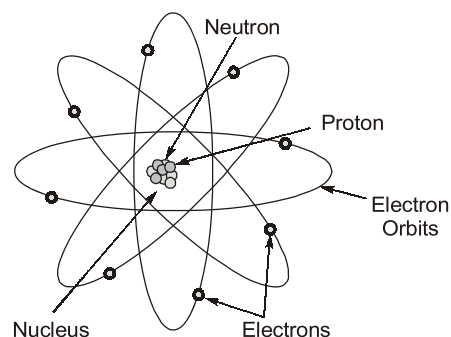
- Matter is made of very tiny particles called atoms.
- Atoms are indivisible structures.
- Atoms can neither be created nor destroyed.
- All atoms of a particular element are similar in all respects including identical mass, physical or their chemical properties.
- Atoms of different elements show different properties and they have different masses and different chemical properties.
- Compounds are formed when atoms of different elements combine in a fixed ratio.

## 2.15 Rutherford Model

Rutherford atomic model, also called solar or nuclear atom or planetary model of the atom, description of the structure of atoms proposed (1911) by the New Zealand-born physicist Ernest Rutherford.

On the basis of his famous alpha particle scattering experiment:

- The model described the atom as a dense, tiny, positively charged core called a nucleus, in which nearly all the mass is concentrated, around which the light negative elements, called electrons, propagate at some distance, similar to planets revolving around the Sun.



**Fig. Rutherford Model**

- Electrons being negatively charged and nucleus being a densely condensed mass of positively charged particles are held together by intense electrostatic force of attraction.
- This model failed in explaining atom stability and linear spectrum of atom.

## 2.16 Bohr Model

Bohr Model is a modification of the earlier Rutherford Model; so it is also called as the Rutherford-Bohr Model.

- Bohr modified this atomic structure model by describing that electrons have motion in fixed shells for which the angular momentum of moving electron is an integral multiple of  $\frac{h}{2\pi}$  and not anywhere in between and he also explained that each shell has a certain energy level.
- Bohr's model consists of a tiny nucleus (positively charged) surrounded by negative electrons revolving around the nucleus in orbits. Bohr found that electrons near to the nucleus have less energy and electron located away from the nucleus has more energy.
- The electrons in an atom shift from lower energy level to higher energy level by obtaining the required energy and an electron moves from higher energy level to lower energy level by losing energy. The amount of energy which an electron released or absorbed is the differences of the energies of the two orbits.

$$h\nu = E_2 - E_1$$

Where  $h$  is Planck's constant,  $E_1$  is the electron energy of lower orbit and  $E_2$  is the electron energy of higher orbit.

- Bohr's model of an atom failed to explain Zeeman Effect (effect of magnetic field on the spectra of atoms).
- It also failed to explain the Stark effect (effect of electric field on the spectra of atoms).
- Bohr model could not explain the uncertainty principle of Heisenberg.
- Bohr Theory has no explanation for elliptical orbits.

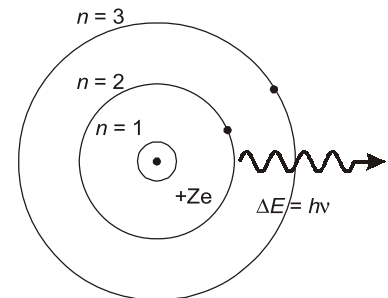


Fig. Bohr Model

## 2.17 Sommer Field's Model

According to Sommer field,

- The path of an electron around the nucleus is an ellipse with the nucleus at one of its foci.
- The velocity of the electron revolving in an elliptical orbit varies at different parts of the orbit. This causes the proportional variation in the mass of the moving electron.

To deal with these two variables, two quantum numbers are introduced

- The principal quantum number  $n$  of Bohr's theory, which determines the energy of the electrons.
- A new quantum number called orbital or azimuthal quantum number ( $l$ ) which has been introduced to characterise the angular momentum in an orbit i.e., it determines the orbital angular momentum of the electron. Its values vary from zero to  $(n - 1)$  in steps of unity.

## 2.18 De Broglie Wave Equation:

In 1924 de Broglie suggested that

- Particles in motion should exhibit properties characteristic of waves. He further proposed that certain basic formulae should apply both to waves and particles.



- The wavelength of such particles e.g., electron, proton, neutron etc. is given by the relation

$$\lambda = \frac{h}{mv} \quad \dots (i)$$

Where  $h$  is Planck's constant,  $m$  is mass of the particle and  $v$  is the velocity of the particle. De Broglie called these waves as matter waves.

Relation (i) gives the mathematical relationship between the momentum ( $p = mv$ ) of a particle which is a dynamical variable tendency of a corpuscle and the wavelength which is characteristic of the associated wave.

- The higher the energy of the electron, the greater will be its momentum  $mv$  and hence the smaller will be the wavelength of the wave function in terms of which its motion can be described.

## 2.19 Octet Rule

Gilbert N. Lewis formulated the "Octet rule" in 1916 which explains chemical combination between atoms known as electronic theory of chemical bonding. He stated that:

- Atoms will react to get in possibly the most stable state because a complete octet is very stable.
- Atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells.
- Atoms with greater stability have less energy, so a reaction that increases the stability of the atoms will release energy in the form of heat or light.

### NOTE



The noble gases rarely form compounds. They have the most stable configuration (full octet, no charge), so they have no reason to change their configuration. All other elements attempt to gain, lose or share electrons to achieve a noble gas configuration.

## 2.20 Boyle's Law (Pressure - Volume Relationship)

Robert Boyle developed relationship of a gas with pressure and volume around 1660 and is known as Boyle's Law. According to this-

"At constant temperature, the pressure of a fixed amount of gas varies inversely with its volume."

Mathematically, it can be expressed as

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

$$P = \frac{k_1}{V}$$

$k_1$  is the constant which is also known as Boyle's constant and the value of  $k_1$  depends upon the amount of the gas, temperature of the gas and the units in which  $P$  and  $V$  are expressed.

$$PV = k_1$$

It means that at constant temperature, product of pressure and volume of a fixed amount of gas is constant.

Suppose  $P_1$  and  $V_1$  are the initial pressure and volume of the given mass of gas. This gas now undergoes expansion at a fixed temperature and the pressure and volume changes to  $P_2$  and  $V_2$ . Now, According to Boyle's law:

$$P_1 V_1 = P_2 V_2 \quad (\text{at constant temperature})$$



## 2.21 Charles Law (Temperature - Volume Relationship)

Charles' law, which states that at constant pressure, the volume of a fixed mass of a gas is directly proportional to its absolute temperature. According to this:

- Volume of a gas increases on increasing temperature and decreases on cooling for a fixed mass of a gas at constant pressure.
- They found that for each degree rise in temperature, volume of a gas increases by  $\frac{1}{273.15}$  of the original volume of the gas at 0 °C.

Let volumes of the gas at 0 °C and at  $t$  °C are  $V_0$  and  $V_t$  respectively then,

$$V_t = V_0 + \left( \frac{t}{273.15} \right) V_0 \quad [\text{at constant } P]$$

$$\Rightarrow V_t = V_0 \left( 1 + \frac{t}{273.15} \right) = V_0 \left( \frac{273.15 + t}{273.15} \right)$$

At this stage, we define a new scale of temperature called the Kelvin temperature scale or Absolute temperature scale such that  $t$  °C on new scale is given by  $T = (273.15 + t)$  K and 0 °C will be given by  $T_0 = 273.15$  K. Thus 0°C on the Celsius scale is equal to 273.15 K at the absolute scale. Kelvin scale of temperature is also called Thermodynamic scale of temperature.

Now Let us assume

$$T_t = (273.15 + t) \text{ K and } T_0 = 273.15 \text{ K}$$

Then

$$V_t = V_0 \left( \frac{T_t}{T_0} \right)$$

Or,

$$\left( \frac{V_t}{V_0} \right) = \left( \frac{T_t}{T_0} \right)$$

We can write it as

$$\left( \frac{V_2}{V_1} \right) = \left( \frac{T_2}{T_1} \right)$$

$$\left( \frac{V_1}{T_1} \right) = \left( \frac{V_2}{T_2} \right)$$

$$\Rightarrow \frac{V}{T} = \text{constant} = k_2$$

Hence,

$$V = k_2 T$$

The value of  $k_2$  depends on the pressure of the gas, its amount and also on the unit of volume  $V$ .

OR

The volume of a gas varies directly with the temperature of the gas when the pressure of the gas is constant.

$$V \propto T \quad [\text{at constant } P]$$

$$\Rightarrow \frac{V}{T} = \text{constant} = k_2$$

**Note:** The lowest hypothetical or imaginary temperature at which gases are supposed to occupy zero volume is called Absolute zero temperature.