THE STRUCTURE OF ATOM

চিত্র অভিষেরন :

The physical and the chemical properties of elements and their compounds are essentially correlated with the structure of atoms. A systematic knowledge of the structure of atoms is, therefore, necessary for the study of modern inorganic chemistry. In fact, the knowledge of structure of atoms has made it possible for the subject of chemistry to be systematized in such a way that it is easier to understand and remember. The chemical reactions and the forces between atoms in molecules can be explained in terms of the structure of atoms. It will be noted that structure and properties of matters are essentially functions of electronic configurations of the atoms of elements.

The Atomic Theory   অণুপরমাণু

It may be mentioned that the idea that matter is constructed of ultimately indivisible particles is as old as science itself. The Greek philosopher, Democritus, is attributed to have originated the atomic concept of matter as opposed to the view of Aristotle that matter is continuous and that there is no limit of its subdivision. The latter view has been completely discarded and in 1803 John Dalton with the help of experiments placed the atomic hypothesis on a useful scientific basis and developed the concept of atomic weights which became the basis for the laws of chemical combinations. The quantitative concepts of atoms subsequently led to a considerable advancement of the science of chemistry both in the theoretical and practical fields. Among the experimental results and relationships supporting the atomic theory mention may be made of Gay-Lussac's law of combination of gases by volume, the law of multiple proportion of Dalton, Faraday's laws of electrolysis and Avogadro's hypothesis

pointing to the existence of molecules and well as atoms. Avogadro's Law provided a basis for the determination of molecular weights. It is the regular arrangement of atoms which gives many solids their crystalline shapes.

Avogadro Number

It may be pointed out that the actual number of molecules in a gram molecule or the number of atoms in a gram atom of any substance has been determined accurately in many different ways which are entirely independent of each other. This number, denoted by N, has a value 6.02×10^{23} molecules per mole (or atoms per gram atom) and is called Avogadro Number. It is a fundamental constant in science with many important applications. The best value for N, 6.023×10^{23}, has been obtained by averaging values from a number of different types of accurate measurements. With the help of Avogadro Number, the weight of a single atom or a molecule can be obtained by dividing the respective atomic or molecular weight by N. For instance, the weight of one single atom of hydrogen is $1.008/6.02 \times 10^{23} = 1.67 \times 10^{-24}$ gram; and the weight of a molecule of carbondioxide is equal to the molecular weight of CO_2 divided by N, i. e. $44.01/6.02 \times 10^{23} = 7.30 \times 10^{-23}$ gram.

A passing reference may be made regarding a notable modification of the atomic theory by Prout in 1815. According to Prout's hypothesis matter was made up of multiples of a fundamental substance which he suggested might be hydrogen. The idea of an ultimate particle in the form of hydrogen atom, of which all other atoms are made, has long been discarded and discredited by accurate determinations of atomic weights, but the idea certainly inspired the scientists for further speculations as regards the composition of matter.

Atoms as Carriers of Electricity

Atoms act as carriers of electricity when an electric current is passed through a salt solution. Faraday discovered that the equivalent weights of different substances were liberated at the electrodes by the passage of the same quantity of electricity. It can be concluded that Faraday's Laws of electrolysis would not have been valid until and unless matter (electrolytes in solution) would have been

made up of electrically charged atoms or ions capable of free movement in solution between two electrodes by the passage of electricity. Accurate determinations have shown that the liberation of 1 gram equivalent of any substance requires the passage of 96,493 absolute coulombs of electricity, and this quantity, represented by F, is known as a *Faraday*. Thus the quantity of electricity which will deposit one g. atom of a monovalent element is called the "*Faraday*". (A coulomb is the quantity of electric charge passing a point in an electrical circuit in one second with one ampere current.)

An obvious deduction from Faraday's laws is that 1 g. equivalent of any ion carries the same amount of electric charge, i. e., F coulombs. Since 1 g. atom contains N number of atoms, it can be deduced that N atoms of a univalent substance carry F coulombs. Similarly, N number of atoms of a bivalent, trivalent and n-valent substances will carry 2F, 3F and nF coulombs respectively. Hence it can be generalized that 1 single atom of an element is associated with nF/N coulombs of electricity where n is the charge of the ion. Again, since n is an integer, it follows that the charge of electricity carried by any single ion is a multiple of the fundamental quantity or smallest unit represented by F/N. This is the unit of electric charge for which Stoney in 1891 proposed the name *electron*. It was not clear whether these units of electricity carried by atoms are positive or negative or whether electrons of both signs exist and form compounds with the originally neutral atoms. The value of

$$\frac{F}{N} = \frac{96.500}{6.023 \times 10^{23}} \text{ coulombs} = 1.60 \times 10^{-19} \text{ coulombs} = 1.60 \times 10^{-20} \text{ emu}$$

(electromagnetic unit), or $= 4.8024 \times 10^{-10}$ esu (electrostatic unit). Hence the charge $e = \frac{F}{N}$ is the smallest charge of an ion. Thus the charge of an ion of Na^+ is e, that of bivalent Mg^{+2} is $2e$, and that of trivalent Al^{+3} is $3e$.

Passage of Electricity Through Gases

Electricity does not pass under normal condition between electrodes. Even if it does, it does in the form of a sudden spark in the presence of air or gases under very high voltage.

But when the gas is enclosed in a glass tube and pressure inside the tube is reduced, the conductivity of the rarefied gases is greatly increased and electricity begins to pass giving luminous and dark spaces at first; when the pressure is

reduced to about 0.01 to 0.001 mm., rays are sent out in straight lines from the cathode, which become evident when these rays strike the sides of the glass tube to produce green fluorescence (Fig. 1—1). These rays are known as cathode rays
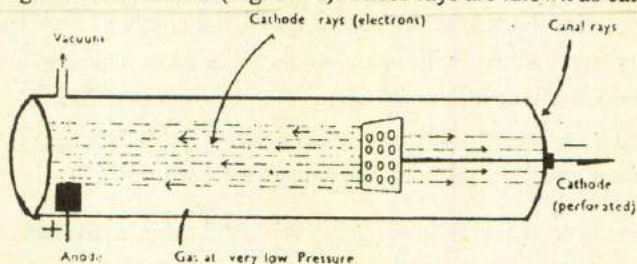

Fig. 1—1. Production of cathode rays and canal rays (positive ions) in a discharge tube.

and are deflected in electric and magnetic fields indicating that these carry electric charge which was proved to be of negative sign by J. J. Thomson.

The deflection of the cathode rays towards the positive pole of the electric field conclusively proves that the rays are associated with negative charges (Fig. 1—2).
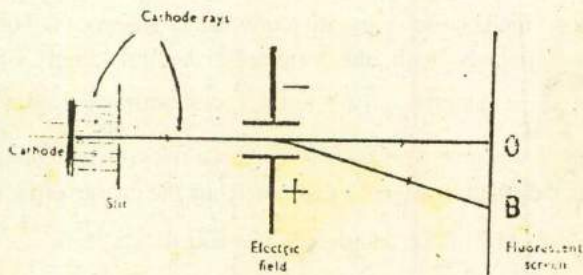

Fig. 1–2 Electrons attracted towards the positive pole of the electric field.

A thin beam of cathode rays strikes at point O on the screen when the electric field in not applied, as shown diagrammatically in Fig. 1-2. When the electric field is applied, the point O moves to B showing that the beam has been attracted towards the positive pole of the electric field.

Determination of e/m: The cathode rays are passed through a small slit (Fig. 1-2) and the narrow beam taken in-between the plates of electric field is

allowed to be focussed on the fluorescent ZnS screen. When the electric field is applied under high vacuum the movement of the bright spot at point O to point B is connected with the charge-to mass ratio of the cathode particle. Similarly, if the cathode beam is subjected to the influence of magnetic field instead of the electric field, the bright spot on the screen describes a circular path. Both the electric and magnetic field are applied simultaneously and the forces are so adjusted that fluorescent spot does not move from its original position at point O. Under this condition the force due to electric field on the cathode particles becomes equal to the force due to the magnetic field.

If e be the charge and m be the mass of a cathode particle moving with velocity v, and I and H be the respective intensities of the electric and magnetic fields then under the conditions of no deflection, we get,

Force due to magnetic fields H.e.v = force due to electric field, I. e; that is,
$$H. e. v = I. e \quad \text{or} \quad v = I/H$$

Thus the velocity of the cathode particles can be found. Now, on subjecting the cathode beam to the action of magnetic field alone and noting the radius r of the circular path, it is observed that the centrifugal force $\dfrac{mv^2}{r}$ is equal but opposite to the force due to applied magnetics field; that is H.e.v $= \dfrac{mv^2}{r}$) or

$$\frac{e}{m} = \frac{v}{rH}$$

Since v = I/H, the ratio e/m can be obtained from the equation:

$$\frac{e}{m} = \frac{I}{rH^2}$$

Thus it was proved that cathode rays consist of particles carrying negative charges and ultimately given the name electron, since they are apparently identical with the unit of electricity associated with the ions in solution suggested by G. J. Stoney. The electrons produced in the cathode rays are in the free state. The properties of the cathode rays were always the same, no matter what gas was used in the tube or what electrode materials were employed. Electrons are also emitted by certain metals when heated to high temperatures. The process is called thermal emission of electrons. Electrically heated metal filaments in vacuum tubes produce electrons which are employed in radio and television. Electrons are also emitted from active metals such as sodium on exposure to light. X-rays also liberate electrons from all types of matter. These photoelectric electrons are employed in photoelectric cells. Radio-elements emit β-rays which are also electrons moving with great speed.

Thus all electrons are identical, irrespective of their source or method of production, and although their velocities vary, their other properties, especially the "charge to mass" ratio e/m remained constant. But a knowledge of e/m did not give the knowledge of the values of e or m of an electron.

Determination of charge e : A number of methods have been developed for determination of charge on an electrical particle, The three important methods are-(i) Wilson's cloud chamber method, (ii) Millikan's oil drop method and (iii) Compton's X-ray diffraction method.

Wilson used two horizontal brass plates in a cloud chamber to study the behaviour of a charged fog in the presence of an electric field. The two plates were kept at distances from 4 to 10 cm apart. On applying electric potential to the parallel plates it was noticed that the fog fell at a different speed than under the normal influence of gravity. The ratio of the two velocities enabled to calculate the electronic charge. But the value of "e" so determined was not very accurate.

Millikan's Oil Drop Method : Small drops of oil can be charged electrically by subjecting them to radiations with X-rays or ultraviolet rays or by radio-elements. Millikan used an apparatus shown schematically in Fig. 1-3 in which electrically charged oil drops were sprayed by means of an atomizer. The upper metal plate has a number of small holes through which a few droplets enter the region between the charged plates. A droplet of oil tends to fall downward due to gravitational force. However, if the top plate is given the charge opposite to that of the drop, the drop is attracted upwards, By adjusting the strength of electric field the droplet may be made to remain suspended and stationary between the two charged plates. This happens when the upward
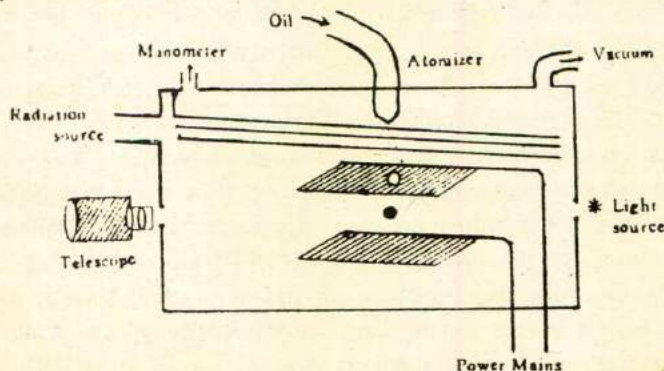

Fig. 1-3.   Schematic sketch of Millikan's apparatus for the determination of e.

electrostatic force becomes equal to the downward gravitational force. This situation is observed between the cross-wires of the telescope while the region between the two plates is illuminated by a source of light.

In a series of experiments Millikan determined the mass of the oil drops (m_o) by measuring the radii (r_o) of the drops and the density of the oil (d_o) by using the relationship

$$m_o = \frac{4}{3}\pi r_o^3 d_o$$

The radii (r_o) of the drops were calculated by observing the velocity of fall (v_1) of the drops under gravity by noting the time taken by the drop to travel between the two sets of cross-wires of the telescope and using the relationship

$$v_1 = \frac{2}{9}\frac{g r_o^2 (d_o - d_a)}{\eta}$$

where g is the acceleration due to gravity, d_o and d_a are the densities of the oil and air respectively and η is the viscosity of air. Under the conditions when downward gravitational force is equal to the upward electrostatic force (charged oil drop remains stationary between the plates) we have

$$\text{I. } e_o = m_o.\, g \quad \text{or} \quad e_o = \frac{m_o\, g}{I}$$

where I is intensity of the electric field, e_o is the charge on the oil drop which can be easily computed.

If the upward electrostatic force, I. e_o, is greater than the downward gravitational force, $m_o g$ (I. $e_o > m_o g$), then the velocity v_2 of the oil drop for upward journey can be measured by timing the distance of rise between the cross-wires of telescope. Under this condition we have

$$\frac{v_2}{v_1} = \frac{\text{I. } e_o. - m_o g}{m_o g}$$

Therefore $e_o = \dfrac{m_o g}{I.v_1}(v_1 + v_2)$

The charge e_o on the oil drops varied from drop to drop in successive experiments but Millikan observed that the values always indicated to be an

integral multiple of a single unit. Millikan concluded that electrical charge is quantized and that any electrical charge must be a some integral multiple of a fundamental unit of charge. The smallest charge or the fundamental unit after modification was found to be equal to 1.602×10^{-19} coulombs per electron or 1.602×10^{-20} electromagnetic unit (emu) or equal to 4.803×10^{-10} electrostatic unit (esu), almost the same value as found from F/N. The mass of an electron was calculated to be equal to $\frac{1}{1839}$th part of the mass of one atom of hydrogen approximately.

From the above discussion it can be seen that the electron is a universal constituent of all matters and that it is much smaller in mass as compared with that of a single atom of hydrogen which is the lightest of all atoms. The comparative figures given below indicate the magnitudes.

Charge of an electron e	$= 1.602 \times 10^{-20}$ emu
	$= 4.803 \times 10^{-10}$ esu
1 emu	$= 10$ coulombs
Mass of one atom of hydrogen	$= 1.67 \times 10^{-24}$ g.
Mass of one electron	$= 9.11 \times 10^{-28}$ g.
$\dfrac{e}{m_{\text{H}}}$ in the case of hydrogen	$= 9.579 \times 10^3$ emu/g.
	$= 9.579 \times 10^4$ coulombs/g.
	$= 2.876 \times 10^{14}$ esu/g.
$\dfrac{e}{m}$ in the case of electron	$\doteq 1.759 \times 10^7$ emu/g.
	1.759×10^8 coulombs/g.
	5.274×10^{17} esu/g.

At this stage a rough idea can be had as to what happens when electric discharge takes place through rarefied gases. Why the conductivity of electricity is increased in high vacua? Under the impact of high voltage, a small portion of the gas in the tube is ionized which means it loses electrons easily. The free electrons are sufficiently accelerated to knock out electrons from other atoms and

molecules by sudden impact. Ultimately a large number of electrons are formed by collision with the gaseous molecules and since the pressure inside the tube is decreased considerably, the "free path" of molecules and ions becomes greater and the charged particles give rise to increased electrical conductivity. A state is finally reached at which a large number of electrons are continually being formed and are accelerated to very high velocities by the repulsive force of the cathode. Thus the cathode rays which constitute the electrons appear to move away form the cathode towards the anode.

It might also be realized that a stream of positively charged particles must also be moving in the opposite direction. Since atoms are electrically neutral and if the negative particles of the atoms are dislodged from it, evidently the positive part would also be produced during the process. Goldstein in 1886 discovered the positively charged ions in the cathode rays tube by a special device, i. e., by using a perforated cathode. The positively charged rays moving away from the anode passed through these perforations or canals and hence are known as *Canal Rays* (Fig. 1-1). The particles constituting the canal rays are found to be heavier than electrons and move very slowly. Determination of the charge to mass ratio in the case of canal rays or positive rays showed that it is not a constant quantity in this case and varied from gas to gas in the vacuum tube. The charges on the positive particles, unlike those on electrons, were found to vary in magnitude. Measurements indicated that each particle carried either a unit positive charge or a simple multiple of this unit. The unit positive charge was equal to the charge on the electron but of opposite sign. The mass of the positive particles was found to be minimum when hydrogen was used in the discharge tube than when any other gas was employed. The neutral atom can be made to form positive ions by the loss of one or more electrons. From this fact it can be concluded that an atom must contain one or more positive units. The simplest atom is obviously that of hydrogen and when it loses its electron the positive hydrogen ion (H^+) is known as *prbton*.

After the discovery of electron in all types of atom, a vague idea was put forward regarding the structure of atom by Thomson. According to Thomson, an atom consists of a number of electrons distributed in a sphere of uniform positive electricity. The idea of nucleus in an atom was quite unknown.

Radioactivity and Atomic Structure

A further advancement in the idea of the structure of atom was provided by the discovery of radioactivity. The term radioactivity applies to the spontaneous disintegration of atoms of certain elements, such as radium and uranium, into simpler elements with the simultaneous production of one or more of the three kinds of radiations emitted during the process. These types of rays are known as alpha (α) rys, beta (β) rays and gamma (γ) rays, These can be characterised by placing the radioactive material in a hole bored in a block of lead, and allowing the emitted rays to pass through strong electric or magnetic field as shown in Fig. 1—4.
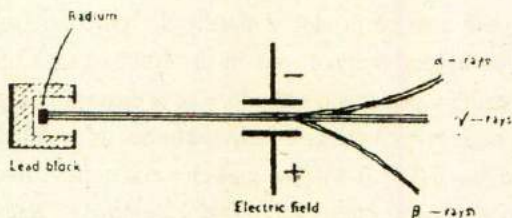

Fig. 1—4. α, β and γ-rays from radium.

The α-rays are deflected towards the negative pole of the electric field and consist of positively charged particles subsequently found to be doubly charged helium ion (He^{+2}). The β-rays are attracted towards the positive pole of the electric field and are, actually electrons moving with tremendous velocity approaching that of light (186,000 miles per second). The γ-rays are not affected by the electric field but are more penetrating having very short wavelengths similar to x-rays and affect photographic plate or film.

Scattering of β-rays by Metal Foils

Since β-rays are electrons moving with great velocities, it was thought that these may force their ways inside an atom and its effect may reveal something about its structure. For this purpose, a narrow parallel beam of β-rays from a radioactive source was directed on thin metal sheets, such as those of aluminium, silver, gold etc. It was noticed that the emergent beam was scattered and

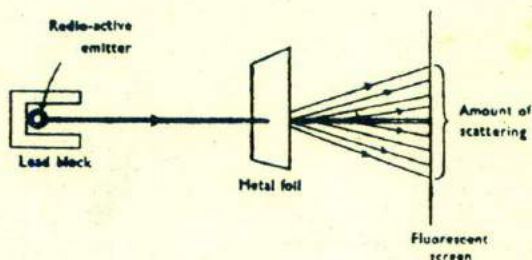divergence could be due to the repulsion of β-rays by the electrons present in the atoms of the metals (Fig. 1—5).

Fig. 1—5. Scattering of β-rays by metal foils.

Form the amount of divergence it was possible to calculate the number of electrons present in the metal atom and this was found to be approximately half of the atomic weight of the metal. Since each electron weighs only $\frac{1}{1\cdot 19}$ th part of one atom of hydrogen, it can be easily seen that the major part of the mass of an atom is associated with the positive electricity.

Scattering of α-rays and the Idea of Nucleus

(α-particles are emitted from radioactive elements with great velocities, on the average about 180,000 miles per second. Rutherford in 1911 projected a beam of α-particles from a radioactive source upon a very thin gold foil. He found that most of the particles passed through the solid gold foil without deflection, and that only a few of them occasionally suffered abrupt back deflection as if the α-particles have met with some obstacles in their onward journey. From this experiment Rutherford assumed that the mass of an atom is concentrated in a central body called the Nucleus which is exceedingly small as compared to the total size of the atom. The electrons can be easily knocked out from the atoms and therefore constitute the external structure of the atom. The nucleus also carry the entire positive charge of the atom. When α-particles come in contact with such a system, there is little or no deflection of α-particles by the tiny electrons because of the mass and size of the particles. But α-particles can only turn back by hitting the nucleus not only because of their

obstacle but also due to repulsion by the positive charges on the nucleus as encounter with a massive shown in Fig. 1—6.
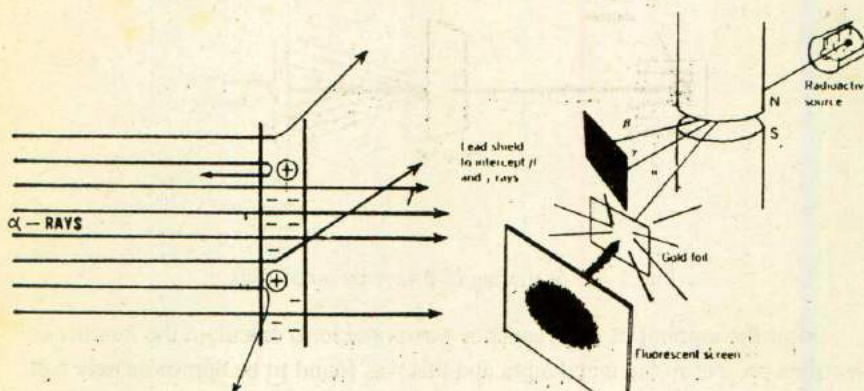

Fig. 1—6. Deflection of α-particles by nuclei in a metal foil.

Rutherford measured the nuclear charges of a large number of atoms and proved that the number of positive charges on the nucleus is, in many cases, approximately one-half the atomic weight of the element and also equal to the number of free electrons in the atom, since its charge is equal to that of all the free electrons.

If there were several nuclei in the atom, the ratio of specific heats at constant pressure Cp, and at constant volume Cv, i. e., Cp/Cv, could not be as high as 1.67 even for monoatomic gases.

Rutherford's Atom Model

Rutherford's solar system atom model may be described as follows :-

(1) An atom consists of a small nucleus containing all the positive charges of the atom and practically the whole of its mass.

(2) The nucleus is surrounded by a number of electrons equal to the number of positive charges on the nucleus.

(3) The electrons are in constant motion round the nucleus like that of planets round the sun in such a way that the electrostatic force of attraction between the electrons and positive nucleus is counterbalanced by the centrifugal force.

As mentioned before, the unit of positive charge in an atom is considered to be due to proton. Here it can be assumed that a nucleus consists of protons which provide all the positive charges and probably almost all the mass of the atom. But this idea is not correct. Since an atom is electrically neutral, it must consist of equal number of positive and negative charges. The problem of atomic weights remained to be solved.

Atomic Number

In 1914, Moseley worked out a method for determining the number of positive charges on the nucleus of an atom. The method used involved the measurement of the wavelengths of x-rays given off by various elements when employed as target. When the metal target is placed in the path of the high velocity cathode rays (electrons), electromagnetic radiations of short wavelengths are produced. These rays are very penetrating and are called x-rays. In order to study the x-rays produced when different elements or their compounds were used as targets, salt crystals such as those of potassium ferrocyanide were used as diffraction gratings to spread the x-rays into a spectrum similar to that when a beam of sunlight is passed through a glass prism.

When the spectra of x-rays produced in this manner are recorded on a photographic film, the lines in the photograph are characteristic of the material of which the target is made. Moseley arranged the x-ray spectra of different elements in the order of increasing atomic weights, and found that the heavier the elements the shorter the wavelengths of the principal lines in the spectra. The wavelength of any element differed from that of the next higher element by the same amount (Fig. 1–7). Thus there is, in an atom, a fundamental quantity which increases by regular steps as we pass from one atom to the next. This quantity can be the charge on the nucleus thus indicating a constant difference of

one proton in the nuclei of the atoms of adjacent elements in the Periodic Table. Thus all the elements can be arranged in the increasing order of the positive

Increasing wavelength ⟶   At. No.

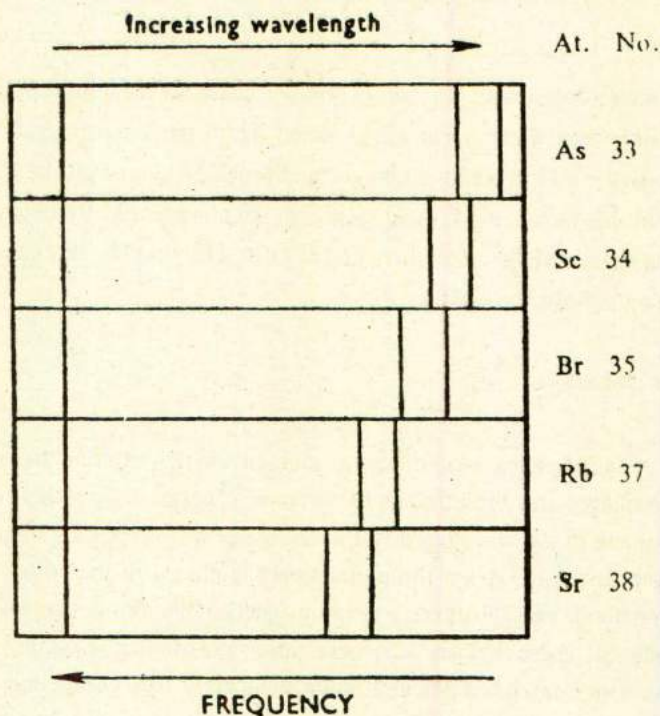As 33

Sc 34

Br 35

Rb 37

Sr 38

⟵ **FREQUENCY**

Fig. 1-7. X-ray spectra of Moseley. Note the greater shift in wavelength between Br (35) and Rb (37).

charge on the nuclei of their atoms instead of the atomic weights beginning with hydrogen. Thus the atomic number of an element can be defined as the number of positive charges on the nucleus of its atom. In effect, the atomic number is the number of protons in the nucleus. The number of electrons outside the nucleus in a neutral atom also gives its atomic number.

Fundamental Particles of Atom

An atom is the smallest particle of an element having its own chemical identity and properties. But the experiments described before indicate that atoms can be subdivided into smaller subatomic particles known as fundamental

particles. Quite a large number of particles have been identified from the subdivision of atoms. Most of the particles are quite unstable and their nature are not clearly known. For the purpose of the study of chemistry the three most important particles, namely *electron, proton* and *neutron*, are regarded as fundamental particles.

Electron : An electron is the smallest of the subatomic particles. As mentioned before, it has the unit electrical charge with negative sign Its mass is about $\frac{1}{1840}$ times less than that of a hydrogen atom or proton. The study of cathode rays provide a great deal of informations regarding the characteristics of electrons. Cathode rays have been proved to be streams of negatively charged electrons moving in an electric field with tremendous speed. These are deflected towards the positive pole of an electric field and also deflected at right angles to the applied magnetic field. The charge to mass ratio, e/m of an electron has been experimentally determined and found to be constant irrespective of the source and the method of production. Electrons appear to constitute the outer structures of atoms, since they are easily dislodged under the influence of electric field. Electrons are emitted from the surface of a substance exposed to the action of x-rays, ultraviolet rays and even on exposure to ordinary light. Electron beams are also produced from electrically heated metal filaments in vacuum tubes. β-rays from radioactive elements are also fast-moving electrons.

The chemical properties of elements and their compounds are mostly dependent upon the arrangement of the electrons in their atoms.

Proton : When an electron is lost from the lightest of all atoms, i. e., hydrogen, a positively charged particle is left. This particle is called a proton. It bears a unit positive charge (i. e., 1.602×10^{-20} emu) but is about 1839 times heavier than an electron. If the gas in the discharge tube is hydrogen, the positive rays formed after the discharge of electrons may consist of protons. The determinations of the charge to mass ratio, e/m, when hydrogen is used in the discharge tube, give the largest value for the positive ions. It is, therefore, assumed that positive ions from this source are the fundamental particles to which the name proton has been given. The value of e/m decreases with the increase in the mass of the particle and this depends upon the gas present in the discharge tube.

Neutron : Rutherford predicted the presence of neutral particles within the nucleus of an atom in order to account for the total mass of the atoms. Since an atom is electrically neutral, it must contain equal number of electrons and protons. But the atomic mass is much greater than the total masses of electrons and protons present in the atom. In 1932, Chadwick discovered neutron as a fundamental unit of atomic structure, He observed that when α-particles are used to bombard thin sheets of beryllium metal, uncharged particles are emitted. These neutral particles are called neutrons. They have a mass equal to 1.0087 on the atomic weight scale (i. e., approximately unity). It was later discovered that under certain conditions a neutron may disintegrate and form a proton and an electron. This may be the origin of the electrons composing the β-rays which are emitted by radioactive elements.

Composition of the Nucleus

The nuclei of atoms contain, for all practical purposes, both protons and neutrons except in the case of hydrogen atom which consists of a single proton. Each neutron and each proton has a mass of approximately 1 (on the basis of atomic weight of carbon, C = 12 *atomic mass unit (amu)*. The atomic weight of an element is approximately equal to the sum of the weights of the total number of protons and the total number of neutrons in the nucleus (neglecting the small weight of the electrons present). The assignment of mass 12 to the isotope of C is defined as the new atomic mass scale by the International Union of Pure and Applied Chemistry (IUPAC) in 1962. Oxygen, O = 16.000, has previously been used as the standard *amu*. But at present the masses of all nucleus are expressed as a ratio of their masses to the mass of $C^{12} = 12.000$.

The protons and neutrons in the nucleus are held together by a force known as nuclear force. The picture of the nucleus is actually much more complex since a very large number of fundamental particles are supposed to be created by the interaction of the neutrons and protons. According to Heisenberg, a neutron in the nucleus sometimes is transformed into an electron and a proton. The electron might escape in the form of β-rays. This is known as *beta decay*. The change in mass for a beta decay is zero.

Mesons : In 1935, Yukawa suggested that when a proton and a neutron interact, a fundamental particle known as meson is absorbed by the neutron. There are two types of mesons having mass between 200 and 300 times that of an electron. The two types of mesons are π mesons and μ mesons. The π mesons at present are known ans *pions* and the μ mesons as *muons*. These may be positive, negative and neutral. In the exchange of positive pion the proton becomes a neutron and the neutron becomes a proton. In the same way a neutron may interact with a proton by emiting a negative pion. These interactions are represented as :

$$p \rightleftharpoons \pi^+ + n$$
$$n \rightleftharpoons \pi^- + p$$
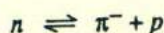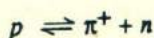
It may be seen in the chapter on Nuclear Chemistry that the emission of an electron or a β-ray from a radioactive nucleus is evidently due to the transformation of a neutron into a proton and electron :

$$n \longrightarrow p + e$$
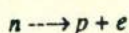
This transformation is known as *beta decay*. In this beta decay, the energy of the neutron should be equal to the energy of the products. But it has been found that both energy and momentum of the particles are changed. In order to preserve the conservation of energy and momentum in beta decay, Pauli suggested that the proton is retained in the nucleus and the electron and another particle called *neutrino* are emitted. Thus :

$$\text{Neutron} \longrightarrow \text{proton} + \text{electron} + \text{neutrino}$$
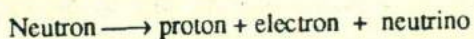
Existence of the free neutrino has since been established experimentally in 1956. Neutrino has charge zero and its mass is either zero or near about zero.

The present-day knowledge of the structure of the nucleus has progressed so far as to present a very complex situation. The multiplicity of fundamental particles has become a subject matter of a vast theoretical and experimental research embodied in the fields of nuclear physics and nuclear chemistry and is beyond the scope of this elementary text book. However, the proton-neutron concept of the nuclear structure will be necessary to understand the elementary

aspects of this subject. The composition of some of the nuclei are given in Table 1.1.
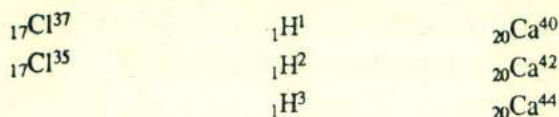
Table 1.1. The composition of the nuclei.

Elements	Symbol	At. Wt.	At. No.	No. of Protons	No. of Neutrons
Hydrogen	H	1.008	1	1	0
Helium	He	4.003	2	2	2
Lithium	Li	6.940	3	3	4
Beryllium	Be	9.013	4	4	5
Boron	B	10.820	5	5	6
Carbon	C	12.010	6	6	6
Nitrogen	N	14.008	7	7	7
Oxygen	O	16.000	8	8	8
Fluorine	F	19.000	9	9	10
Neon	Ne	20.183	10	10	10

Isotopes

The atomic weights of the various elements in Table 1.1 are not at all whole numbers. This has been found to be due to the fact that most elements are composed of mixtures of two or more kinds of atoms of different atomic masses, but similar in chemical properties. For example chlorine, with an atomic weight of 35.46, is composed of two kinds of chlorine atoms containing masses 35 and 37. But both types of the atoms of chlorine have atomic number 17. This means that both have 17 protons in the nucleus. The difference is, therefore, due to the number of neutrons in the nuclei of the different types of atoms. Chlorine 35 has 18 neutrons and chlorine 37 has 20 neutrons. The atoms having the same atomic number but different atomic masses are called *isotopes*. The only difference in the composition between different isotopes of the same element is in the number of neutrons in the nucleus. These isotopes, as a rule, occupy the same place in the periodic classification of elements. It is to be remembered that the atomic weight of an element is an average of the weights of the isotopes of element in the proportions in which they normally occur in nature. The atomic weight of chlorine 35.46 indicates that the atoms of isotopic weight or mass number 35

are more abundant than the isotope of chlorine having mass number 37. Isotopes of an element are generally written by the following symbols :

$$_{17}Cl^{37} \qquad\qquad _1H^1 \qquad\qquad _{20}Ca^{40}$$
$$_{17}Cl^{35} \qquad\qquad _1H^2 \qquad\qquad _{20}Ca^{42}$$
$$\qquad\qquad\qquad\quad _1H^3 \qquad\qquad _{20}Ca^{44}$$

The subscript stands for the atomic number of the element and the superscript denotes the mass number. There are more than 1,000 isotopes, natural and artificial, that have been identified of the known elements.

Atomic Spectra and Electronic Structure

The present-day knowledge of the structure of atom, particularly as regards the arrangements of extra-nuclear electrons is based upon the spectrum analysis and the lines which appear in them. When white light is passed through a glass prism, diffraction occurs and the white light becomes separated into its component coloure known as spectrum. Light consists of waves which is transverse. Of the visible colours, red has the greatest wavelength and violet, the shortest. The region between red to violet constitutes the visible region of the spectrum. But there are lights of greater wavelengths beyond the visible red and constitute the invisible infra-red region of the spectrum. Similarly there are
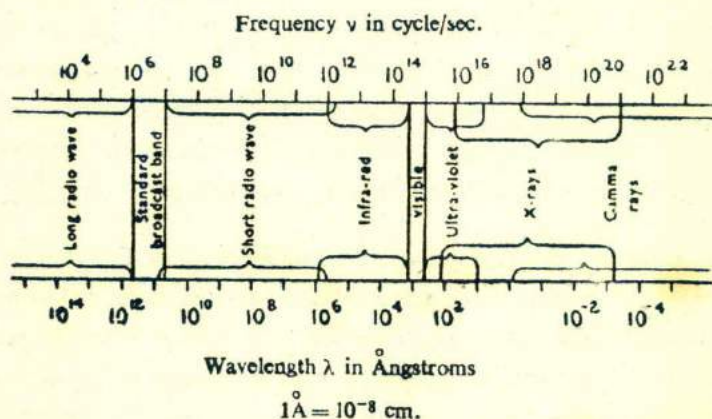

Fig. 1—8. Different regions of the spectrum.

lights of shorter wavelengths beyond the visible violet and constitute the invisible ultra-violet region of the spectrum. These invisible regions i. e., the infra-red and ultraviolet regions may be detected and recorded photographically. The different regions of the spectrum are shown in Fig. 1—8.

When a solid in heated to incandescence, it gives more or less a continuous spectrum. But gases and vapours under the same conditions or when subjected to electric discharge in a vacuum tube give spectrum often consisting of lines and bands occupying definite positions, i. e., with definite wavelengths. Thus we have "line spectra" and "band spectra". It was later shown that the line spectra are due to atoms and the band spectra are due to molecules.

It is from the atomic spectra consisting of sharp lines that informations regarding the extra-nuclear electrons are obtained. Many attempts have been made to explain how an excited atom radiates energy and why it radiates the particular wavelength or frequencies. Why the lines in the spectrum are sharp and well-defined?

It was also known that an element in the excited state, i. e., heated condition, in flame, during passage of electricity, subjected to electric arc or spark, exposure to exciting radiation etc. gives bright lines corresponding to the colours of the region in the visible spectrum. This is called "emission spectrum". But if white light is passed through the same element (gas or vapour) that is not glowing, the spectrum shows dark lines exactly at the same position characterised by the wavelengths where bright lines are obtained under excited conditions. The spectrum with dark lines is called "absorption spectrum".

Bunsen and Kirchhoff discovered that any given spectral line defined by its wavelength (or frequency) is characteristic of a type of atom, so that one may detect by means of an spectroscopic analysis what element is present in a given sample. The interpretation of Fraunhofer lines in the solar spectrum had led to the belief that absorption spectra or dark lines are caused by the presence of various elements in the sun, such as H, He, Na, Mg, Ca, Fe, etc.

In 1885, Balmer studied the hydrogen spectrum in the visible region and accurately measured the wavelengths of all the lines. The series of lines in the
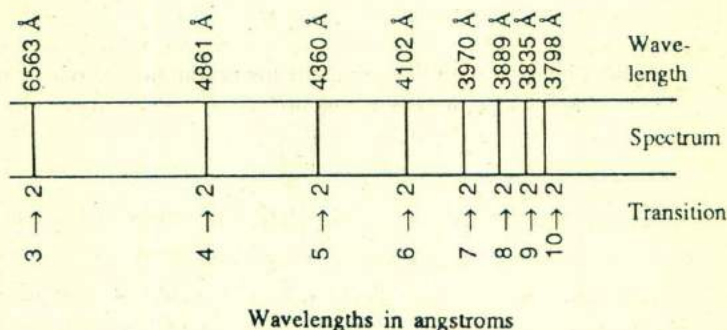
6563 Å	4861 Å	4360 Å	4102 Å	3970 Å	3889 Å 3835 Å 3798 Å	Wave-length
						Spectrum
2 ↑ 3	2 ↑ 4	2 ↑ 5	2 ↑ 6	2 ↑ 7	2 2 2 ↑ ↑ ↑ 8 9 10	Transition

Wavelengths in angstroms

Fig. 1–9 Balmer series spectrum of hydrogen in the visible region.

spectrum is known as Balmer series (Fig. 1—9). The values of the wavelengths so obtained by Balmer remarkably fitted into a general equation

$$\lambda = K \; \frac{n^2}{n^2-4}$$

where λ = wavelength and n is an integer greater than 2 and K is a constant.

The modified form of the equation is,

$$\frac{1}{\lambda} = R \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

$$\text{or, } \bar{\upsilon} = R \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

where $\bar{\upsilon}$ is the reciprocal of wavelength, i. e., $\frac{1}{\lambda}$ and is known as wave number, R is a constant known as Rydberg Constant named after its discoverer and represents a fundamental wave number and is very nearly the same for all elements, n is an integer and has values 3, 4, 5 etc. for the first, second, third etc. line in the hydrogen spectrum (represented as $H\alpha$, $H\beta$ $H\gamma$ etc.).

The wave number $\bar{\upsilon}$ is also related to the frequency υ by the relationship $\upsilon = \bar{\upsilon}.c$, where c is the velocity of light (3×10^{10} cm. per second). The

frequency υ is the number of vibrations (wavelengths) per second whereas the wave number $\bar{\upsilon}$ is the number of vibrations (wavelengths) per centimetre.

Similarly, Lyman in 1906 studied the ultraviolet region of the hydrogen spectrum and observed a number of lines, having the wavelengths in excellent agreement with the equation,

$$\bar{\upsilon} = R \left(\frac{1}{1^2} - \frac{1}{n^2} \right)$$

Where n is an integer having values 2, 3, 4, 5 etc. The series of lines in the ultraviolet region of the hydrogen spectrum is known an Lyman series. In 1908, Paschen discovered the series of lines in the infra-red region of the hydrogen spectrum and a general equation was also derived in which the Paschen series of lines fitted remarkably well. This equation follows the same pattern,

$$\bar{\upsilon} = R \left(\frac{1}{3^2} - \frac{1}{n^2} \right)$$

Where n is an integer having values 4, 5, 6, etc.

All the above three equations can be further generalized and expressed by a single equation for all the series of lines in the hydrogen spectrum :

$$\bar{\upsilon} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\text{or,} \quad \upsilon = Rc \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right). \qquad (\because \upsilon = \bar{\upsilon} . c)$$

Where c is the velocity of light, n_1 and n_2 are integers. These equations are all empirical. Rydberg constant and the equations were discovered merely by observation, calculation and hunting for a general rule.

The interpretation of the regularity and remarkable generalization was given for the first time by the theory of Bohr in 1913.

Limitations of Rutherford Atom Model

According to Rutherford, the nuclear model of atom consists of a positively charged nucleus, containing practically all the mass surrounded by a planetary system of electrons. The negative charges of the electrons are equal to the positive charges on the nucleus. It is also necessary to assume that the electrons

are in rapid motion about the nucleus so that the attractive electrostatic force of the nucleus is exactly counterbalanced by the outward centrifugal force produced by the motion of electrons. Obviously this picture of the atom is based upon Newton's Laws of motion and gravitation. Bohr pointed out that the Rutherford atom model is extremely unstable for the following reasons :-

(1) Newton's Laws of motion and gravitation can only be applied to neutral bodies such as planets and not to charged bodies such as tiny electrons moving round a positive nucleus. The analogy does not hold good since the electrons in an atom repel one another, whereas planets attract each other because of gravitational forces. Besides, there is electrostatic attraction in a nuclear atom model.

(2) According to Maxwell' stheory, any charged body such as electrons rotating in an orbit must radiate energy continuously thereby losing kinetic energy. Hence the electron must gradually spiral in towards the nucleus. The radius of the electron will gradually decrease and it will ultimately fall into the nucleus, thus annihilating the atom model.

(3) since the process of radiating energy would go on continuously, the atomic spectra should also be continuous and should not give sharp and well-defined lines.

In order to overcome these difficulties Bohr made some revolutionary suggestions in an attempt to arrive at a solution. He succeeded to some extent in correlating the empirical knowledge of atomic spectra and Planck's theory of radiation. According to Planck's theory of radiation, energy is radiated or absorbed by a body discontinuously in a definite fundamental unit or in an integral multiple of the fundamental unit. This unit of energy was called by Planck "a quantum". The magnitude of the unit of energy depends upon the frequency of rediation and thus a quantum of energy is directly proportional to the frequency of the radiation υ. In equation form this is expressed as,

$$E \propto \upsilon$$

$$\text{or, } E = h\upsilon$$

This quantum of energy is known as photon resulting from one electronic transition. E is the unit of energy and h, the Planck's constant. To convert

frequency υ to the equivalent energy in ergs, Planck used a conversion factor of 6.62×10^{-27} erg. sec. This factor is called 'h'. Thus the radiation of energy from a body will take place discontinuously in the unit $h\upsilon$ or a simple multiple of $h\upsilon$, i. e., $nh\upsilon$, where n is an integer (1, 2, 3, 4 etc.).

Bohr's Atom Model

Bohr constructed a theory of hydrogen atom in particular and to some extent of atomic structure in general. Bohr's theory consists of the following postulates :-

1. Postulate of Energy Levels

(a) An atom has a number of stable orbits in which an electron can revolve without the radiation of energy. These orbits are referred to as "Energy Levels". The electrons in these orbits possess an integral multiple of the quantum of energy i, e., $h\upsilon$, but do not radiate it.

(b) If the electron moves in a circular orbit, its motion is subject to the ordinary laws of electrical and centrifugal forces. These orbits are decided by the condition that the angular momentum of the electron in such orbits must be an integral multiple of $\dfrac{h}{2\pi}$, that is,

$$mvr = n \cdot \frac{h}{2\pi} ,$$

Where m is the mass of the electron, v is its velocity, r is the radius of the orbit and n is 1, 2, 3, 4, 5 etc. (h is the Planck's constant).

2. Postulate of Frequency or Radiation

According to this postulate an electron can, however, jump from one orbit to another. An atom radiates energy as light only when an electron passes from a higher energy level to another of lower energy giving definite spectral lines in emission spectra. The jump of an electron from a lower energy level to that of a higher energy level is manifested by absorption of energy giving dark lines. The quantity of energy radiated or absorbed is equal to the difference between the energies the atom possessed before and after the electron changed orbits.

If E_1 and E_2 are the energies of the electron in the initial and final levels respectively, the difference of energy radiated when the electron passes from the higher to the lower energy level is given by the relation :

$$E_2 - E_1 = h\upsilon,$$

where h is the Planck's constant and υ is the frequency of radiation.

On the basis of his theory, Bohr was able to account satisfactorily for the bright lines in a number of different atomic spectral series particularly in that of hydrogen.

The angular momentum of the electron is defined as the product of the velocity (v) of the electron in its orbit, mass (m) and radius of its orbit (r), i. e., $m\omega == m$vr (Fig. 1-10), where ω is the angular velocity.

According to Bohr's postulate the angular momentum must be a simple multiple of $\dfrac{h}{2\pi}$ that is, $m$vr $= n\dfrac{h}{2\pi}$ where n has values 1, 2, 3, etc. and is
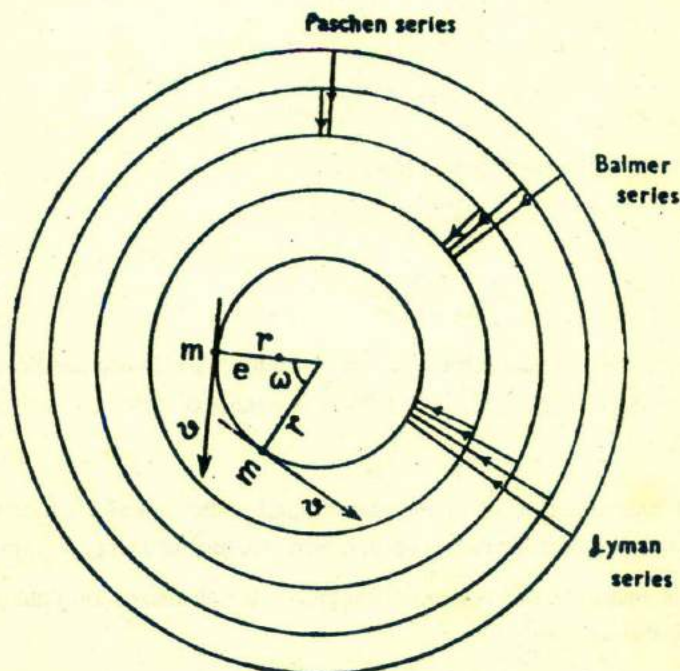

Fig. 1-10. Bohr hydrogen atom. Origin of spectral lines.

referred to as "quantum numbers". The total energy of the electron in an orbit is made up of kinetic and potential energies and can be calculated by applying the laws of mechanics and electrostatic forces of attraction. For an electron in an orbit of radius r, the electrostatic force of attraction between the nucleus with charge Z. e (where Z is the atomic number) is given by $\frac{Z.e^2}{r^2}$ This attraction is counterbalanced by the centrifugal force $\frac{mv^2}{r}$ (Fig. 1—10). Thus :

$$\frac{mv^2}{r} = \frac{Z.e^2}{r^2}$$

$$\text{or,} \quad v^2 = \frac{Z.e^2}{mr} \qquad \dots\dots \quad \dots\dots \quad \dots\dots \text{ (1)}$$

Bohr's postulate gives the quantum condition in which

$$m\text{vr} = n \cdot \frac{h}{2\pi}$$

$$\text{or,} \quad v = \frac{nh}{2\pi mr}$$

$$\text{or,} \quad v^2 = \frac{n^2h^2}{4\pi^2 m^2 r^2} \qquad \dots\dots \quad \dots\dots \quad \dots\dots \text{ (2)}$$

Combining the equations (1) and (2),

$$\frac{n^2h^2}{4\pi^2 m^2 r^2} = \frac{Z.e^2}{mr}$$

$$\text{or,} \quad r = \frac{n^2h^2}{4\pi^2 m.Z.e^2} \qquad \dots\dots \quad \dots\dots \quad \dots\dots \text{ (3)}$$

solving the equation for n = 1 for hydrogen, (Z = 1), the radius of the first orbit, r = 0.53 x 10^{-8} cm., or = 0.53 $\overset{\circ}{A}$ is obtained (10^{-8} cm. = 1 angstrom unit, $\overset{\circ}{A}$).

The total energy E of an electron is equal to the sum of the kinetic energy (K. E.) and the potential energy (P. E.). Now, the kinetic energy $= \frac{1}{2} mv^2$ and the potential energy of an electron of charge Z. e at a distance r from the nucleus is given by the equation :

$$\text{P. E.} = - \frac{Ze^2}{r} .$$

The total energy E of an electron in any orbit is given by the equation:

$$E = K.\,E. + P.\,E.$$

$$E = \frac{mv^2}{2} - \frac{Ze^2}{r}$$

Since,

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2}$$

therefore,

$$E = \frac{Ze^2}{2r} - \frac{Ze^2}{r} = -\frac{Ze^2}{2r}$$

Substituting the value of r from (3) we get,

$$E = -\frac{2\pi^2 Z^2 e^4 m}{n^2 h^2} = -\frac{13.6}{n^2} \quad \text{electron volts} \quad \ldots\ldots\ldots (4)$$

Where E is the total energy of the electron in the orbit designated by the quantum number n, e is the charge and m, the mass of the electron, Z is the number of electrons involved or the atomic number and this is 1 in the case of hydrogen atom, h is the Planck's constant.

Thus $E_1 = -13.6$ ev, $E_2 = -\frac{13.6}{2^2} = -\frac{13.6}{4} = -3.4$ ev

According to Bohr's postulate when an electron passes from one orbit to another of lower energy, radiation of energy occurs having the energy equal to the energy difference between the initial and final orbit or levels. If E_2 is the energy of the higher level and E_1 that of the lower level, the difference may be expressed as,

$$E_2 - E_1 = h\upsilon$$

The difference of the total energy of an electron in the orbits n_1 (using equation 4) may be shown by the equation,

$$E_2 - E_1 = h\upsilon = \frac{2\pi^2 Z^2 e^4 m}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Therefore, $\upsilon = \frac{2\pi^2 Z^2 e^4 m}{h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right),$

where μ is the frequency of radiation in cycles/second.

The difference in energies of the first level and second level, $E_2 - E_1 = -3.4 - (-13.6) = 10.2$ electron volts.

Since $\upsilon = \bar{\upsilon}\, c$, therefore, $\bar{\upsilon} = \dfrac{2\pi^2 Z^2 e^4 m}{h^3 c}\left(\dfrac{1}{n_1{}^2} - \dfrac{1}{n_2{}^2}\right)$

All the terms in $\dfrac{2\pi^2 Z^2 e^4 m}{h^3 c}$ are constant ; Z, the number of positive charges on the nucleus, is 1 in the case of hydrogen atom.

The value of $\dfrac{2\pi^2 Z^2 e^4 m}{h^3 c}$ for hydrogen has been calculated to be $=109,737.31 \text{cm}^{-1}$. This value is the same as found for Rydberg constant in the equation $\dfrac{1}{\lambda} = R\left(\dfrac{1}{n_1{}^2} - \dfrac{1}{n_2{}^2}\right)$. Since wave number $\bar{\upsilon} = \dfrac{1}{\lambda}$. hence the relation becomes :

$$\bar{\upsilon} = R\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right)$$

This equation is identical with the general equation for the wave number of any spectral line in all the region of the spectral series of the hydrogen atom. This discovery was perhaps, the most sensational evidence in favour of Bohr's theory when it was first published.

Origin of spectral Lines : The electron in the hydrogen atom exists normally in the *ground state* or lowest energy level when n_1 or $n = 1$, i. e., nearest to the nucleus. If, however, the atom is excited, the electron will move to some higher energy level ; from this it will tend to drop back to the lowest energy level in the stable position if not ionized. This happens either directly or through intermediate steps. When the electron is returning form a higher energy level to a lower one, excess energy will be liberated as radiation of some definite frequencies according to Bohr's theory. This will give rise to emission spectra. The absorption spectra will be produced in the reverse way. Since the same orbits are involved, the same spectral lines will be observed in emission and absorption spectra.

Thus, for all the lines in the Lyman series, $n_1 = 1$ in the general equation $\bar{\upsilon} = R\left(\dfrac{1}{n_1{}^2} - \dfrac{1}{n_2{}^2}\right)$, and $n_2 = 2, 3, 4, 5$ etc. energies will be emitted or absorbed giving definite lines in the spectrum.

Hence according to Bohr's theory the Lyman series of lines in the hydrogen spectrum are produced when an electron jumps from any higher level to the lowest level. In excited atoms all the electrons will not be raised to the same
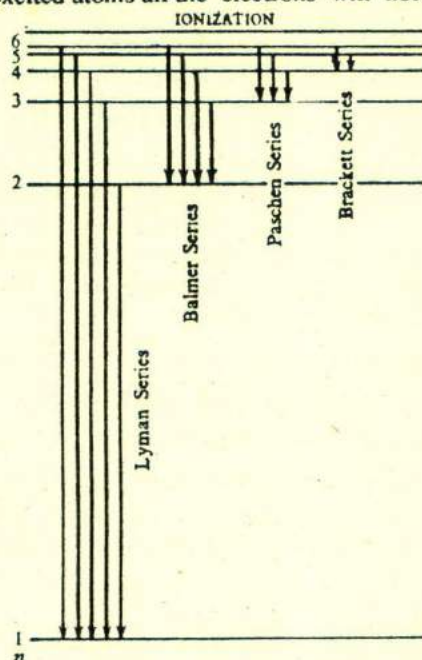

Fig. 1—11. Origin of emission spectra of hydrogen.

levels and consequently when these electrons fall back to the lowest level, a series of spectral lines will be produced as shown in Fig. 1—11. This happens in the ultraviolet region of the spectrum.

Similarly, the electrons in the various hydrogen atoms in the excited state will tend to fall back to the second energy level $n_1 = 2$ from outer levels. This takes place in the visible region and produces the Balmer series of lines. All electron transitions ending at $n_1 = 3$ from outer levels are indicated by Paschen series in the infra-red region. This theory, therefore, was remarkably successful in accounting for the main features of the hydrogen spectrum.

Limitations of Bohr Theory : As mentioned before, Bohr Theory was eminently successful in explaining the spectrum of hydrogen but failed to predict the energy states of more complicated atoms in which there are more than

one electron. Bohr presented a somewhat pictorial representation of the fact and is far from exact physical reality. Periodic motion around a central body usually
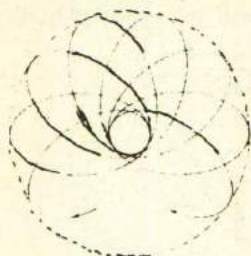
follows an elliptic path rather than a circular path which has been assumed in the case of Bohr Theory. If electrons follow elliptical path, the velocity along the path does not remain constant. Fig. 1-12 indicates the precession of electron orbit due to changes in the velocity of the electron in elliptical orbit with the nucleus at one of the foci.

Fig. 1—12. Precession of the electron orbit due to changes in the velocity of the electron.

Moreover, according to Heisenberg, both the position and the momentum of an electron in an atom cannot be fixed simultaneously. This is known as Heisenberg's Uncertainty Principle. High resolving power spectroscope shows multiple lines in the atomic spectra and the multiplicity of lines has not been explained by Bohr Theory. Also the mass of an electron, m, moving with great speed v is not the same as the mass at rest, m_0 and is given by the equation,

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$$

where c is the velocity of light.

when $v = c$. then $1 - \frac{v^2}{c^2} = 0$ and the rest mass $m_0 = 0$. This is the case with photon which has the rest mass zero but other material particle has a real rest mass.

Quantum Numbers

The Principal Quantum Number : The nuclei of the more complex atoms are surrounded by orbital electrons which are arranged in a series of energy levels or spherical shells concentric with the nucleus. These electrons are classified in terms of their energy levels. One of the original assumptions of the Bohr theory was to fix the motion of an electron in a circular orbit with angular momentum equal to a simple multiple of $\frac{h}{2\pi}$, i.e., $mvr = \frac{n.h}{2\pi}$. the integer n is

designated as the Principal Quantum Number and represents any particular circular orbit. The value of n gives roughly the binding force and distance between the nucleus and the electron. This quantum number represents the size of the electron orbit. When $n = 1$, it represents the first energy level ; $n = 2$ represents the second energy level and so on. The first energy level is the one nearest the nucleus.

The Subsidiary Quantum Number : Sommerfeld modified the Bohr atom by adding elliptical orbits in order to explain the fine structure of the spectral lines. According to this modification the electrons in any particular energy level could have either a circular orbit or a number of elliptical orbits about the nucleus. Only those elliptical orbits are selected in which the electron possesses the angular momentum given by the equation

$$mvr = \frac{h\sqrt{l(l+1)}}{2\pi}$$

where l stands for subsidiary or azimuthal or orbital quantum number. This gives a measure of the angular momentum of an electron in its orbital motion about the nucleus.

Thus the subsidiary quantum numbers describe the shapes of the electron's orbit. The main energy level (or shells) of electron may be considered as being made up of one or more sub-levels (sub-shells). The number of sub-levels are limited by quantum condition so that if n is the principal quantum number, then the number of sub-levels will be equal to n. For $n = 3$, the number of possible sub-levels are 3. The term l may have values from 0 to $n-1$ Hence for the first energy level where $n = 1$, l can have only a value of 0. This means that energy level and sub-level coincide with each other. For $n = 2$, l can have values 0 and 1. Thus the second energy level has two sub-levels. Since the values of l in the mathematical treatment gives the shapes of the orbit, the orbits are circular when $l = n-1$ and have elliptical shapes when l is different from $n—1$. Fig. 1—13 shows the orbits with $n = 4$.

The Magnetic Quantum Number : Zeeman in 1896 observed the splitting of spectral lines in a magnetic field. This is known as Zeeman effect.

The third quantum number was introduced to explain the orientation of electronic arbit in space particularly under the influence of an applied magnetic
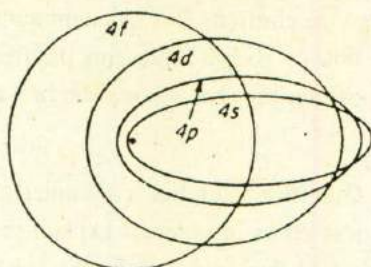

Fig. 1—13. Bohr-Sommerfeld orbits for principal quantum number n = 4.

field. This is known as the magnetic quantum number and is designated by m. The magnetic quantum knumber is associated with the translational motion of the electron in the atom. The values of m, i. e., the number of possible orientations depends to an extent upon the shape of the electron level. Mathematically, the magnetic quantum number may be expressed by the equation :

$$\text{Total angular momentum} = \frac{mh}{2\pi},$$

when m can have values from $-l$ to $+l$ including 0. Thus, when n = 1, then l = 0 and m can have only one value of 0. When n = 2, l can have values 0 and 1, and therefore, when l=0, m is also 0 and for l=1, m can have value –1,0 and +1.

The Spin Quantum Number : Stern and Gerlach (Fig 1—14) found that atoms having odd number of electrons such as H, Li, Na, Cu etc. possessed
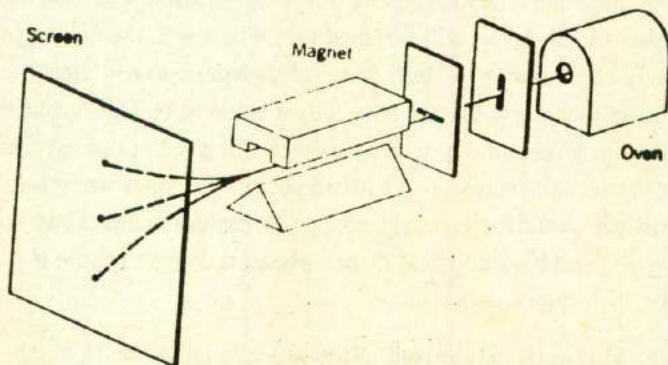

Fig. 1—14. Stern-Gerlach Experiment

magnetic moments caused by the spin of the electrons about their axis. The spin quantum number represents the direction of the electron spin and is denoted by s. The direction of spin is investigated in presence of external magnetic field and it is found that all electrons spin either in one direction (say, clockwise direction) or in the direction directly opposite (anti-clockwise). Mathematically, the spin quantum number is defined by the equation :

$$mvr = \frac{h\sqrt{s(s+1)}}{2\pi}$$

Where mvr is the angular momentum and the spin quantum numbers can have values $+\frac{1}{2}$ or $-\frac{1}{2}$ which are the mathematical notations for the spin direction of the electrons. The spin of the electrons appears to be quantized and is limited to only two values, $+\frac{1}{2}$ and $-\frac{1}{2}$ for s (spin quantum number).

The Physical Significance of Quantum Number

Four quantum numbers are necessary to describe an electron in an atom. These quantum numbers in effect describe the electron orbit in terms of (1) size, (2) shape, (3) orientation in space and (4) direction of spin of electron in its axis.

The principal quantum number, n, determines the size of the orbit and also gives a measure of the energy of the electron. The subsidiary quantum number, l, determines the shape of the orbit and indicates whether the orbit is circular or elliptical. The magnetic quantum number, m, determines the number of possible orientations in space or the number of planes in which the orbits are situated. The spin quantum number s stands for spin directions and the symbols $+\frac{1}{2}$ and $-\frac{1}{2}$ are mathematical notations of spin rather than that of physical rotation. Each electron going into an atom takes the four quantum numbers and has the lowest energy. This does not mean that all electrons in each of the elements should have values $n = 1$, $l = 0$ $m = 0$ and $s = \pm\frac{1}{2}$ which, in fact, are the lowest possible values of the four quantum numbers.

The principal and subsidiary quantum numbers representing the principal and secondary energy levels appear to be adequate descriptions of the energy states of an electron in isolated atoms. If the excited atoms from which electromagnetic radiation is being emitted is placed between the poles of a very powerful

magnetic field, a large increase in the number of different frequencies of radiation is observed. It is assumed that the secondary energy levels are further subdivided into other energy levels by the presence of magnetic field. These subdivisions of the secondary energy levels are called orbitals.

It is obvious that in the absence of a magnetic field the orbitals represent the same potential energy for an electron. A schematic diagram in Fig. 1—15 gives the resolutions of the energy levels to show the splitting of the spectral lines. It is to be noted that s energy levels are not split in a magnetic field, whereas
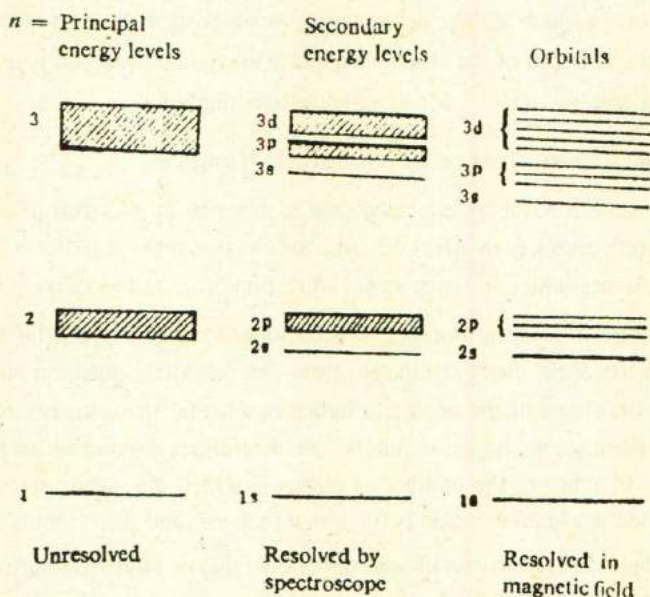
Fig. 1—15. Interpretation of spectral lines in magnetic field.

p type secondary levels appear to consist of three orbitals. The distribution of electrons in an atom is governed by the famous rule known as Pauli Exclusion Principle enunciated by W. Pauli in 1925.

Pauli Exclusion Principle : This principle may be stated in several ways, e. g.,

1.   "No two electrons in the same atom can have the same values for the four quantum numbers."

2.   "No two electrons in the same atom can have identical sets of four quantum numbers. "

3.   "No more than one electron can have given values for the four Quantum Numbers."

The above rule appears to be analogous to the law : "Two bodies cannot be placed in the same position at the same time." Thus, two electrons of the same atom can have the same values for three of their quantum numbers, but the fourth quantum number must be different for the two electrons. Thus two electrons may have orbits of the same size, shape and orientation in space provided they have opposed spins. It is noted that each atomic orbital can hold a maximum number of two electrons provided their spins are opposed.

Types of Electrons : Based on the values of the quantum numbers the electrons are classified into **s. p. d** and **f** types. Electrons having subsidiary quantum numbers $l = 0, 1, 2, 3$ are called **s, p, d** and **f** electrons respectively. Thus, each value of l is represented by a different small letters.

Value of l	Electron symbol	Maximum No. of electrons of each type
0	s	2
1	p	6
2	d	10
3	f	14

The letters, **s, p, d** and **f** thus represent the possible sub-levels in addition to the principal quantum number. For instance, an electron having $n = 1$ and $l = 0$ is designated as 1s electron ; an electron with $n = 4$ and $l = 3$ is designated as 4f electron.

The maximum number of electrons in the various energy levels permitted by Pauli Exclusion Principle have been shown in Table 1. 2.

Table 1.2. Distribution of electrons on various energy levels based on quantum numbers.

Principal quantum number n	Subsidiary quantum number l	Magnetic quantum number m	Spin quantum number s	Sub-total of electrons	Type of electron	Total number of electrons
1	0	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$	2	s	2
2	0	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$	2	s	
	1	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		+1	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		−1	$+\frac{1}{2}$			
			$-\frac{1}{2}$	6	p	8
3	0	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$	2	s	
	1	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		−1	$+\frac{1}{2}$			
			$-\frac{1}{2}$	6	p	
		+1	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
	2	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$			

Principal quantum number n	Subsidiary quantum number l	Magnetic quantum number m	Spin quantum number s	Sub-total of electrons	Type of electron	Total number of electrons
		+1	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		−1	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		+2	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		− 2	$+\frac{1}{2}$			
			$-\frac{1}{2}$	10	d	18
4	0	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$	2	s	
	1	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		+1	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		−1	$+\frac{1}{2}$	6	p	
			$-\frac{1}{2}$			
	2	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		+1	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		−1	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		+ 2	$+\frac{1}{2}$			Contd.

Principal quantum number n	Subsidiary quantum number l	Magnetic quantum number m	Spin quantum number s	Sub-total of electrons	Type of electron	Total number of electrons
			$-\frac{1}{2}$			
		-2	$+\frac{1}{2}$			
			$-\frac{1}{2}$	10	d	
	3	0	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		$+1$	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		-1	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		$+2$	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		-2	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		$+3$	$+\frac{1}{2}$			
			$-\frac{1}{2}$			
		-3	$+\frac{1}{2}$			
			$-\frac{1}{2}$	14	f	32

Distribution of Electrons in the Atoms of Elements

As we proceed from one element to another beginning from hydrogen, the number of electrons in the atom increases by one in each instance. The electrons are not distributed at random but are arranged among the known elements in seven main energy levels designated by the quantum numbers $n = 1, 2, 3, 4, 5, 6$ and 7. These principal energy levels are divided into sub-levels indicated by s, p, d and f. The first energy level (n =1) which has only one sub-level is designated as 1s. The second energy level ($n = 2$) has two sub-levels designated

as 2s and 2p, the third ($n = 3$) energy level has three sub-levels designated as 3s, 3p and 3d and the fourth energy level $n = 4$ has four sub-levels 4s, 4p, 4d and 4f. The sub-levels are further divisible into orbitals. An s sub-level is made up of one orbital; a p sub-level-three orbitals; a d sub-level—five orbitals; and an f sub-level—seven orbitals.

Each electron orbital can accommodate a maximum of two electrons of opposed spins. Thus 1s orbital can hold a maximum of two electrons. The three p orbitals can hold a maximum of 6 electrons. These results are given in Table 1.3. The number in front of the sub-level symbol is the principal quantum number and the superscript is the number of electrons in the particular orbital.

Table 1.3. Electron distribution in orbitals.

Principal quantum number	Maximum number of electrons	Number of electrons distributed in orbitals
1	2	$1s^2$
2	8	$2s^2\,2p^6$
3	18	$3s^2\,3p^6\,3d^{10}$
4	32	$4s^2 4p^6 4d^{10} 4f^{14}$
5	32	$5s^2\,5p^6\,5d^{10}\ 5f^{14}$

Thus the maximum number of electrons which the different types of atomic orbitals can accommodate are :

Sub-level	No. of orbitals	Total No. of electrons
s	1	2
p	3	6
d	5	10
f	7	14

In arriving at the electronic structure of atoms of the various elements, it is convenient to consider the sub-levels in which electrons would enter if these atoms were built up in the order of increasing atomic number, beginning with hydrogen. As each additional electron enters the atom, it will tend to occupy the available orbital of lowest energy. The higher orbitals are filled up only after lower energy orbitals have been completed.

The electron configurations of the elements are given in Table 1.4. Note that the electron configurations of chromium and copper and some other elements do not conform with the generalization stated above. In the case of chromium, the 3d level becomes half-filled (containing 5 electrons) and with copper 3d level becomes completely filled up with 10 electrons. The extra-

Table 1.4. Electron distribution in the atoms of the elements.

	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
H	1	1																	
He	2	2																	
Li	3	2	1																
Be	4	2	2																
B	5	2	2	1															
C	6	2	2	2															
N	7	2	2	3															
O	8	2	2	4															
F	9	2	2	5															
Ne	10	2	2	6															
Na	11	2	2	6	1														
Mg	12	2	2	6	2														
Al	13	2	2	6	2	1													
Si	14	2	2	6	2	2													
P	15	2	2	6	2	3													
S	16	2	2	6	2	4													
Cl	17	2	2	6	2	5													
Ar	18	2	2	6	2	6													
K	19	2	2	6	2	6		1											
Ca	20	2	2	6	2	6		2											
Sc	21	2	2	6	2	6	1	2											
Ti	22	2	2	6	2	6	2	2											
V	23	2	2	6	2	6	3	2											
Cr	24	2	2	6	2	6	5	1											
Mn	25	2	2	6	2	6	5	2											

Contd.

	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
Fe	26	2	2	6	2	6	6	2											
Co	27	2	2	6	2	6	7	2											
Ni	28	2	2	6	2	6	8	2											
Cu	29	2	2	6	2	6	10	1											
Zn	30	2	2	6	2	6	10	2											
Ga	31	2	2	6	2	6	10	2	1										
Ge	32	2	2	6	2	6	10	2	2										
As	33	2	2	6	2	6	10	2	3										
Se	34	2	2	6	2	6	10	2	4										
Br	35	2	2	6	2	6	10	2	5										
Kr	36	2	2	6	2	6	10	2	6										
Rb	37	2	2	6	2	6	10	2	6			1							
Sr	38	2	2	6	2	6	10	2	6			2							
Y	39	2	2	6	2	6	10	2	6	1		2							
Zr	40	2	2	6	2	6	10	2	6	2		2							
Nb	41	2	2	6	2	6	10	2	6	4		1							
Mo	42	2	2	6	2	6	10	2	6	5		1							
To	43	2	2	6	2	6	10	2	6	6		1							
Ru	44	2	2	6	2	6	10	2	6	7		1							
Rh	45	2	2	6	2	6	10	2	6	8		1							
Pd	46	2	2	6	2	6	10	2	6	10									
Ag	47	2	2	6	2	6	10	2	6	10		1							
Cd	48	2	2	6	2	6	10	2	6	10		2							
In	49	2	2	6	2	6	10	2	6	10		2	1						
Sn	50	2	2	6	2	6	10	2	6	10		2	2						
Sb	51	2	2	6	2	6	10	2	6	10		2	3						
Te	52	2	2	6	2	6	10	2	6	10		2	4						
I	53	2	2	6	2	5	10	2	6	10		2	5						
Xe	54	2	2	6	2	6	10	2	6	10	—	2	6						
Cs	55	2	2	6	2	6	10	2	6	10	—	2	6	—	—	1			
Ba	56	2	2	6	2	6	10	2	6	10		2	6			2			

Contd.

	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
La	57	2	2	6	2	6	10	2	6	10		2	6	1		2			
Ce	58	2	2	6	2	6	10	2	6	10	2	2	6			2			
Pr	59	2	2	6	2	6	10	2	6	10	3	2	6			2			
Nd	60	2	2	6	2	6	10	2	6	10	4	2	6			2			
Pm	61	2	2	6	2	6	10	2	6	10	5	2	6			2			
Sm	62	2	2	6	2	6	10	2	6	10	6	2	6			2			
Eu	63	2	2	6	2	6	10	2	7	10	7	2	6			2			
Gd	64	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
Tb	65	2	2	6	2	6	10	2	6	10	9	2	6			2			
Dy	66	2	2	6	2	6	10	2	6	10	10	2	6			2			
Ho	67	2	2	6	2	6	10	2	6	10	11	2	6			2			
Er	68	2	2	6	2	6	10	2	6	10	12	2	6			2			
Tm	69	2	2	6	2	6	10	2	7	10	13	2	6			2			
Yb	70	2	2	6	2	6	10	2	6	10	14	2	6			2			
Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
Ta	73	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
W	74	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
Re	75	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
Os	76	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
Ir	77	2	2	6	2	6	10	2	6	10	14	2	6	7		2			
Pt	78	2	2	6	2	6	10	2	6	10	14	2	6	9		1			
Au	79	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
Hg	80	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
Tl	81	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
Pb	82	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
Bi	83	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
Po	84	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
At	85	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
Rn	86	2	2	6	2	6	10	2	6	10	14	2	6	10	—	2	6		

	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
Fr	87	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
Ra	88	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
Ac	89	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
Th	90	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
Pa	91	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
U	92	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
Np	93	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
Pu	94	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6		2
Am	95	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6		2
Cm	96	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
Bk	97	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
Cf	98	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2
En	99	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
Fm	100	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
Md	101	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2
No	102	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2
Lr	103	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2
Rf	104	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	2	2
Db	105	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	3	2
Sg	106	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	4	2
Bh	107	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	5	2
Hs	108	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	5	3
Mt	109	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	7	2

(N. B. The claims for the discovery and naming of the elements upto 112 are controversial.)

electrons needed for this arrangement appear to come from the 4s orbital, leaving it with only one electron. It has been shown that half-filled and completely filled energy levels represent conditions of stability. (See page 154)

Energy Level Diagram

A diagram representing roughly the energies of the electrons in the atoms is given in Fig.1-16. The energy of an electrons in an orbital is indicated by the vertical coordinate in the diagram. At the bottom, ls orbital of lowest energy and greatest stability has been given. Generally, the increasing electrons in the atom may be expected to occupy the orbitals in the order as they appear in the diagram. Each set of orbitals are being filled before electrons enter the next

higher orbitals. This scheme holds strictly only for the elements of low atomic numbers. The elements of higher atomic number have electron arrangements slightly different from that shown in the diagram. The relative energies of the higher orbitals do not change to the same extent.
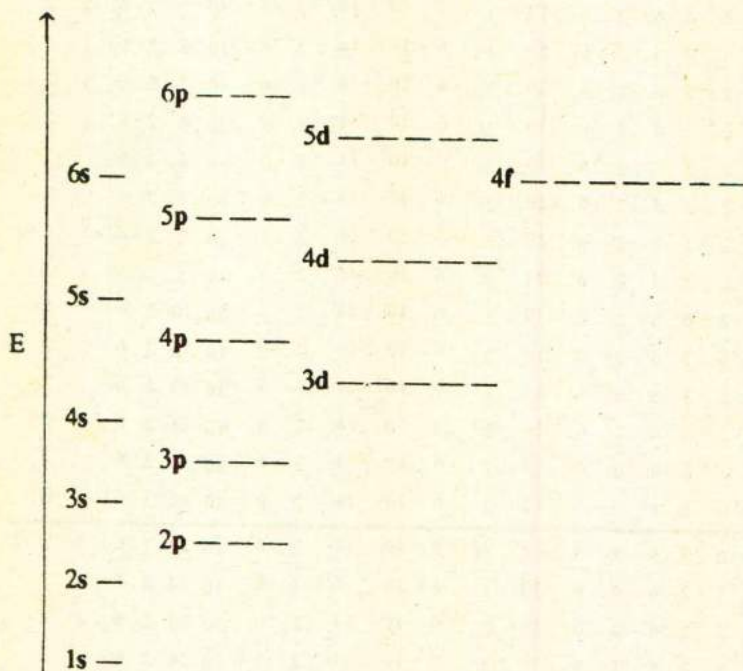
Fig. 1—16. Energy level diagram for atomic orbitals.

The above diagram may also be represented as follows to indicate the increasing energies of the atomic orbitals :

$$1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4f<5d<6p<6p<7s<5f<6d.$$
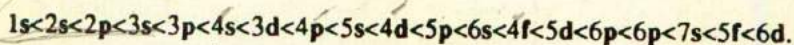
The order of filling of orbitals may be easily remembered by following the diagram in Fig. 1—17. Thus starting with 1s, proceed towards the head of the arrow and then start with the tail of the next arrow. The order of filling up is, therefore, 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f and 6d.

The inert gases have the electron configuration just before crossing the vertical line in Fig. 1-17 from right to left. The electron configurations of Cr

(24) ($1s^2 2s^2 2p^6 4s^1 3d^5$) and that of Cu (29) ($1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$) occur because of the irregularities due to extra stabilities of filled and half-filled
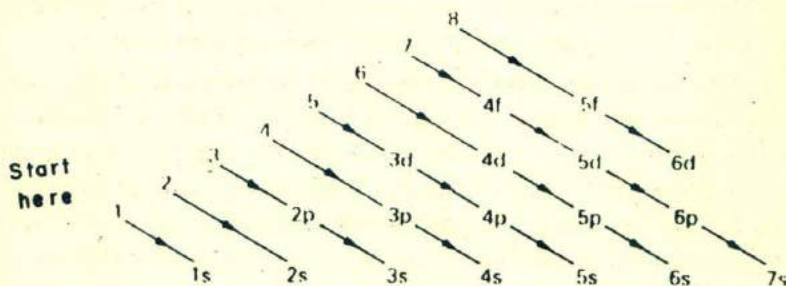
Fig. 1—17. Order of the filling of orbitals.

orbitals. The electron configuration of Ce (58) may be easily written as,

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^2$.
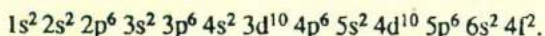
According to electronic configurations, four types of atoms can be easily distinguished :-

(i) Inert gases, He, Ne, Ar, Kr, Xe and Rn having outer group of electrons of considerable stability. These have complete s^2p^6 outer electron groupings except He ($1s^2$).

(ii) Atoms having all except the outermost electron groupings incomplete. These are alkali, alkaline earth metals etc. These have s^1 and s^2 electrons in the outermost levels respectively

(iii) Atoms having the two outermost electrons groupings incomplete. These include transition elements and d orbitals are being filled up.

(iv) Atoms having the three outermost electron groupings incomplete. These are rare-earth (lanthanides) and actinides in which mainly f electrons levels are being filled up.

Valence Electrons

It is to be emphasised that the electrons in the outermost orbital of an atom largely determine the chemical properties of the element. The electrons which are present in the outermost energy level of an atom are known as valence electrons

and these electrons determine the manner in which atoms combine with one another. Sodium metal is a very good conductor of electricity since the loose outer electron of sodium moves from one atom to the next giving rise to a flow of electrons through the sodium metal. In general, a metal is a good conductor of electricity because the valence electrons are comparatively lightly held by the atom and are free to move successively from one atom to the other.

Atoms having large number of electrons in the valence level have tendency to draw electrons to achieve stability. For instance, chlorine has 5 electrons in 3p orbital and takes up one electron to complete the 3p orbital having 6 electrons. In general, it may be seen that atoms having less than four electrons in the outer orbital tend to take up electrons. Generally it will be observed that elements classified as metals have tendency to give up valence electrons while non-metals usually take up electrons. Certain elements (metalloids) have both the tendencies of losing and gaining electrons and, therefore, exhibit the properties of both metals and non-metals.

Similarities of Structure

The electrons in the outermost energy level determine the chemical properties of the element. It is expected that group of elements having the same outer-configurations will exhibit quite similar chemical properties. It is for this reason that the groupwise chemical properties of, say, alkali metals, halogens etc. are similar. The electronic configurations of alkali metals, halogens and alkaline earth metals are given in Table 1.5.

Table 1.5. Electronic configurations of some chemically similar elements.

Elements	Atomic No.	Electronic configurations
Na	11	$1s^2 2s^2 2p^6 3s^1$
K	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Rb	37	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$
F	9	$1s^2 2s^2 2p^5$
Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Br	35	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
Be	4	$1s^2 2s^2$
Mg	12	$1s^2 2s^2 2p^6 3s^2$
Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

The Nature of Atomic Orbitals

Heisenberg Uncertainty Principle : The idea of fixed orbits of electron with fixed angular momentum is no longer acceptable, for, it is impossible to determine accurately both the exact position and the exact energy of an electron simultaneously. This is known as the Heisenberg Uncertainty Principle and maintains that the more accurately we measure the energy of a moving electron, the less accurately we can determine its position and vice versa. Therefore, the picture of an electron as a material particle of matter moving in a circular or elliptical orbit about a nucleus has little significance because such picture deals with great uncertainty as regards its position and momentum or its velocity. The best solution to this problem has been found in considering the electrons to possess the probability of being found at given location within the atom. An electron may be visualized to be in rapid motion in a relatively large region, spending most of its time in certain region of high probability, It is easier to imagine the electron as a cloud of negative charge with the cloud being dense in regions of high probability and more diffuse in regions of low probability. It is the electron clouds which are more appropriately called as *atomic orbitals*. The larger the number of the principal quantum number, the greater is the volume of the corresponding orbital. Thus a 2s electron has a larger orbital than a 1s electron, a 3s electron has a larger orbital than a 2s electron and so on. It may be noted, however, that outer orbitals and orbitals occupied by inner electrons in an atom do overlap and penetrate each other.

Wave Nature of Electrons :

The wave character of the electron was first suggested by L. de Broglie. He assigned a wavelength to the moving electron given by the equation,

$$\lambda = \frac{h}{mv},$$

Where v is the velocity and m is the mass of the electron, h is the Planck's universal constant (6.625×10^{-27} erg. sec) and λ is the wavelength. Experimentally the wave nature of electrons was established by the fact that crystals produce diffraction patterns similar to that produced by x-rays.

By the proposition of de Broglie, not only the electron is associated with wavelength λ, but also a photon of light has a mass m. Schrodinger incorporated the de Broglie concept in a wave equation describing the behaviour of electrons in atoms in terms of their wave nature, their energy states and their mass. This treatment ignores the fixed or restricted orbits of Bohr and Sommerfeld and allows the probability of finding each electron in a space around the nucleus.

An electron moving in a closed orbit is considered as describing a stationary or standing wave. In such electron wave Planck's equation applies so that energy E is directly proportional to the frequency υ or

$$E = h\upsilon \qquad \text{(h is the Planck's constant)}$$

Using Einstein's equation, $E = mc^2$, where m is the mass of photon moving with the velocity of light c, we have

$$mc^2 = h\upsilon$$

or
$$mc = \frac{h\upsilon}{c} = \frac{h}{\lambda}, \qquad \text{since } \upsilon = \frac{c}{\lambda}$$

Hence
$$\lambda = \frac{h}{mc}$$

Applying the above equation on electron moving with velocity v and associated with wavelength λ, the de Broglie relationship is obtained

$$\lambda = \frac{h}{mv}$$

An electron describing an stationary wave in an atom may be represented as in Fig. 1-18. If there are n number of wavelengths in the stationary wave in a
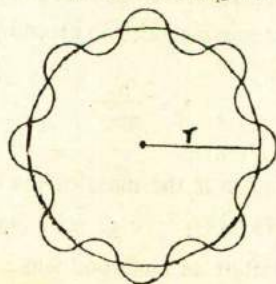
Fig. 1-18. Electron cloud of a stationary wave.

circle of circumference $2\pi r$ (r being the radius), then

$$2\pi r = n\lambda$$

or
$$\lambda = \frac{2\pi r}{n}$$

Since de Broglie relationship gives

$$\lambda = \frac{h}{mv}$$

Therefore,
$$\frac{2\pi r}{n} = \frac{h}{mv}$$

or
$$mvr = n.\frac{h}{2\pi}$$

Thus the angular momentum, mvr, of an electron is an integral multiple of the quantity $\frac{h}{2\pi}$ which may be considered as the unit of angular momentum for the particle in motion describing the stationary wave around the nucleus.

According to the wave-mechanical calculations, the average distance from the nucleus and speed of an electron in any particular quantum orbit corresponds with that calculated by Bohr. But the angular momentum, however, is different. In particular, the electron in the normal quantum level is not moving around the nucleus with angular momentum $\frac{h}{2\pi}$, but is moving to and fro around the nucleus with zero angular momentum. The wave mechanical concept of the electron seeks to relate mathematically the energy, spin, momentum and other characteristics of the electron to the probability of finding the electron in a space around the nucleus.

Because atoms exhibit spherical symmetry, it is more convenient to represent electronic wave forms by polar coordinates r, θ and ϕ instead of the Cartesian co-ordinates x, y and z. The relationship between the two systems are shown in Fig. 1—19.

The relationship between the two coordinate systems is easily obtained as,

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta \quad \text{and} \quad r^2 = x^2 + y^2 + z^2$$

Instead of locating the electron in an orbit in three-dimentional directions as a function of x, y and z, it is covenient to represent the wave function Ψ, as a product of three functions Θ, Φ and R. that is,

$$\Psi = \Theta(\theta). \ \Phi(\phi). \ R.(r)$$
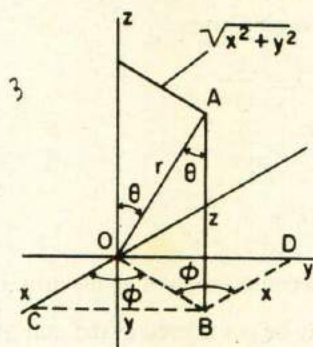
Fig. 1—19. The radial vector in three-dimensional space.

Where Θ is a mathematical expression of the variation of electron density as the angle θ varies. Φ is a mathematical expression of the change of electron density as the angle ϕ varies. R is a mathematical expression of the variation of electron density as the distance r increases to different distances from the nucleus of the atom.

Thus the behaviour of electron as a wave is described by a wave function represented by ψ. In the case of a standing wave described by an electron in an atom the probability of finding the electron at any point in an orbital is proportional to the square of its wave function, ψ^2. Mathematically, the probability $P = c^2 \psi^2$, where c is a constant. Any event that is sure to occur is given a mathematical probability = 1. Hence the probability of the electron to be in its orbital is $P = 1$. Under this condition the orbital is *normalized*. The normalization of orbital is expressed by the function

$$c^2 \int \psi^2 \, dv = 1$$

Where dv = small increase in the volume of electron density and c = constant which, in this case = 1, Since $v = 4/3 \ \pi r^3$, then $dv = 4 \ \pi r^2 dr$. Hence

$$c^2 \int 4\pi r^2 \psi^2 \, dr = 1$$

If the separate orbitals in the same atom are normalized each containing one electron so that each orbital is independent, then the orbitals are said to be

orthogonal. Now, since atoms are considered to be spherical the electron density of any atomic orbital is represented as being in a spherical volume. Thus it is possible to sketch three-dimensional units of space within which the electron may, most probably, be found in a state corresponding to an orbital. In other words, it is in the space through which the charge of the electron is distributed in the orbitals in terms of the radial function and angular functions.

Alternatively, the electron may be imagined as a charged cloud carrying negative electricity and spreading over a relatively large area. The charged cloud is thick in region of high probability and more diffuse in low probability region. No experiment has yet been devised to prove or distinguish the above interpretation, although the "charge cloud" interpretation is more widely used.

There are various ways of representing electron charge cloud or probability of electron density around a nucleus. The simple hydrogen atom may be shown diagrammatically as in Fig. 1—20.
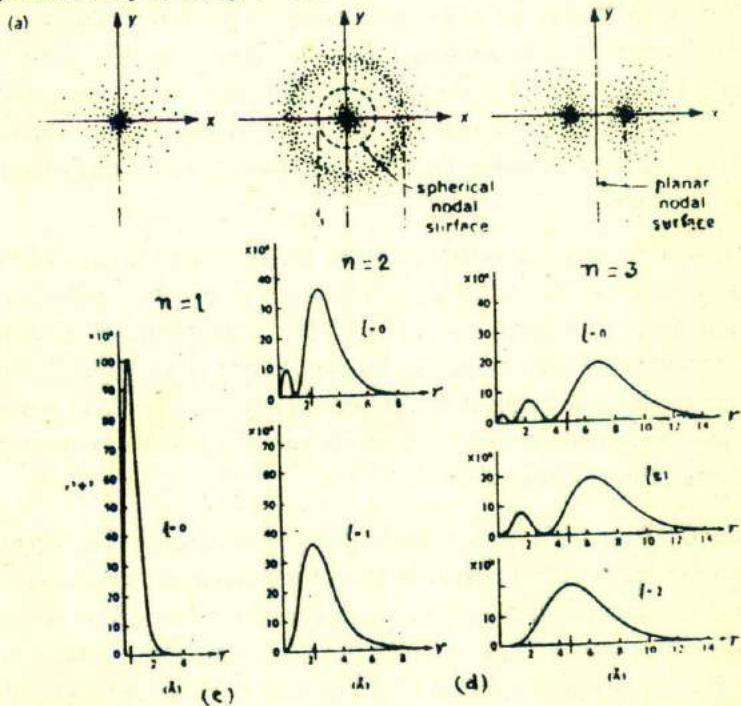
Fig. 1—20. Electron distribution in the hydrogen atom ($n = 1$). The charge cloud distribution (a). Probability density against distance from the nucleus (b). Probability density per unit volume against distance from the nucleus (c) The radial distribution of electron density for a 2s and 2p electrons (d).

The electron charge cloud has its greatest density nearest to the nucleus and becomes diffuse as the distance from the nucleus increases. Thus the probability of finding an electron in the hydrogen atom (s orbital, $n = 1$) is greatest in the small volume surrounding the nucleus in space. But there is also a finite probability that electron will be found away from the nucleus indicated by the diffuse dots in Fig. 1—20 (a). The same effect is represented in Fig. 1—20 (b) where the probability of electron density Ψ^2 has been shown graphically against the distance from the nucleus. The shape of the curve indicates that the electron is strongly attracted by the nucleus. When the electron charge cloud per unit volume $4\pi r^2 \Psi^2$ is plotted against the distance from the nucleus, the probability is less close to the nucleus, since less space is available—attains a maximum point at a particular distance and then gradually falls off as the distance increases. This effect is represented in Fing. 1—20 (c) (for $n = 1$). In the case of hydrogen atom the total probability of finding an electron at all points (radially) is greatest when the distance from the nucleus, r, becomes equal to the Bohr radius. The plot shows a maximum at 0.53Å which is the Bohr radius for hydrogen atom. In the case of $n = 2$, as represented in Fing 1—20 (d), the two maxima correspond to the 2s energy level. However, the curve corresponding to 2p energy level has a single maximum.

Although the large maximum probability for locating an electron in the 2p level is closer to the nucleus than the maximum probability for finding the electron in the 2s level, as shown in Fig. 1—20 (d), an electron in the 2s level is at a slightly lower potential energy than an electron in the 2p level. This is due to the greater penetration of a 2s electron as compared to an electron in 2p level. Since there are three 2p orbitals, an electron in any one of the three states has the same probability disance.

Atomic Orbitals : It is possible to sketch three-dimensional patterns of space within which the electron may be found corresponding to an orbital. These are the spaces through which the electron moves over a long period of time or the charge of the electron is distributed in those spaces corresponding to the orbital. Thus the charge distribution for s type atomic orbitals are spherical and possess no directional characteristics because in these orbitals only the radial wave function is involved. It is more proper to consider the 1s charge distribu-

tion to be a hollow sphere with maximum of charge at a distance of $r = 0.53$ Å from the nucleus. The charge distribution for an electron in 2s orbital resembles two concentric hollow spheres with a minimum (node) in-between. But all the s type atomic orbitals are represented as a single sphere as shown in Fig. 1—21.
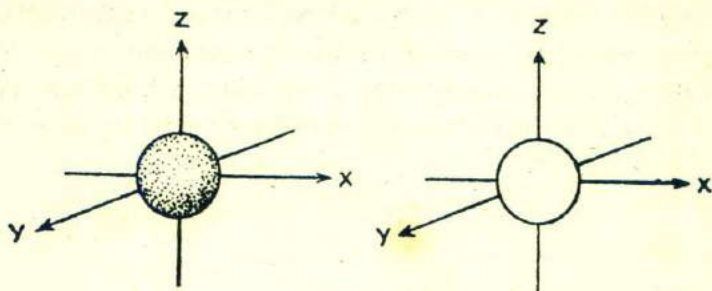
Fig. 1—21. Atomic s orbitals.

The charge distributions for electrons in p orbitals are directed in space and in terms of the Cartesian co-ordinates x, y and z-axes in such a way that the orbitals consist of two ellipsoids lying across each axis giving a dumb-bell shape. The directional characteristics arise because both the radial and angular wave functions are involved. The p orbitals are designated by subscripts p_x, p_y and p_z corresponding to x, y, z cartesian coordinates (Fig. 1—22).
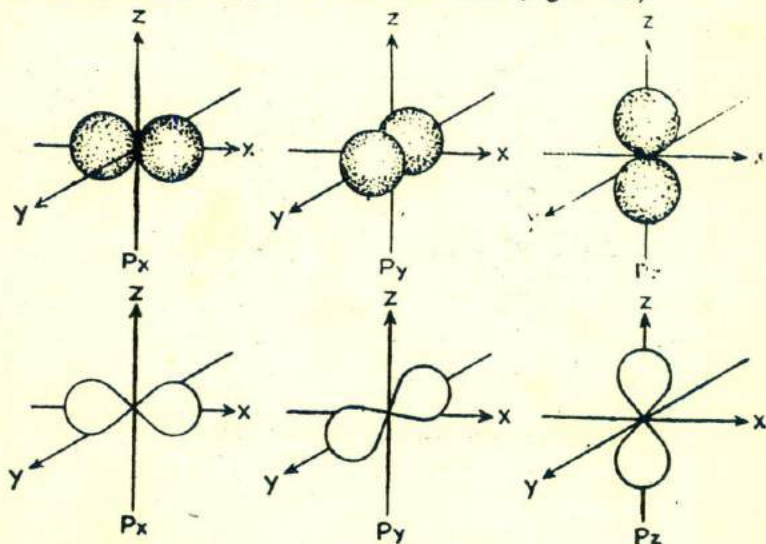
Fig. 1—22. Directional characteristics of atomic p orbitals.

The charge distribution corresponding to the five d orbitals are rather comples. Three of these consist of four lobes, each directed in between the axes xy, yz, and xz planes respectively. These are designated as d_{xy}, d_{yz} and d_{xz} orbitals. Another d orbital consists of four lobes directed along the x and y axes. This is designated as dx^2-y^2 orbital. The other d orbital consists of two lobes directed along z-axis but is encircled by a ring of charge distribution in the xy plane. This is called d_z^2 orbital. The different d orbitals are shown in Fig. 1—23.
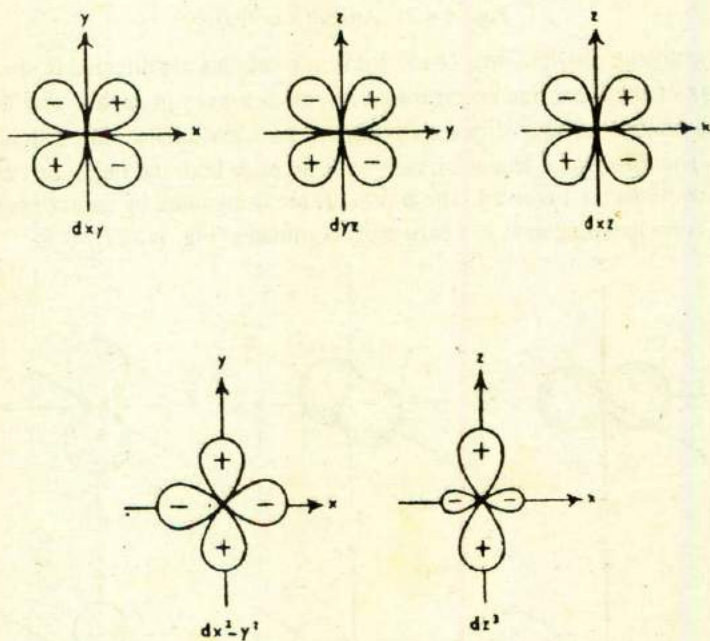
Fig. 1—23. Cross-section diagrams of d orbitals

THE SCHRÖDINGER EQUATION, THE QUANTUM NUMBERS AND ENERGY LEVELS

In 1926, Erwin Schrödinger developed an equation consistent with the wave properties of the electron. His basic equation was similar to an equation that is used to describe standing waves in general.

When the concepts of the Heisenberg uncertainty principle, the electron as a standing wave, and the de Broglie relationship are combined, the result is the wave-mechanical theory of the atom, expressed usually in the form of the Schrödinger wave equation :

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi + \frac{8\pi^2 m}{h^2}(E-U)\psi = O$$

E is the sum of the kinetic energy and the potential energy of the atom. U is the potential energy of the atom, m is the mass of the electron, h is Planck's constant, and ψ is the wave function describing the electron in a particular orbital. For example, the wave function for an electron in a 1s orbital is

$$\psi = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2} e^{-r/a_o}$$

where a_o is the Bohr radius with n = 1) and r is any radius from the nucleus.

The differential $\dfrac{\partial^2}{\partial x^2}+\dfrac{\partial^2}{\partial y^2}+\dfrac{\partial^2}{\partial z^2}$

is a mathematical operation from the calculus. $\dfrac{\partial^2 \psi}{\partial x^2}$, for example, is read, "the second derivative of ψ with respect to the x coordinate of a three-dimensional system". Performing this mathematical operation gives the change in the rate of change of ψ along the x coordinate.

Although to know the intricacies of the mathematics of the Schrödinger equation is important in checking the limitation of this model of the atom, perhaps more important here is to understand the utility of the theory in explaining chemical properties of matter.

Solving the Schrödinger equation yields energy levels and wave functions for electrons in particular orbitals in an atom, specifically in the hydrogen atom. Each orbital can contain a maximum of two electrons and is a different stable energy level which these electrons can have within the atom. The student should not

confuse these orbitals with the Bohr orbits. In the first place, the orbitals have nothing to do with the path of an electron; if an electron is in a particular orbital, this simply means that the electron has a particular energy and a probable location within the atom. But the orbital information does not specify the movement of the electron. In the second place, the energies of the orbitals are subdivisions of the energies of the Bohr orbits.

Probabilities of locating electron within an atom and quantum numbers are two properties of orbitals which emerge from the solutions of the Schrödinger equation. Quantum numbers are used to describe the energy and the assignment of an electron to possible orbitals within the atom. Probabilities give the chance of finding an electron at a given location within an atom. The actual solution of the Schrödinger equation involves rather sophisticated calculus and consequently, we shall not solve it.

Questions and Problems

1.   How do you prove the existence of electrons in an atom?

2.   Devise an experiment to show that electrons carry negative charges.

3.   What is a proton and a neutron?

4.   (a) Name three important fundamental particles of atom and give short description of each.

      (b) Explain the solar system atom model and construct models of the following atoms :-

      (i) Neon, (ii) Sodium, (iii) Beryllium.

5.   How will you prove the presence of a nucleus in an atom?

6.   Write short notes on :-

      (a) Atomic number ; (b) Nuclear charge.

7.   What is meant by an excited atom? How could you excite an atom?

8.   How will you define a Bohr atom model?

9.   Explain energy levels of electrons in atoms.

10.   What is the relationship between spectrum of an element and its atomic structure? What are quantum numbers?

11. Show the distribution of electrons in the atoms of Be (4), Mg (12) and Ca (20).

12. Give an account of the structure of atoms with reference to the arrangement of orbital electrons.

    Explain the term "Quantum numbers".

13. Why four quantum numbers are necessary to describe an electron in an atom?

14. What is the origin of the s, p, d and f types of electrons?

15. What is the maximum number of electrons in 5f and 3f energy levels?

16. Why hydrogen atom should give so many lines in its spectrum although there is only one electron in hydrogen atom?

17. Calculate the wavelength of Hα & Hβ using the round figure value of $R = 109, 300 \ cm^{-1}$.

18. What is Pauli Exclusion Principle? How does it govern the distribution of electrons in the atoms of H and Na?

19. Show the distribution of electrons in Ca (20) and Cr (24).

20. The atoms contain electrically charged particles, yet they are neutral. Explain.

21. What is meant by the following notations : $1s^1$, $2p^5$, $3d^0$, $4f^{10}$, $3p^3$ and $3d^5$?

22. What do you understand by the term "Isotopes"? How will you write symbolically the isotopes of chlorine and hydrogen?

23. Write a concise account of the modern concept of the structure of atoms with particular reference to the distribution of orbital electrons.

24. Why are four quantum numbers necessary to formulate the electronic configuration of atoms? Show the relations amongst them.

25. Write short note on Fundamental Particles.

26. Give an account of Quantum Numbers.

27. Write brief account of :
    (a) Bohr's concept of atomic model and the origin of spectra in a hydrogen atom.

    (b) Pauli Exclusion Principles.

28. (a) Give a brief account of the modern concept of the structure of atoms.
    (b) Explain the terms :
    Pauli Exclusion Principle; Quantum Numbers; Planck constant.

29.   (a) What are quantum numbers? Indicate their significance. (b) Briefly discuss
       the principle for the building up of atoms in respect of the arrangements of
       extranuclear electrons. (c) Write the electronic configurations of Cr ($Z = 24$)
       and Ce ($Z = 58$).

30.   Draw the sketches of p and d orbitals showing the directional characteristics.

31.   For the proton and electron the e/m are respectively 2.88×10^{14} esu/g and
       5.28×10^{17} esu/g. Calculate masses of the proton and electron.

32.   Why has thé Bohr model of the atom become outmoded ?

33.   Calculate the wave length of light emitted from H for the electronic transition
       from energy level n $= 3$ to n $= 2$ using R $= 109600$ cm^{-1}.

34.   A bar of iron at high temperature is red. Is the light emitted from the glowing
       bar due to electrons moving from low energy to high energy or dropping from
       a high energy to lower energy levels ?

35.   Derive relationships to show that frequency varies with energy and also
       wavelengths varies with energy.

THE CHEMICAL BOND

The Concept of Chemical Bond

When it is considered that a molecule is formed by combination of two or more atoms either of the same or of different elements the question naturally arises as to what are the forces which ordinarily hold the atoms together in a molecule. Before the discovery of the electronic structures of atoms the nature of the forces holding atoms together in molecules or crystals was mysterious and generally chemical bond was considered to be formed due to the combining capacity of different elements with atoms of hydrogen or oxygen or chlorine. This combining capacity or "valency" was considered to be the number of other atoms with which an atom of an element can combine. The classical concept of chemical bond formation has been largely replaced by the electronic concepts and the modern progress in the field of structural chemistry presents a great landmark in the advancement of our knowledge regarding the structure of matter.

The Electronic Concept

The combination or joining together of two atoms, such as that of H to H_2 appears at the first sight a mysterious phenomenon, if not an impossible one, since both the atoms are electrically neutral and should not combine with each other because of repulsion between the electron clouds of the two H atoms.

It is to be remembered that electrons play a very important role in the formation of chemical bonds. These are the electrons in the outermost energy level which undergo rearrangement or regrouping to form more stable arrangement. The electronic concept of chemical bond was advanced by W. Kossel and G. N. Lewis in 1916 independently.

The Fundamental abilities of the atoms of various elements to combine with each other depend largely upon the extent to which their electron levels are

completed. It has been considered that since the inert gases are chemically inactive, the atoms of the elements containing a total of 2, 10, 18, 36, 54 and 86 extra-nuclear electrons apparently impart a greater electronic stability than elements intermediate between them.

As regards the electronic arrangements we have classified atoms into four groups : (i) Atoms with complete electronic groupings. (ii) Atoms having all but the outermost electronic trouping incomplete. (iii) Atoms having two outermost electron levels incomplete. (iv) Atoms with three outermost energy levels incomplete. This concept was based on inert gases' electronic configurations which have incomplete levels except He and Ne.

The inert gases with stable electronic configurations do not normally enter into chemical combination and have two electrons (in the case of He) and eight electrons (in the case of other inert gases) in the outermost electron levels. Therefore, these electron arrangements represent complete groupings. Electrons containing less than eight electrons in the outermost energy level are incomplete and belong to the second type. The third and the fourth type of atoms having two and three outermost electron groupings incomplete enter into chemical combination in a variety of ways which are discussed latter.

In effect, the following principles may be enunciated to understand the early electronic theory of chemical bonding.

Principles of Electronic Theory of Chemical Bond :

(1)   Chemical combination between atoms of the same or different elements takes place due to the tendency by the outermost electron groups to attain the stable arrangement of inert gases.*

(2)   The attainment of inert gas electron configuration may take place by complete transference of electrons from one atom to another. The resulting electrically charged atoms (or ions) are held together by electrostatic force of attraction. The chemical bond so formed is known as electrovalent or *ionic bond.*

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*   It needs some extension because these also include other stable electronic groupings beside those of inert gases which is more generally applicable.

(3) The attainment of inert gas configuration may occur by sharing of electrons (in pairs) between two atoms. The chemical bond so formed is called *covalent bond*.

(4) The attainment of electron groupings of inert gases may also happen by both transference and sharing of electrons between atoms in pairs. The bond so formed is known as *coordination bond*.

The Ionic Bond

The ionic bond is formed when one or more electrons are transferred from one atom to the other to complete the orbitals in each case. In both cases, the electronic arrangements of the resulting ions is identical to that of an atom of one of the inert gases. Such elements are generally those which immediately precede and those which closely follow the inert gases in the periodic classification. Table 2.1 shows the electronic arrangements of neon and argon and some of the elements that immediately precede and follow them in the Periodic Table.

Table 2.1. Electronic arrangement of inert gases and adjacent elements.

Elements	At. No.	Electron arrangement
O	8	$1s^2\,2s^2\,2p^4$
F	9	$1s^2\,2s^2\,2p^5$
Ne	10	$1s^2\,2s^2\,2p^6$
Na	11	$1s^2\,2s^2\,2p^6\,3s^1$
Mg	12	$1s^2\,2s^2\,2p^6\,3s^2$
S	16	$1s^2\,2s^2\,2p^6\,3s^2\,3p^4$
Cl	17	$1s^2\,2s^2\,2p^6\,3s^2\,3p5$
Ar	18	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6$ --
K	19	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$
Ca	20	$1s^2\,2s^2\,2p^6\,4s^2\,3p6\,4s^2$

It is noted from Table 2.1 that the gas neon (Ne) has 8 electrons in its outer energy level. The sodium atom which follows neon has the electronic structure of neon plus an electron in the next higher energy level. When the sodium atom loses the extra electron, it would then have an electronic arrangement identical to

that of neon (2,8) and sodium atom will form positively charged ion because it has now 11 protons but 10 electrons. This may be represented more simply as,

$$Na^\circ\ (1s^2\ 2s^2\ 2p^6\ 3s^1)\ -\ 1e\ \longrightarrow N\ ^{+}a(1s^2\ 2s^2\ 2p^6)$$
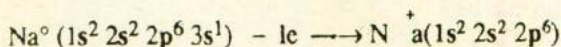
the dot $(^\circ)$ in Na represents the single electron in the outermost level $(3s^1)$

Similarly, the formation of negatively charged fluoride ior (F^-) from neutral fluorine atom F, having 7 electron in the outermost energy level and placed just before Ne in the Periodic Table may be illustrated as follows :

$$F\ (1s^2\ 2s^2\ 2p^5) + 1e\ \longrightarrow\ F^-\ (1s^2\ 2s^2\ 2p^6)$$
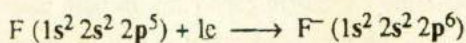
Thus the fluorine atom by entering into chemical reactions gains one electron and the electronic arrangement of the resulting fluoride ion (F^-) is identical to that of neon. The fluoride ion has one electron more than the fluorine atom :

$$\text{:}\overset{\bullet\bullet}{\underset{\circ\circ}{F}}_\circ\ +\ 1e\ \longrightarrow\ \text{:}\overset{\circ\circ}{\underset{\bullet\bullet}{F}}\text{:}\ ^-$$
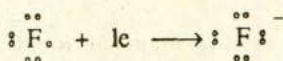
Now, when a sodium atom and a fluorine atom are brought together, the sodium atom loses one electron to form a stable positive ion, Na^+, and the fluorine atom gains this electron to form a stable negative ion, F^-. The two ions Na^+ and F^- are now held together by the electrostatic force of attraction to for─ molecule of NaF. Thus the chemical bond formed between oppositely cha─ ions is known as ionic bond that hold the resulting compound. It is to be n─ that the transfer of electron from the electron cloud of sodium atom to t─e electron cloud of fluorine atom constitutes the chemical change represented by the equation,

$$Na^\circ\ +\ \overset{\times\times}{\underset{\times\times}{\times\,F\,\times}}\ \longrightarrow\ Na^+\left[\overset{\times\times}{\underset{\times\times}{\text{:}F^\times_\times}}\right]^-\ \longrightarrow NaF$$
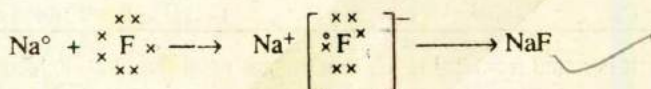
Similarly, the bond between magnesium and oxygen in magnesium oxide (MgO) involves two electrons.

Mg $1s^2\, 2s^2\, 2p^6\, 3s^2$

Mg^{+2} $1s^2\, 2s^2\, 2p^6$ (Neon structure)

O $1s^2\, 2s^2\, 2p^4$

O^{-2} $1s^2\, 2s^2\, 2p^6$ (Neon structure)

$$^{\circ}Mg^{\circ} + \overset{\circ\circ}{\underset{\circ\circ}{:\ddot{O}:}} \longrightarrow Mg^{+2} + \left[:\overset{\circ\circ}{\underset{\circ\circ}{\ddot{O}}}:\right]^{-2} \longrightarrow MgO$$
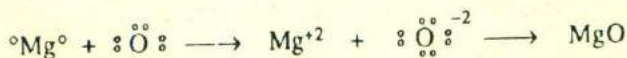
Thus when magnesium atom enters into combination, it gives up 2 electrons to form a dipositive magnesium ion, Mg^{+2}, which has an electronic arrangement identical to that of neon. The oxygen atom by gaining two electrons becomes O^{-2} ion again having the neon arrangement. When magnesium and oxygen react with each other, two electrons are transferred from magnesium atom to oxygen atom and the resulting $Mg^{+2}O^{-2}$ or MgO are, therefore, held together by ionic bond.

Extending the arguments to other compounds such as CaS and KCl, it can be proved that Ca^{+2} and K^+ assume the electronic configuration of argon (2, 8, 8) by losing 2 electrons and 1 electron respectively. The sulphur atom takes up 2 electrons and then has an electronic arrangement identical to that of argon. Chlorine atom gains 1 electron from potassium and has the electron configuration of argon. Hence in CaS, positive Ca^{+2} ion is combined to S^{-2} ion by means of ionic bond. Similarly, K^+ ion and Cl^- ion combine by means of ionic bond to form KCl. In short, the electrovalent bond or ionic bond results from a coulombic attraction between the excess charges on the oppositely charged ions.

Similarly, K_2S and $CaCl_2$ may be represented as :

$$K^+ \qquad \left[:\overset{\times\times}{\underset{\times\times}{S}}\times\right]^{-2}$$
$$K^+$$

$$K_2S$$

$$Ca^{+2} \quad \begin{array}{l}\left[\overset{\times\times}{\underset{\times\times}{\times\ Cl\ \times}}\right]^{-} \\[8pt] \left[\overset{\times\times}{\underset{\times\times}{\times\ Cl\ \times}}\right]^{-}\end{array}$$

$$CaCl_2$$
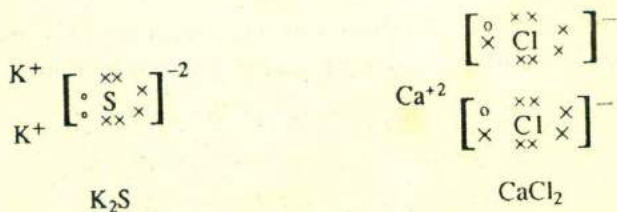
The cations with inert gas configurations are generally those of the following metals.

Li^+,	Be^{+2}			He structure
Na^+,	Mg^{+2},	Al^{+3}		Ne structure
K^+,	Ca^{+2},	Sc^{+3}		Ar structure
Rb^+,	Sr^{+2},	Y^{+3},	Zr^{+4}	Kr structure
Cs^+,	Ba^{+2},	La^{+3},	Ce^{+4}	Xe structure

The anions having inert gas structure are mainly the halides, oxides and nitrides.

Halides	F^-	Ne structure
	Cl^-	Ar structure
	Br^-	Kr structure
	I^-	Xe structure
Oxides	O^{-2}	Ne structure
Nitrides	N^{-3}	Ne structure

Limitations of Ionic Bond.

(1) It is seen that there is a limit to gain and loss of electrons by an atom to form positive and negative ions mainly because of the energy considerations. When a neutral atom loses more than one electron, more work will be required to remove them against the attraction of positive nucleus. Similarly, gaining of successive electron makes the negative charge on the negative ion greater and thereby oppose the approach of further electrons. Thus F will form F^- but not F^{+7}; similarly, N^{+3} is formed but not isolated N^{+5}. Also C^{+4} and C^{-4} are normally not formed. Ions carrying high charges are rare because of the large amount of energy involved in electron transfer.

(2) Many cations do not always have inert gas structure. There are cations which have the outer $s^2 p^6 d^{10}$ structure instead of $s^2 p^6$ groups. Thus

Cu^+,	Zn^{+2},	Ga^{+3}	have outer $3s^2 3p^6 3d^{10}$ groupings.
Ag^+,	Cd^{+2}	In^{+3},	Sn^{+4} have outer $4s^2 4p^6 4d^{10}$ groupings
Au^+,	Hg^{+2},	Tl^{+3},	Pb^{+4} have outer $5s^2 5p^6 5d^{10}$ groupings

These are not much stable and show variable structures

Cu— $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

Cu^+— $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

Cu^{+2}--$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$
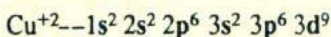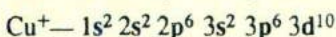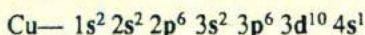
Similarly, Ag^+, Ag^{+2}, Au^+ Au^{+3} etc. are also formed. Ag^+ and Au^{+3} are most stable cations in the group.

(3) The electron grouping $s^2 p^6 d^{10}$ in Zn^{+2}, Cd^{+2} and Hg^{+2} appear to be stable since no extra electron is lost from these cations.

(4) Transition metal cations show variable charge and do not have either inert gas $s^2 p^6$ or 18 electron $s^2 p^6 d^{10}$ structures.

Fe— $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Fe^{+2}— $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

Fe^{+3}— $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
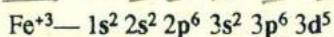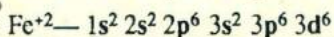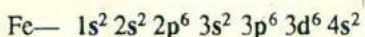
Similarly, Co^{+2}, Co^{+3}, Mn^{+2} etc. have variable charges.

General Properties of the Ionic Bond

Since the ionic bond results from the electronic attraction between the positive and negative ions, the strength of the bond so formed can be calculated roughly from the product of the charges on the ions and distance between the effective centres of the ions. The ionic bond is neither rigid nor directed. The electrostatic field of the ions extend in all directions. Consequently, a crystal of ionic compound is actually a cluster or aggregate of ions. The molecule is also called polar since it develops a positive and a negative pole or electrically charged ends separated by a finite distance. The following important properties of ionic bond may by mentioned:—

(1) **Crystalline State** : Ionic crystals are composed of cluster of ions in the crystal lattice or the atomic network and produce geometric shapes because of the arrangements of ions in space. For instance, in sodium chloride each sodium ion is surrounded by six choloride ions and each chloride ion is surrounded by six sodium ions in the cubic crystal lattice or atomic network in space. The proof is based upon the diffraction of x-rays produced by the crystals of sodium chloride.

This structure of sodium chloride has been shown in Fig. 2—1 and gives cubic crystals.

● Na$^+$ ion

◯ Cl$^-$ ion

(a)

(b)
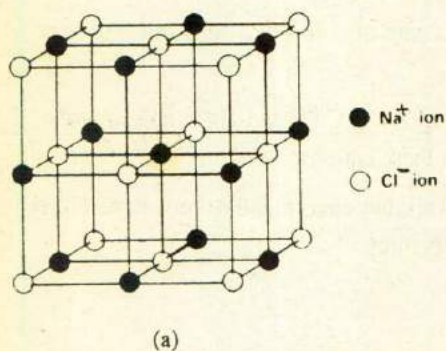
Fig. 2—1 (a) The crystal pattern of sodium chloride
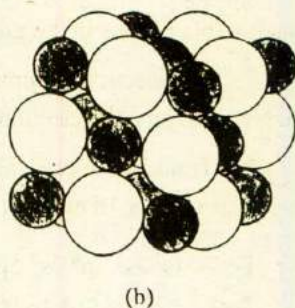
Fig. 2—1 (b). The packing of the ions in sodium chloride.

(2) *Electrical Conductivity* : Ionic compounds either in the fused state or in solutions are good conductors of electricity. It may be easily visualized that in the fused state or in solutions, ions are dissociated and because the restraining forces of the crystal lattice are no longer present, the ions are free to move under the influence of electric field. Such solutions or melts are good conductors of electricity.

(3) *Isomorphism* : Ionic crystals having the same crystalline structures have been related to the electron arrangements of the ions in the solids. The different compounds containing ionic bonds have ions which assume the same electron arrangements in their molecules and hence show similar crystalline forms. For instance NaF is isomorphous with MgO, and K_2S has the same crystalline form as that of $CaCl_2$.

$$Na^+ \qquad 1s^2\,2s^2\,2p^6 \qquad F^- \qquad 1s^2\,2s^2\,2p^6$$

$$Mg^{+2} \qquad 1s^2\,2s^2\,2p^6 \qquad O^{-2} \qquad 1s^2\,2s^2\,2p^6$$
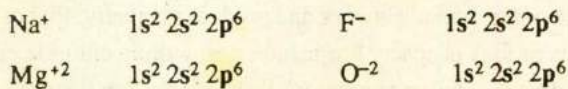
Similarly, in the case of K^+, S^{-2}, Ca^{+2} and Cl^- ions, the electron groupings are identical.

(4) Dielectric Constant : When a dipolar or polar molecule is placed in an electrostatic field the positive end of the dipole is directed towards the negative pole of the electric field and *vice versa*. The oriented dipole oppose the

<div align="center">Field off   Field on</div>
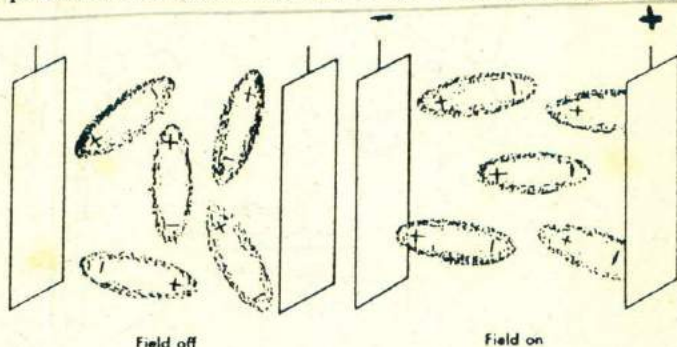
Fig. 2—2. Orientation of dipolar molecules in an electric field.

field and the intesity of the electric field is reduced. The reducing tendency is measured by the dielectric constant or the specific inductive capacity of the polar substance. The substances containing ionic bonds have high dielectric constant.

(5) Melting and Boiling Points : Molecules which possess dipoles may show a tendency to "dipole association" on account of mutual attractions of the opposite poles. Thus in the ionic crystals the ions exert a powerful electrostatic force on each other. The tendency to dipole association gives rise to "abnormal" behaviour in liquids and since the molecules with strong dipoles have stronger mutual attractions, a considerable amount of work is needed to separate them from one another. Thus it is natural to suppose that ionic compounds have high melting and boiling points. For instance, NaCl boils at 1470°C whereas the nonionic (covalent) CCl_4 bolis at 77°C only. It is to be noted that on heating. the kinetic energy of the particles within the solid is increased. The increased vibrations of the particles overcome the forces holding the particles together and they break away from their fixed positions.

(6) Reactivity : The reactions between ionic compounds generally take place with great speed, for instance, during the precipitation reactions in aqueous solution. Drastic methods are required to bring about reactions between non-ionic compounds.

—5

(7) *Solubility* : Ionic compounds are generally more soluble in polar than in non-polar solvents. For instance, sodium chloride dissolves in water but
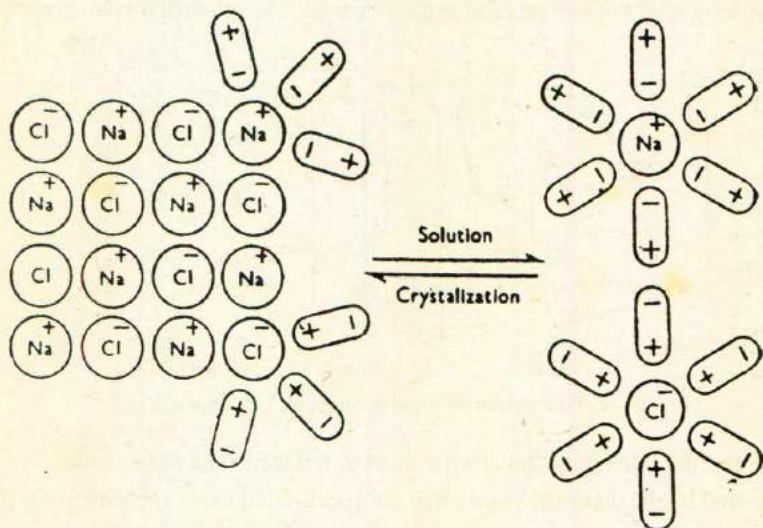
Fig. 2—3. Schematic diagram of the solution process of an ionic compound, NaCl.

not in benzene. Similarly, naphthalene dissolves in benzene but not in water. In the process by which an ionic solid of the type of NaCl enters into solution in water, the molecules of water, because of their high dipole moments, align their negative pole towards the positive ions (Na^+) and the positive pole of H_2O towards the negative ions (Cl^-) at the surface of the crystal. The dipole forces exerted by the oriented water molecules render the inter– ionic attraction within the crystal much weaker than before and some of the ions are thereby pulled away into solution. Assuming that six water molecules are attached to each ion, the schematic representation of the phenomenon of solubility of ionic compounds may be represented as in Fig. 2—3.

The Covalent Bond

Lewis Theory : Atoms may combine with each other chemically by sharing of electrons. A chemical bond of this type is called a covalent bond, and compounds containing these bonds are called covalent compounds. This type of chemical bond was first suggested by G. N. Lewis in 1916.

Atoms of different elements or atoms of same element may enter into combination by sharing of electrons to form covalent bond. It may be noted that when the atoms of the same element combine by covalent bond, molecules of the element are formed. When atoms of different elements are covalently bonded, they give rise to molecules of compounds.

Sharing of electrons between atoms always occurs in pairs, and in each pair of shared electrons one is contributed by each atom. Covalent bonds are, therefore, also known as electron pair bonds. One pair of electrons corresponds to a single bond, two pairs to double bond, three pairs of shared electrons to triple bond.

For example, when two hydrogen atoms combine to form a hydrogen molecule, the two hydrogen atoms contribute its single electron to form a pair of electrons shared by both. The resulting electronic arrangement of each hydrogen atom thereby attains the stable electronic arrangement of helium, He(2). The shared electron pair constitutes the covalent bond between the two atoms. The $1s^1$ electron of hydrogen atoms becomes paired up and may be simply represented as,

$$H° + \times H \longrightarrow H \overset{\times}{\cdot} H \quad or \quad H—H \quad (H_2)$$
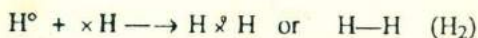
Similarly, fluorine molecule is formed by combination of two fluorine atoms. Fluorine atom having electron arrangement of $1s^2 2s^2 2p^5$ has one electron less than the neon atom, $1s^2 2s^2 2p^6$. Hence if two fluorine atoms combine, one electron from each paired up atoms is shared in common by both the atoms to produce the stable electronic arrangement of neon for the two fluorine atoms.

$$\overset{\circ\circ}{\underset{\circ\circ}{\colon F°}} \quad + \quad \overset{\times\times}{\underset{\times\times}{\times F \times}} \quad \longrightarrow \quad \overset{\circ\circ}{\underset{\circ\circ}{\colon F}} \overset{\times\times}{\underset{\times\times}{\times F \times}} \quad or \quad F—F \quad (F_2)$$
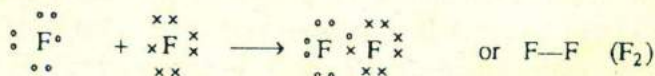
In both the above examples of the formation of H_2 and F_2 molecules, only one pair of electrons are shared. However, the formation of oxygen and nitrogen molecules by the electron pair bonds can be represented with the help of two pairs and three pairs of electrons respectively. The underlying principle, as discussed before, is the attainment of the stable electronic configurations of the inert gas. Thus,

$$\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}} + \overset{\times\times}{\underset{\times\times}{\times N}} \longrightarrow \overset{\times\times}{:}N\overset{\times}{\underset{\cdot}{\cdot}}\overset{\times}{\underset{\cdot}{\cdot}}\overset{\times}{N}\overset{\times}{\underset{\times}{}} \qquad N \equiv N \qquad (N_2)$$

$$\overset{\cdot\cdot}{\underset{\cdot\cdot}{:O}} + \overset{\times\times}{\underset{\times\times}{O\times}}\times \longrightarrow \overset{\cdot\cdot}{:O:} \overset{\times\times}{\underset{\times}{\times O\times}} \qquad O = O \qquad (O_2)$$
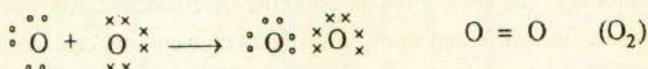
The covalent bond may also link together atoms of different elements to form a molecule of a compound. The combination of a hydrogen atom with an atom of chlorine to form a molecule of HCl may be shown as follows :

$$H^\circ + \overset{\times\times}{\underset{\times\times}{\times Cl}}\overset{\times}{\underset{\times}{}} \longrightarrow H \overset{\circ}{\underset{\times}{}} \overset{\times\times}{\underset{\times\times}{Cl}}\overset{\times}{\underset{\times}{}}$$
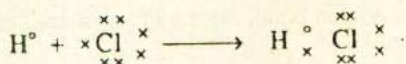
In the molecule of HCl, both H and Cl are surrounded by an electron cloud like that of helium and argon atoms respectively.

An atom can combine by sharing electrons with more than one atom. For instance, in the case of methane, CH_4, ammonia, NH_3, and H_2O, carbon, nitrogen and oxygen have combined with 4, 3 and 2 atoms of hydrogen respectively as illustrated below :

$$\begin{array}{ccc} H & H & H \\ \overset{\times\circ}{H\overset{\circ}{\underset{\circ}{\times}}C\overset{\times}{\underset{\times}{\circ}}H} & H\overset{\times}{\underset{\times}{\overset{\times\circ}{N}}}\overset{\times}{\underset{\times}{}} & \overset{\times\circ}{\underset{\times\times}{\times O\times}}H \\ H & H & \end{array}$$
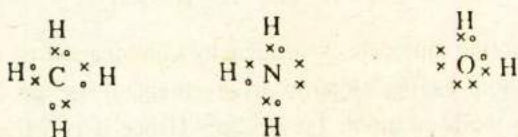
Each of the atoms in CH_4, NH_3 and H_2O has a stable electronic arrangement similar to that of an inert gas. It may be noticed that in NH_3 molecule, there is one pair of electrons which are not shared. These are of special significance and will be discussed latter. Similarly, in the molecule of PCl_3 and SCl_2 each atom contributes an unpaired electron to form an electron pair shared by the two atoms indicated by lines —. Thus,

$$\begin{array}{cc} & Cl \\ & | \\ C\!-\!\overset{\times}{\underset{\times}{P}} & \\ & | \\ & Cl \end{array} \qquad \begin{array}{c} \overset{\times\times}{\times S}\!-\!Cl \\ | \\ Cl \end{array}$$
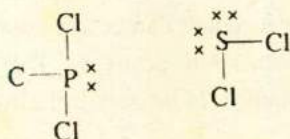
The electronic formula of carbon compounds are easily represented in terms of the formation of covalent bonds.

Limitations of Lewis Concept of Covalent Bond

1. The Lewis theory of covalency stressed tendency of reacting atoms to attain the electronic arrangement of inert gas. It, however, did not offer any reason why such a structure was stable. Also no explanation was available why a shared pair of electrons constituted a stable chemical bond. This theory did not present any real understanding of the nature of chemical bond.

2. There are a few molecules in which one of the atoms has not completed the required number of eight electrons. Thus in the case of BF_3, the boron atom has the electron configuration $1s^2 2s^2 2p^1$. It may be expected that boron would give up its three outermost electrons to give B^{+3}; but these electrons are tightly held. Instead boron shares three electrons with other atoms, say F, to form covalent BF_3. But boron atom does not conform to the stable configuration since it has only 6 electrons in BF_3.

$$F$$
$$\overset{\text{xo}}{F \overset{\text{o}}{\underset{\text{x}}{} B \overset{\text{o}}{\underset{\text{x}}{}} F}$$
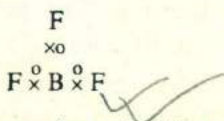
3. Similarly, electronic arrangements for molecules such as PCl_5, ICl_5, SF_6 do not correspond with the Lewis theory and apparently sharing of electrons in pairs involves more than 8 electrons (10 in PCl_5 and 12 in SF_6). Each line represents two electron bonds.
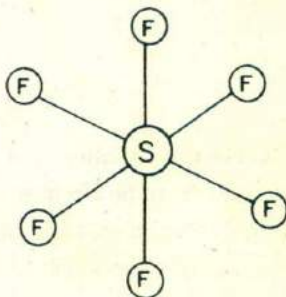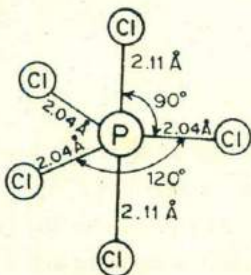
4. Lewis structure of oxygen atom does not explain the magnetic properties of oxygen molecule.

5. There are a large number of compounds where more than one Lewis structures can be shown, although only one compound exists, for example, N_2O, HN_3, CO_2 etc.

Coordination Bond

Langmuir Theory : In some molecules one of the atoms may supply both electrons, i. e., both the shared electrons come from the same atom. A covalent bond formed by the donation of a pair of electrons from one atom to another atom in the molecule is called a *coordination bond.*

The electron-dot formula of ammonia and boron trifluoride molecules are represented as,

Ex.

```
        H                    F
        ••                   ••
     H : N :              B : F
        ••                   ••
        H                    F
```
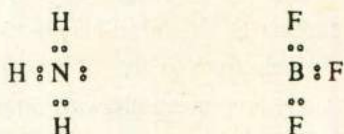
A pair of electron in NH_3 is available for further interaction. A pair of electron of this sort is known as "lone pair" . Since there are only 6 electrons around the boron atom in BF_3, it requires 2 electrons to attain the inert gas configuration. It is known experimentally that gaseous ammonia and gaseous boron triflouride react together to give solid compound $NH_3:BF_3$. This can be understood if nitrogen atom shares its lone pair of electrons with the boron atom.

```
      H  F                         H    F
      ••  ••                       |    |
   H : N : B : F        or      H—N→ B—F
      ••  ••                       |    |
      H  B                        H    F
```
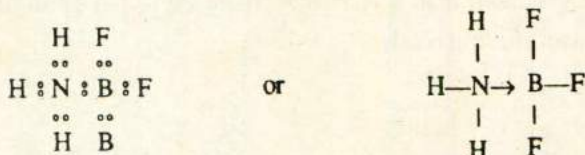
Donor-Acceptor Atoms : In the above case since nitrogen atom supplies or donates both the electrons to form a coordination bond, it is known as donor atom. The atom that accepts the lone pair of electron is known as acceptor atom. The bond between the donor and the acceptor atoms constitutes the coordination bond.

Coordination bonds occur very often in chemical compounds. As mentioned before, two conditions are necessary for the formation of this type of bond :-

(i)   One atom, molecule or ion must have an electron pair available for sharing with other atom by donation.

(ii) One atom, molecule or ion must be capable of sharing the lone pair of electrons by acceptance.

Electronic configurations of some donor and acceptor molecule are given below :-

Donors : $H : \ddot{F} :$, $: \ddot{F} : ^-$, $H : \ddot{O} : H$ $\overset{H}{\underset{H}{: \ddot{P} :}}^-$

Acceptors : H^+ $\overset{Br}{\underset{Br}{Br : Al}}$ $: \ddot{S}$
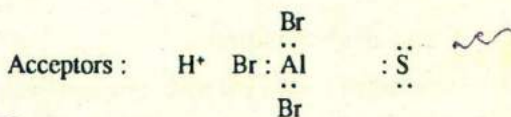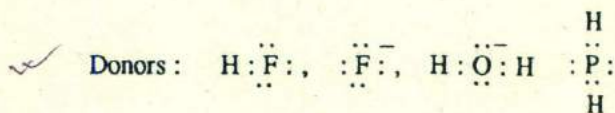
For example

Coordination bonds are particularly important in compounds containing oxygen. For example, a molecule of H_2SO_4 containing 2 H, 1S and 4 O have both covalent and coordinate bonds. The formulation may be represented as,

$$2H. + \overset{\times\times}{\underset{\times\times}{\times\, S\, \times}} + 4\ddot{O}: \longrightarrow H \overset{..}{\underset{..}{:} O} \overset{:O:}{\underset{:O:}{\overset{\times\times}{\underset{\times\times}{: S :}}}} O : H$$
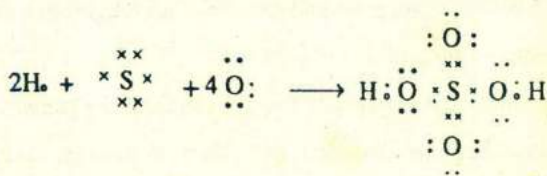
Notice that there are covalent bond between oxygen and hydrogen, covalent bond between sulphur and two oxygen atoms which are joined with the two hydrogen, and two coordination bonds between sulphur and the other two oxygen atoms. This is also represented as :

$$\begin{array}{c} O \\ \uparrow \\ H-O-S-O-H \\ \downarrow \\ O \end{array}$$
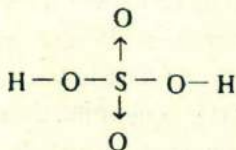
Ammonium ion also can be represented as formed by the combination of H^+ ion with ammonia molecule by coordination bond.

$$
\begin{array}{ccccccc}
& H & & & H & & \left[\begin{array}{c} H \end{array}\right]^+ \\
& | & & & | & & | \\
H\!-\!N: & + & H^+ & \longrightarrow & H\!-\!N:H^+ & \text{or} & H\!-\!N\!-\!H \\
& | & & & | & & | \\
& H & & & H & & H
\end{array}
$$

The electronic structure of $POCl_3$ is,

$$
\begin{array}{c}
:\overset{..}{\underset{\times\ \bullet}{Cl}}: \\[4pt]
:\overset{..}{\underset{..}{Cl}} \overset{\bullet}{\underset{\times}{}}\ P\ \overset{\times}{\underset{\times}{}}\overset{..}{\underset{..}{O}}: \\[4pt]
:\overset{\times\ \bullet}{\underset{..}{Cl}}:
\end{array}
$$
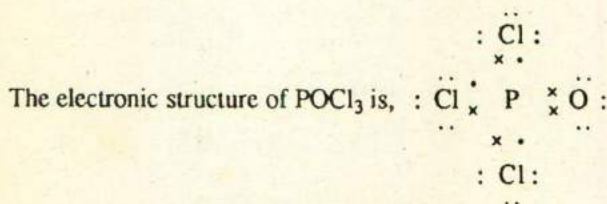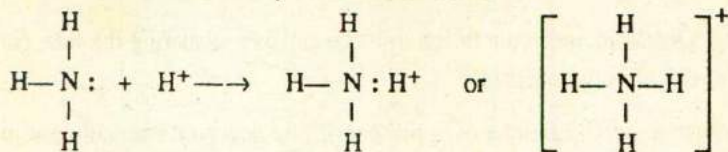
Recent Theories of Covalent Bonding

It can be easily visualized that when one hydrogen atom with its proton and electron combines with another hydrogen atom with a similar system of proton and electron, there are both forces of attraction and repulsion acting between them. The forces may be classified as :

(a) Repulsion between electron and electron.

(b) Attraction between electrons and protons of each hydrogen atom.

(c) Repulsion between proton and proton.

(d) Electronic interactions between the two electronic systems.

It is necessary here to illustrate the potential energy diagram for the formation of a chemical bond when two atomic systems such as those of two H atoms having their own charge clouds of electrons approach each other. When the two atoms are at infinite distance apart, there is no interaction between their electron clouds. As they approach each other and if there is no chemical bond formation, the energy required to force the two atoms to come close to each other will be very high as indicated by the curve I in Fig 2—4. This shows increasing external energy to force them nearer to each other. On the other hand, the formation of chemical bond between the two atomic systems through electronic interaction leads to the rearrangement of the electron clouds giving rise to the lowering of energy as shown by the curve II in Fig 2—4. The two atomic
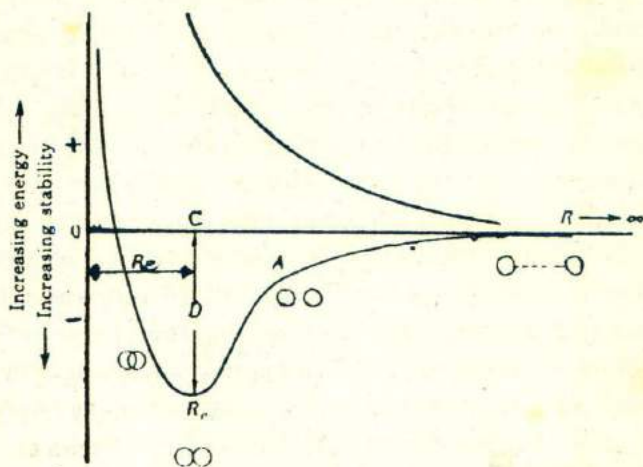
Fig. 2—4. Potential energy diagram for the formation of a diatomic molecule as a function of internuclear distance. Re = Internuclear distance at equilibrium on bond formation. D = Bond dissociation energy.

systems form a molecule with increased stability at the equilibrium internuclear distance between the two atoms. The lowering of energy occurs in chemical bond formation because of the rearrangement of electron clouds of the two systems. The formation of a stable molecule through initially excited states also involves lowering of energy as indicated by Fig. 2—5.
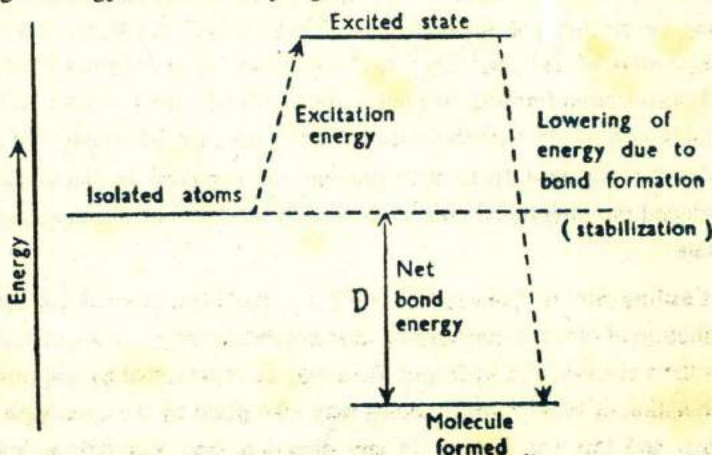
Fig. 2—5. Energy changes during the formation of bond.

Thus in the case of H_2, theoretical treatment predicts a cloud of two electrons with paired spins between two nuclei. In other cases also the treatment deals with the question of solutions as to how the clouds of valence electrons interact as the atoms are brought together. The treatment is highly mathematical and is beyond the scope of this elementary text book. The entire picture is based upon the wave mechanical approach considering the wave nature of electrons. Briefly it may be mentioned that two main methods have been developed in the application of wave mechanics to the electrons involved in chemical bonding. One of these advanced by Heitler and London in 1927 and extended by Pauling and Slater in 1931, accounts for the directional properties of covalent bond and is known as "valence-bond method". The other method was developed by Hund and Mulliken and postulates the formation of molecular orbitals by superimposition of atomic orbitals to form covalent bond. This method is known as "molecular orbital method".

The Valence-Bond Theory (VBT)

Heitler-London Theory : The Heitler-London concept of covalent bond is based upon the pairing of electrons and resultant neutralization of opposed spins. If the electron spins are opposed when two atoms such as that of hydrogen approach each other, attractive forces result on account of the availability of each orbital in the hydrogen atom for occupation by two electrons without violation of Pauli Exclusion Principle. An atom combines with another atom through the pairing of electrons of opposed spins. Thus nitrogen having the outer electron configuration of $2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$ can share three unpaired electrons with, say, fluorine atom forming NF_3 but cannot form NF_5 since no more orbitals are available in $n = 2$. Phosphorus does form PF_5 because $3d$ orbitals are available besides the unpaired $3p$ to accommodate the unpaired $3s$ electrons. Pauling introduced the directional characteristics on the basis of the shapes of atomic orbitals.

Pauling-Slater Concept of VBT : It has been pointed out before that distribution of electron densities in various orbitals are geometrical in character. Thus the s electron of a hydrogen atom may be represented by a sphere and the combination of two hydrogen atoms may take place by the overlapping of two spheres and this can happen in any direction since s orbitals are spherically

symmetrical as shown in Fig. 2—6 (a). The overlap of two p orbitals in x direction is shown in Fig. 2—6 (b). But, since the p orbitals are directed in
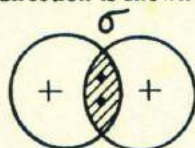
(a) Overlap of s-type orbitals.   (b) Overlap of p-type orbitals
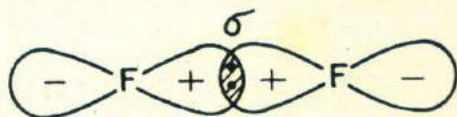
Fig. 2—6. Overlap of s and p orbitals. Notice the + and – signs which must have the same sign for combination of orbitals.

space along x, y and z axes, and are at right angles to each other, it follows that bonds involving these orbitals must be similarly directed. Pauling and Slater put forward the concept of directed bond based upon the consideration that strong covalent bonds are formed by maximum overlapping of atomic orbitals which gives the resultant maximum electron densities in the bond regions. However, there are certain conditions for the combination of atomic orbitals which may be stated, in short, as follows :

1. The orbitals must have similar energies.

2. The orbitals must overlap to a considerable extent.

3. The orbitals must possess the same symmetry about the molecular axis.

4. According to Pauli Exclusion Principle, each bonding orbital contains two electrons of opposed spin.

Thus **s** orbitals can combine with another **s** or **p** or **d** orbitals in the direction of the bond. A p_x orbital can combine with another p_x orbital but not with p_y orbital in the same system. If two p_y orbitals combine they do so sideways or laterally. These are illustrated in Fig. 2—7.

In the case of water, oxygen atom with $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ electron configuration containing two unpaired electrons combine with two s electrons of opposite spins of two hydrogen atoms to form H_2O. But P_y and P_z orbitals are at right angles to each other; the two O—H bonds in H_2O are expected to be at right angles $(90°)$ as shown in Fig. 2—8. In practice the bond angles in H—O—H has been found to be about $105°$ instead of $90°$. This has been assumed to be due to repulsion between the charged clouds of two H atoms. Similar is the case in H_2S but the bond angle is $92°$ in this molecule. The larger angles than $90°$ in H_2O have been assumed to be due to the formation of *hybrid* bonds by O rather than simple overlap of s and p orbitals.
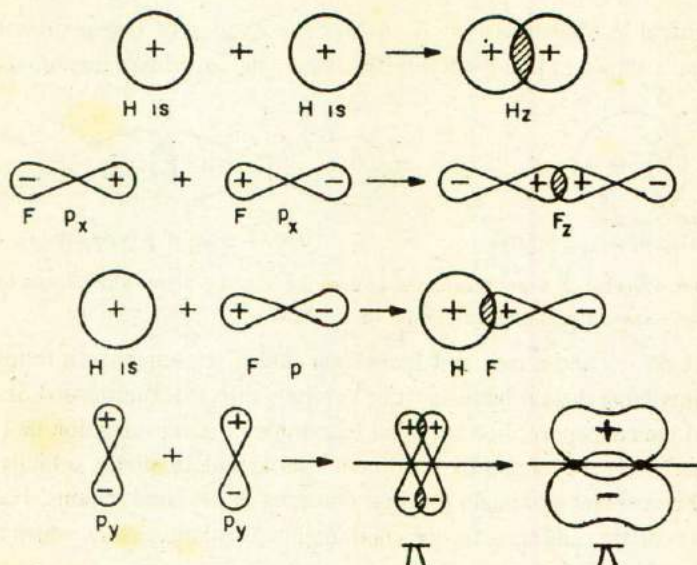
Fig. 2—7. Overlap of atomic orbitals. The signs (+ or −) of the combining orbitals must be the same. No overlap takes place when the orbitals are of opposite sings.

Nitrogen has three p electrons occupying singly the p_x, p_y and p_z orbitals. These combine with the s orbitals of three hydrogen atoms in a similar manner forming NH_3 having the three bonds at right angles (Fig. 2—8) to each other. In

H₂O   NH₃

H—O—H angle 90°   Each H — N—H angle 90°
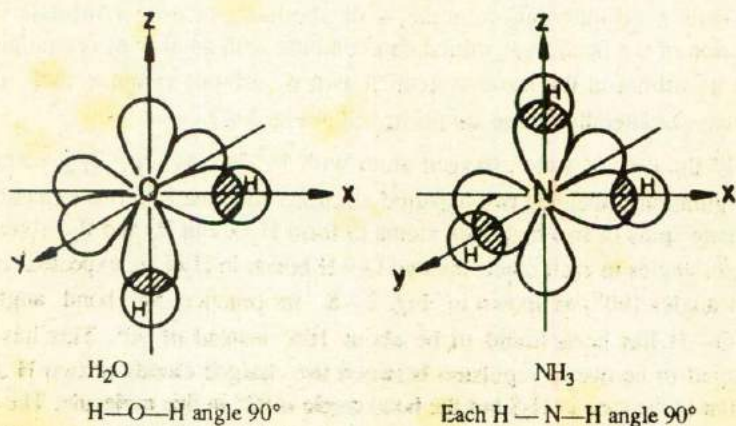
Fig. 2—8. Overlap of orbitals in H_2O and NH_3 molecules without the use of hybrid orbitals gives wrong structures.

practice the angles between H—N—H in NH_3 has been found to be about $107°$. This has been suggested as due to the repulsion of the hydrogen atoms. But this is now explained on the basis of hybrid bonds in which N uses four hybrid tetrahedral orbitals rather than simple orbitals. Similar is the case of O in H_2O.

Hybrid Bonds

The bonds in simple molecules such as $BeCl_2$, BF_3, CCl_4, H_2O, NH_3, PCl_3, PCl_5 etc. can be best explained on the basis of valence bond theory in terms of the formation of hybrid bond orbitals by the central atoms in the molecules. Beryllium having $1s^2 2s^2$ in the ground state has paired electrons. Similarly, B with $1s^2 2s^2 2p^1$ appears to be monovalent and C with $1s^2 2s^2 2p^2$ or $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^o$ should be at best a divalent atom. But these atoms use different hybrid bonds.

sp Hybrid Bonds :

In $BeCl_2$, the two bonds Be—Cl are linear and equivalent in all respects. Similarly in BF_3, CCl_4 etc. the bonds are equivalent and the molecules have definite geometry. The ground state and the excited state of the electron configurations in the atoms of Be. B, C are expressed as

Be—$1s^2 2s^2$	excited	$1s^2 2s^1 2p_x^1$
B—$1s^2 2s^2 2p_x^1$	excited	$1s^2 2s^1 2p_x^1 2p_y^1$
C—$1s^2 2s^2 2p_x^1 2p_y^1$	excited	$1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$

The two bonds of Be in $BeCl_2$ are not formed separately by the overlap of Be $2s^1$ with one Cl p_x^1 and then Be $2p_x^1$ with another Cl p_x^1 since in this way Cl—Be—Cl would not have been linear. It is, therefore, concluded that Be $2s^1$ and $2p_x^1$ orbitals combine to form two sp hybrid orbitals at $180°$ to each other. The bonds in $BeCl_2$ are formed by the overlap of p_x orbitals of two Cl atoms with the hybrid sp orbitals of Be atom as given in Fig. 2—9.

sp^2 Hybrid Bonds

Similarly, B atom in BF_3 does not use $2s^1$, $2p_x^1$ and $2p_y^1$ orbitals separately to form bonds with three F atoms, but a combination of $2s^1$, $2p_x^1$ and $2p_y^1$ orbitals giving rise to hybrid sp^2 bond orbitals situated in space at the
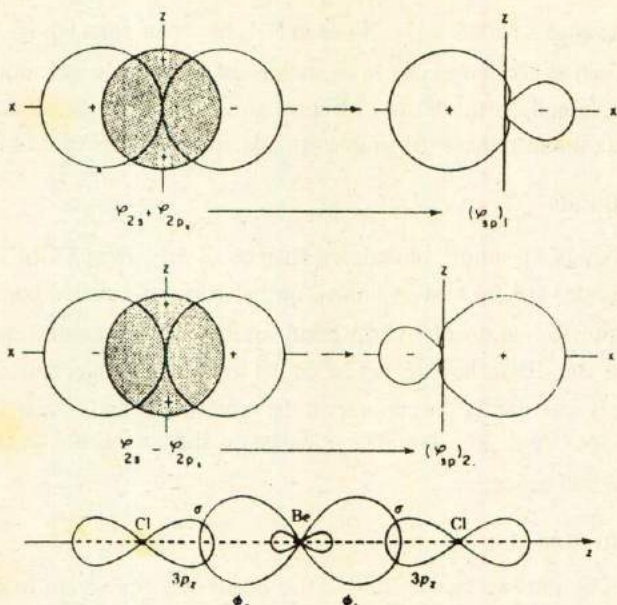
Fig. 2—9. Formation of sp hybrid orbital by combination of separate s and p orbitals. Overlap of p orbitals of two Cl atoms with sp hybrid orbital of Be forming σ bonds.

corners of an equilateral triangle giving each F—B—F angle equal to 120°. This is illustrated in Fig 2—10.
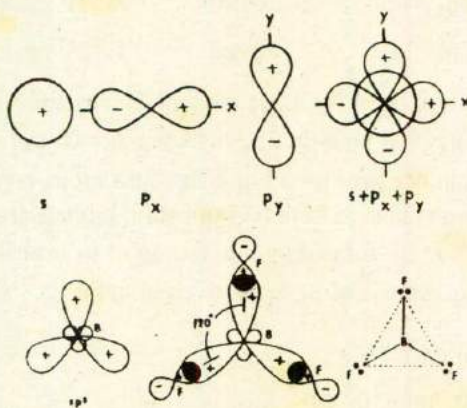
Fig. 2—10. Formation of sp^2 hybrid orbitals of B from one s and two p orbitals. Formation of BF_3 molecule .

sp³ Hybrid Bonds :

The electronic configuration of an isolated carbon atom is $1s^2 2s^2 2p^2$. In terms of the orbital theory there are three p orbitals, each of which initially contains one electron because of the same energy before pairing occurs. The detailed configuration of carbon atom may be written as $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^\circ$. The vacant p orbital is written as p_z°. Thus the valence electrons of carbon in the ground state are—

$$2s^2 \ 2p_x^1 \ 2p_y^1 \ 2p_z^0$$
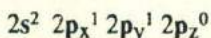
Since carbon forms four covalent bonds, the above arrangement of the valence electrons does not explain this nature of the carbon atom. It only indicates that carbon can form only two covalent bonds. It is, therefore, considered that an excited state of carbon atom is attained by promoting one of the $2s^2$ electrons to the vacant $2p_z^0$ orbital. The excited state of the carbon has the electronic arrangement of the valence shell as,

$$2s^1 \ 2p_x^1 \ 2p_y^1 \ 2p_z^1$$
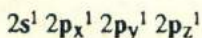
Thus the carbon atom can now form four covalent bonds by sharing 4 electrons from another atom or atoms with one electron of 2s and three electrons of 2p orbitals. One may expect that carbon atom will, therefore, form one bond of one kind and three bonds of another kind. But the four bonds of carbon are equivalent in all respects and there is no difference in the four bonds of either CH_4 or CCl_4.

```
        H                              Cl
        |                              |
   H— C—H                        Cl— C —Cl
        |                              |
        H                              Cl
```
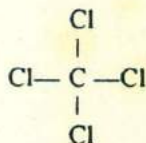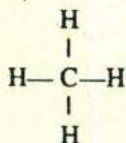
Actually, the one 2s orbital and the three 2p orbitals of carbon atom combine to form four hybrid orbitals which are now completely equivalent to one another. These four hybrid orbitals are directed in space at the corners of a regular tetrahedron.

$$s + p_x + p_y + p_z = sp^3 \text{ hybrid orbitals.}$$
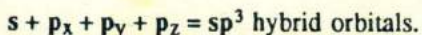
These hybrid orbitals of C form four bonds with 1s orbital of 4 H atoms or p_x orbital of 4 Cl atoms in CH_4 and CCl_4 respectively.

These four hybrid bonds are stronger than either **s** or **p** bond orbitals when formed separately. This is the reason that four bonds of carbon are tetrahedral having bond angles of 109°28′ (Fig. 2—11).
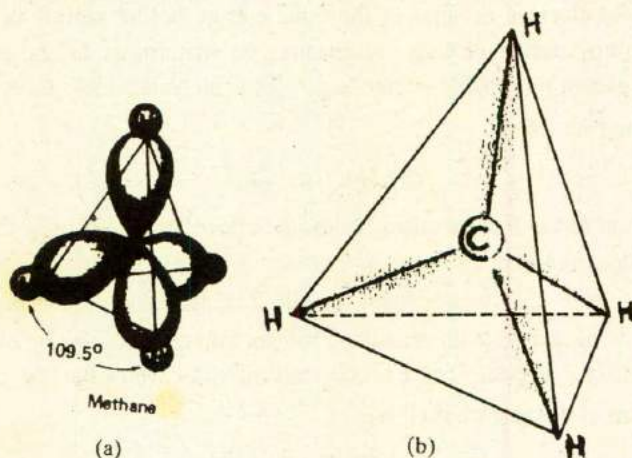
Fig. 2—11. (a) Tetrahedral sp^3 bond of carbon as in CH_4. (b) Overlap of sp^3 hybrid orbitals of C with **s** orbitals of H. The four C—H bonds are shown by the solid lines in (b).

Similarly, other types of hybrid bonds are formed having directional characteristics by combination of different atomic orbitals. Some of them are designated as sp, sp^2, dsp^2, sp^3, sp^3d, d^2sp^3 etc. which have linear, triangular, planar, tetrahedral, trigonal bipyramidal and octahedral arrangements respectively.

Hybrid orbitals	Geometry of molecules	Examples
sp	Linear	$BeCl_2$, $HgCl_2$
sp^2	Triangular	BBr_3, BF_3
sp^3	Tetrahedral	CH_4, $SiCl_4$
dsp^2 or sp^2d	Square planar	$Ni(CN)_4^{-2}$, XeF_4
sp^3d or dsp^3	Trigonal bipyramidal	PCl_5
d^2sp^3, or sp^3d^2	Octahedral	SF_6, $Co(NH_3)_6^{+3}$

Other forms of hybrid orbitals have been described in appropriate places.

We notice that the geometry of a specific molecule is described by converting atomic orbitals into *HYBRID ATOMIC ORBITALS* (These are formed by

mathematical combination of two or more pure atomic orbitals). Thus a hybrid orbital is different from a pure orbital in contour and directions in space. A tetrahedral hybrid atomic orbitals are each described as having $\frac{1}{4}$ s and $\frac{3}{4}$ p atomic orbital character. A trigonal plane hybrid orbital has $\frac{1}{3}$ s and $\frac{2}{3}$ p character. The linear hybrid orbital is constituted by combination of $\frac{1}{2}$ s and $\frac{1}{2}$ p character.

The Bonding operation, thus in the case of hybrid orbitals are due to overlapping of the hybrid orbitals with pure or another hybrid orbitals according to Linear Combination of Atomic Orbitals (LCAO). Since the hybrid orbitals have equal bond length, bond energy and bond strength, these are also known as equivalent orbitals.

Diagramatically the energetics involved in the formation of some hybrid orbitals are shown in Fig. 2—12 to Fig 2—22.
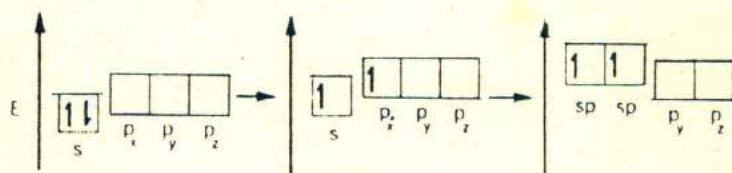
Fig 2—12, Energy diagramme for the formation of sp hybrid atomic orbitals.
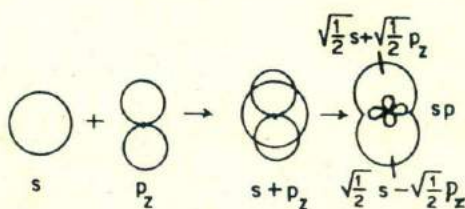
Fig 2—13, Mathematical combination of two sp hybrid orbitals
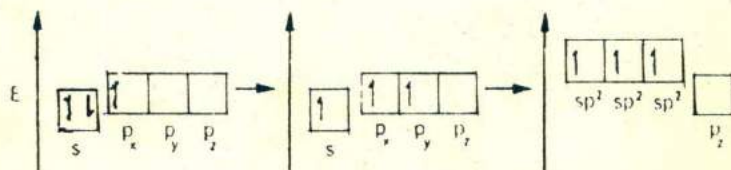
Fig 2—14, Energy diagramme of sp^2 hybrid orbital.

$$\sqrt{\frac{1}{3}}\,s - \sqrt{\frac{1}{6}}\,p_x + \sqrt{\frac{1}{2}}\,p_y$$

$$\sqrt{\frac{1}{3}}\,s + \sqrt{\frac{2}{3}}\,p_x$$

$$sp^2$$

$$s + p_x + p_y$$

$$\sqrt{\frac{1}{3}}\,s - \sqrt{\frac{1}{6}}\,p_x - \sqrt{\frac{1}{2}}\,p_y$$
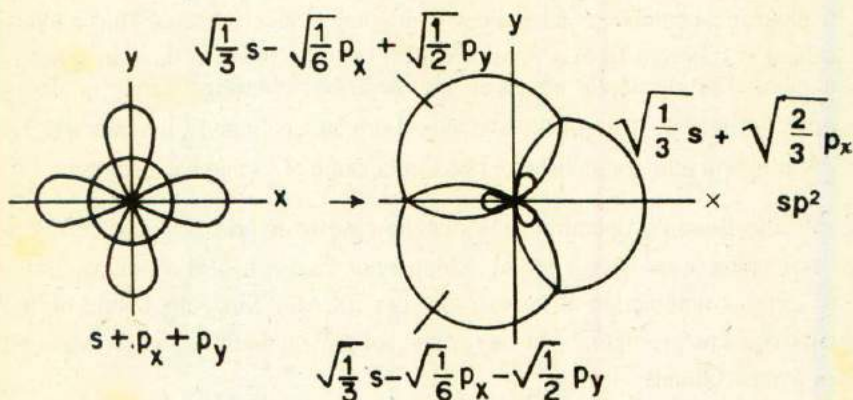
Fig 2—15, Combination of $s + p_x + p_y$ orbitals to give sp^2 hybrid orbitals and their orientations.
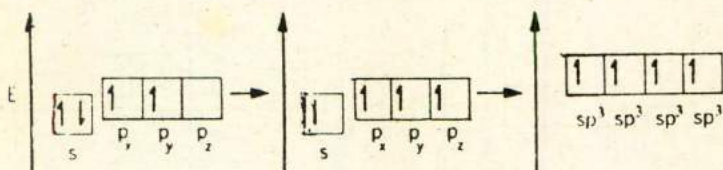
Fig. 2—16 Sequence of Energy Diagrams representing the formation of sp^3 Hybrid Atomic Orbitals from Pure Atomic Orbitals

Hybridize to form

sp^3
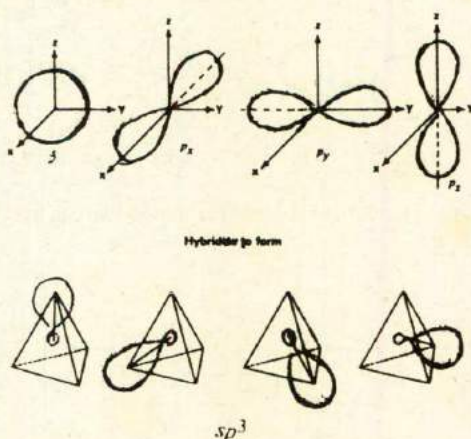
Fig. 2—17 A Tetrahedral Assemblage of Four sp^3 Hybrid Atomic Orbitals
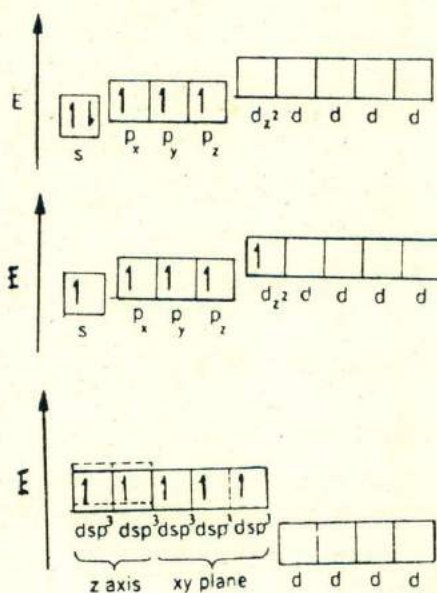
Fig. 2—18 Sequence of Energy Diagrams representing the formation of **dsp³** Hybrid Atomic Orbitals from Pure Atomic Orbitals

$$s + p_x + p_y + p_z + d_{z^2}$$

. Hybridise to form

Trigonal Bipyramid (90°, 120°)
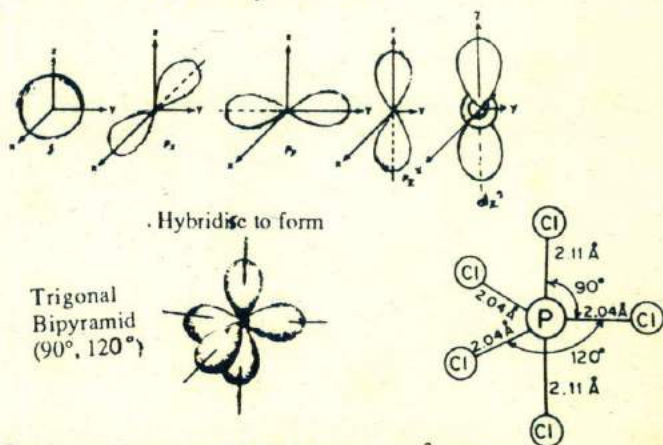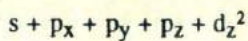
Fig. 2—19. Structure of PCl_5 Molecule. (sp³d bonds)
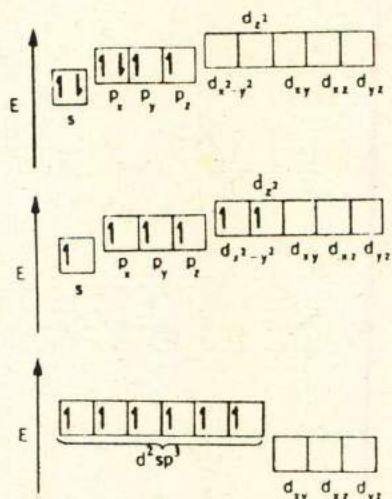
Fig. 2—20. Sequence of Energy Diagrams representing the formation of d^2sp^3 Hybrid Atomic Orbitals from Pure Atomic Orbitals in a Sulphur Atom

$$s + p_x + p_y + p_z + d_{x-y}^2{}^2 + d_z{}^2$$
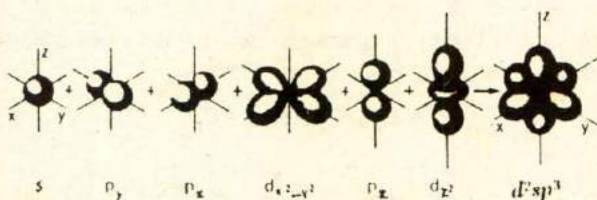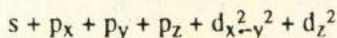
Fig. 2—21. Pictorial Representation of the Mathematical Interpretation of the formation of Six d^2sp^3 Hybrid Atomic Orbitals
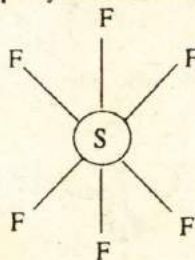
Fig. 2—22. Pictorial representation of the Mathematical Interpretation of the formation of a Molecule of SF_6 using sp^3d^2 hybrid orbitals of S

Resonance

NO_3^-, CO_3^{-2}, SO_3^{-2}, O_3 etc indicate different electron distributions in their respective molecular species according to Lewis method. For instance in the Nitrate (NO^{-3}) ion, the N—O bond lengths are the same and all the O—N—O angles are equal to $120°$. NO^{-3} may be shown to have electron distribution as :

$$: O : \text{—}$$
$$O : : N : O :$$
$$+$$
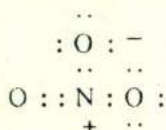
But the experiment shows that NO_3^- must have electron distribution as :

$$: O : \text{—}$$
$$\text{—} : O : N : O :$$
$$+2$$
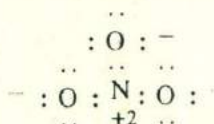
But the charge separation is too great to accept this electron distribution. Thus the nature of bonding in NO^{-3} CO_3^{-2}, etc. may be represented by several different structure having different positions of the double bonds as :
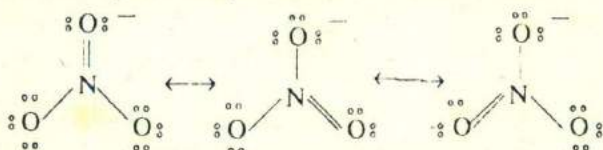
Such molecules or ions may be considered to have resonance structures having different positions of the electrons and do not have a single formula. In this case it may be assumed that each bond between N—O is formed by $1\frac{1}{8}$
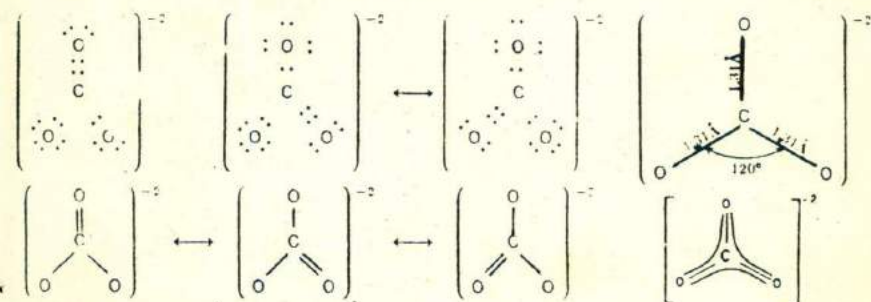
electron pairs. The chemical structures in which the bond orders are not integers (whole numbers) are called hybrid structures or resonating structures. The resonance characteristics demands that the molecular models have a series of bond symbols as in the case of CO_3^{-2}

Rules for Resonance

The following rules have been formulated for the resonance structures :

1. A resonance hybrid structure of a chemical species must have two or more conventional bond symbols.
2. The relative positions of the component atoms must be fixed in the various forms having similar electron arrangements.
3. Each conventional structural formula of a hybrid molecule must have the same number of unpaired electrons.
4. The different resonance hybrid must have similar energy and the resultant structure must be of lower energy for the species to be stable.
5. The change in the electron positions between the hybrid structures is made in the $\pi-$ bonding system.
6. The maximum effect of resonance appear in planar chemical structures because of $\pi-$ bondings.
7. Unlike charges in the stable molecular structures are least separated and like charges are greatly dispersed.
8. The greater the number of contributing structures, the more stable is the hybrid molecule or species.

    Considering the NO_3^- ion in the orbital forms in which N—O bonds have the same character, the resulting picture shows three p_z orbitals of each oxygen having two electrons, N has a vacant p_z orbital giving $\pi-$ bonding.
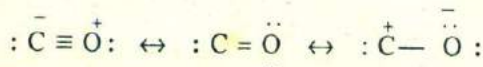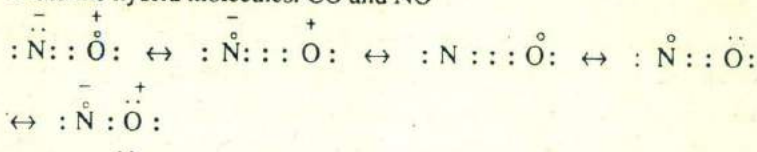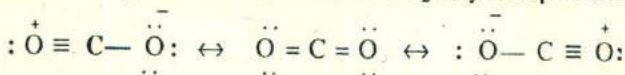

NO_3^-
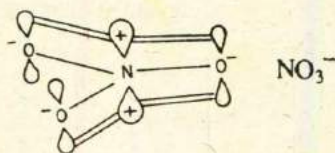
O_3 molecule may be represented as :
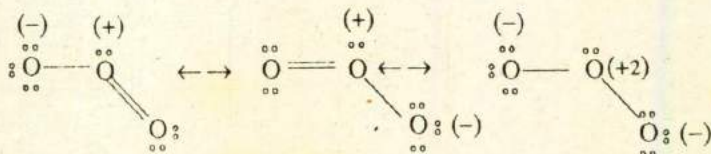
Types of π- bonded systems having Resonance Structures

1. Diatomic hybrid molecules: CO and NO

$$: \overset{-}{\underset{}{N}} : : \overset{+}{\overset{\circ}{O}} : \leftrightarrow : \overset{-}{N} : : : \overset{+}{O} : \leftrightarrow : N : : : \overset{\circ}{O} : \leftrightarrow : \overset{\circ}{N} : : \overset{..}{O} :$$

$$\leftrightarrow : \overset{-}{\overset{\circ}{N}} : \overset{+}{\overset{..}{O}} :$$

$$: \overset{-}{C} \equiv \overset{+}{O} : \leftrightarrow : C = \overset{..}{O} \leftrightarrow : \overset{+}{C} - \overset{-}{\overset{..}{O}} :$$

2. Triatomic hybrid molecules such as CO_2 may be represented as:

$$: \overset{+}{O} \equiv C - \overset{-}{\overset{..}{O}} : \leftrightarrow \overset{..}{O} = C = \overset{..}{O} \leftrightarrow : \overset{-}{\overset{..}{O}} - C \equiv \overset{+}{O} :$$

3. Tetratomic molecules having conjugated double bonds as in butadiene $H_2C = CH - CH = CH_2$.

4. Hexagonal planar structure of benzene is one of the historical example of the resonance structure showing several hybrid structures having double delocalized π- electron clouds on top and the bottom of the 6C—C ring systems as shown belows :

(b)
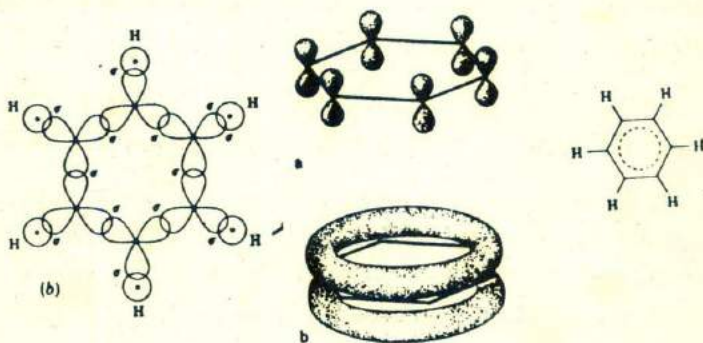
Wave mechanical representation of a benzene molecule (a) represents p_z atomic orbital overlap of C to form continuous π-electron cloud above and below the plane of C nuclei. (b) represents the three-dimensional wave clouds.

Experimental Evidence of Resonance : 1. Shortening of bond length measured by x-ray diffraction, 2. Benzene does not give reactions of isolated double bonds, 3. Infrared frequency indicate resonance, 4. Measured heat of formation differ from the calculated value, 5. Dipole moment measurements indicate resonance.

The Molecular Orbital Theory (MOT)

According to the molecular orbital theory of chemical bond, each electron is placed in a molecular orbital which is polynuclear, that is, it is associated with all the atomic nuclei present in the molecule. the electrons are placed into the available molecular orbitals one at a time, the lowest energy molecular orbital being filled first. In terms of Pauli Exclusion Principle each molecular orbital can accommodate a maximum of two electrons provided their spins are opposed.

The fundamental principles involved in the molecular orbital theory for the combination of atomic orbitals are the same as those of the Valence Bond Theory, namely,

(i) The orbitals must have similar energy;

(ii) The orbitals must overlap to a considerable extent ;

(iii) The orbitals must have the same symmetry about the molecular axis.

The mathematical treatment for the combination of atomic orbitals in order to obtain the molecular orbitals is known as the Linear Combination of Atomic Orbitals or in short LCAO approximation method. The linear combination of two atomic orbital wave functions, ψ_A and ψ_B, combine to form two new molecular wave functions expressed by equations,

$$\psi_+ = C_A\psi_A + C_B\psi_B \qquad \psi_+^2 = C_A^2\psi_A^2 + 2C_A\psi_A C_B\psi_B + C_B^2\psi_B^2$$

$$\psi_- = C_A\psi_A - C_B\psi_B \qquad \psi_-^2 = C_A^2\psi_A^2 - 2C_A\psi_A C_B\psi_B + C_B^2\psi_B^2$$

ψ_+ and ψ_- are the molecular orbital wave functions and C_A and C_B are the mixing coefficients of atoms A and B respectively. For a homonuclear diatomic molecule A_2 when A = B, the wave functions ψ_A and ψ_B are equal and $C_A^2 + C_B^2 = 1$, i. e., $C_A = C_B$ (mathematical details omitted). Then $C_A^2 = C_B^2 = \frac{1}{2}$ for a homonuclear bond and for a heteronuclear bond (ionic bond) $C_A^2 = C_B^2 = 1$, $C_A^2 = 0, C_B^2 = 1$

In a purely covalent bond the bonding electron wave is distributed equally between A and B and the limiting condition of a completely ionic bond, the bonding electron wave reside within the valence level of atom B to produce a negative charge atom. A having none of the electron wave in the valence level, has a residual positive charge. Thus $C_A^2 = 0$ and $C_B^2 = 1$.

Thus the combination of two atomic orbitals gives two molecular orbitals (one of higher energy and the other of lower energy) which accommodate the available electrons. Each orbital contains a pair of electrons of opposed spins. The molecular orbitals which are at a lower energy than the original atomic orbitals are known as *bonding molecular orbitals*. The molecular orbitals which are at a higher energy than the original atomic orbitals are known as *antibonding molecular orbitals*. Electrons which are placed in a bonding molecular orbital are known as *bonding electrons* and signify attraction. Electrons which are placed in an anti-bonding molecular orbital are known as *anti-bonding electrons* and signify repulsion. Electrons present in the deep-seated non-bonding orbitals do not take part in bonding and are known as *non-bonding* electrons.

In the formation of a stable molecule, the number of bonding electrons must be more than the number of anti-bonding electrons. These effects are illustrated in Fig. 2—23 showing the formation of hydrogen and helium molecules by the LCAO method. The hydrogen molecule contains two bonding electrons in the lowest energy bonding orbital labelled as 1s. This can be written as,

$H (1s^1) + H(1s^1) = H_2 [\sigma 1s)^2]$. The upper anti-bonding orbital labelled as $\sigma^* 1s$ is empty.

That a molecule of helium gas He_2 is not formed, is easily explained on the basis of the molecular orbital theory as shown in Fig. 2—23. The number of electrons in the bonding σ 1s and antibonding σ^* 1s are equal and hence the attraction and repulsion between the electrons of the two atoms of helium are equal. Thereby helium molecule He_2 is not formed.

Similarly, a nitrogen molecule is formed by the union of two atoms of nitrogen having configuration $1s^2 2s^2 2p^3$. The $1s^2$ electrons nearest the nucleus are non-bonding and may be omitted for simplicity. The $2s^2$ and $2p^3$ electrons of the two nitrogen atoms take part in bonding interactions. Thus $N(1s^2 2s^2 2p^3) + N(1s^2 2s^2 2p^3) = N_2[KK (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p)^2 (\pi 2p)^4]$. KK symbols indicate K shells containing the non-bonding electrons in the 1s levels. Of the four 2s electrons from the two atoms of nitrogen, two become $(\sigma 2s)^2$ bonding electrons and two become $(\sigma^* 2s)^2$ which are anti-bonding. The effect of the two molecular

orbitals $\sigma 2s$ and $\sigma^* 2s$ in the N_2 molecule each containing 2 electrons is cancelled out and they do not take part in the bonding system of N_2.
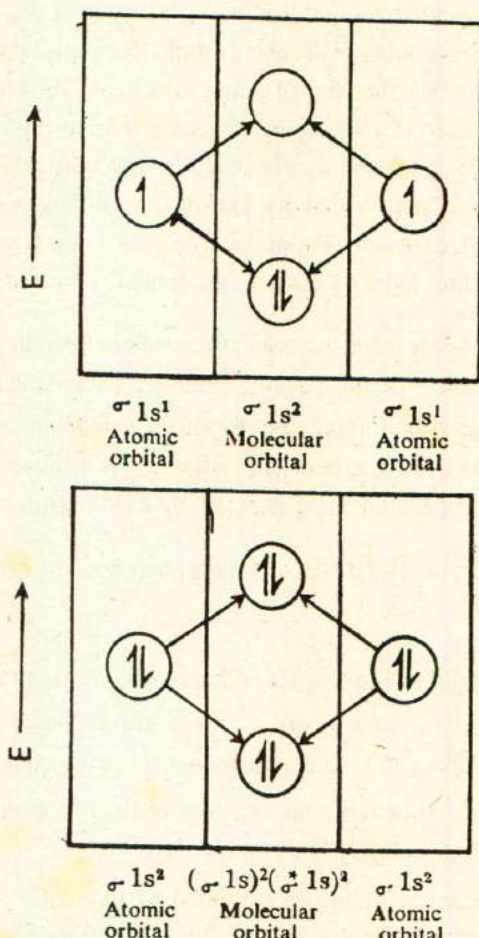

$\sigma 1s^1$ $\sigma 1s^2$ $\sigma 1s^1$
Atomic   Molecular   Atomic
orbital   orbital   orbital

$\sigma 1s^2$ $(\sigma 1s)^2(\sigma^* 1s)^2$ $\sigma 1s^2$
Atomic   Molecular   Atomic
orbital   orbital   orbital

Fig. 2—23. Formation of H_2 molecule (top) and repulsion of He atom (bottom)

The p orbitals of the two nitrogen atom can combine in two different ways. The direct head-on or end-on combination of p orbitals, as in the case of two p_x atomic orbitals, form a bonding molecular orbital known as $\sigma 2p_x$ molecular

orbital and another anti-bonding molecular orbital σ^*2p_x. Another way of combination of **p** orbitals takes place side-ways or laterally. If two $2p_y$ orbitals are combined side-ways to give two molecular orbitals, the bonding molecular orbital is labelled as $\pi2p_y$ and the anti-bonding molecular orbital is designated as π^*2p_y. Similarly, the combination of the p_z orbitals gives $\pi2p_z$ bonding and π^*2p_z anti-bonding molecular orbitals. The six p electrons of the two N atoms consisting of two sets of $2p_x^1$, $2p_y^1$ and $2p_z^1$ atomic orbitals which interact to form two $\sigma2p_x$ or $(\sigma2p_x)^2$ and four electrons become $\pi2p_y^2$, $\pi2p_z^2$ and all are bonding electrons because of lower energy than in the isolated atoms. The six bonding electrons produce a $N \equiv N$ triple bond, one bond being σ and other two π in character. The formation of nitrogen and oxygen molecules according to molecular orbital treatment is shown in Fig. 2—24.
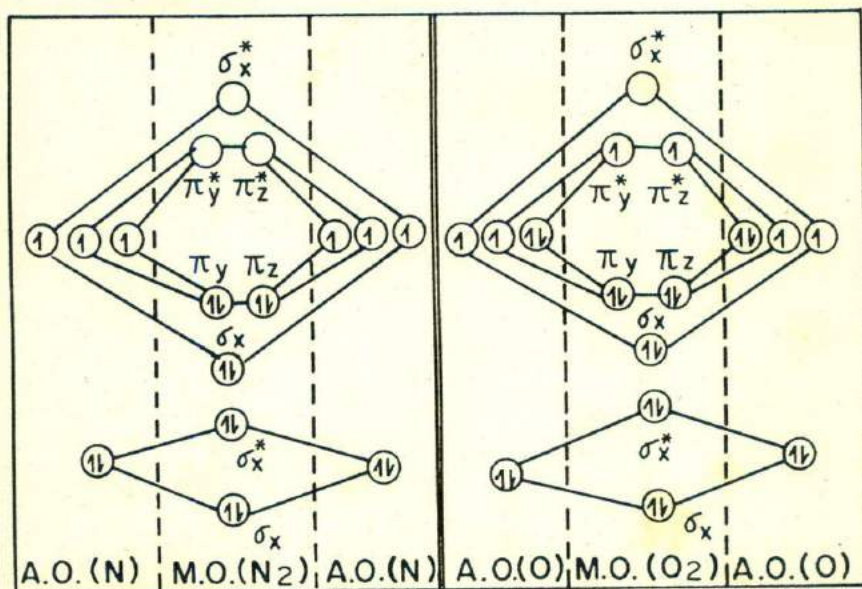

Fig. 2—24 Formation of (N_2). and (O_2) molecular orbitals. Bond order, $N_2 = 3$
Bondorder for $O_2 = 2$. Notice 2 unpaired electrons in the O_2 molecule.

Bond Order:

Bond order is defined as equal to half the total number of electrons in the bonding orbitals (Nb) minus half the number of electrons in the anti-bonding orbitals

(Na). That is : Bond order $= \frac{1}{2}$ (Nb—Na). For a stable molecule the number of electrons in the bonding orbitals must be greater than the number of electrons in the anti-bonding orbitals. Bond orders in some diatomic homonuclear molecules and the relationship with some important properties are given in Fig. 2—25. The two dimensional overlap of s and p orbitals according to MOT are given in Fig. 2—26.
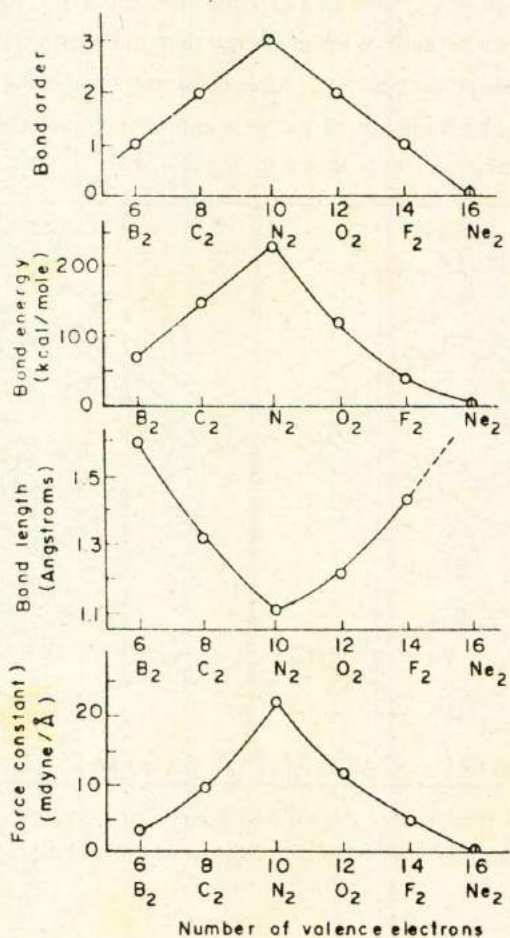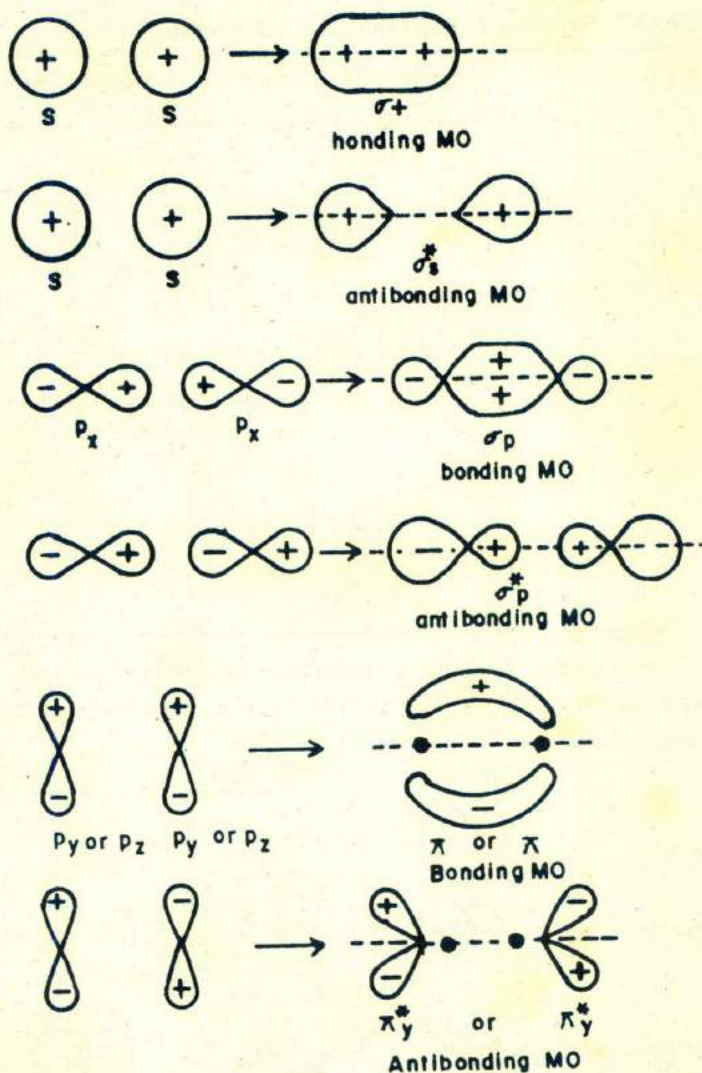
Fig. 2—25. Bond orders and bond properties in some homonuclear diatomic molecules.

Fig. 2—26 Cross-section of approximate shapes of MO's in homonuclear molecules.

The combinations of atomic orbitals to form molecular orbitals are governed by energy and symmetry consideration and the permitted combinations are given in Table 2.2.

Table 2.2 Permitted combinations of atomic orbitals.

Atomic orbital Ψ_A		Atomic orbital Ψ_B			Type of molecular orbital formed
s	s	p_x	$d_{x^2-y^2}$	d_z^2	σ
p_x	s	p_x	$d_{x^2-y^2}$	d_z^2	σ
p_y		p_y	d_{xy}		π
p_z		p_z	d_{xz}		π
$d_{x^2-y^2}$	s	p_x	$d_{x^2-y^2}$	d_z^2	σ
d_z^2	s	p_x		d_z^2	σ
d_{xy}		p_y	d_{xy}		π
d_{xz}		p_z	d_{xz}		π
d_{yz}			d_{yz}		δ
$d_{x^2-y^2}$			$d_{x^2-y^2}$		δ

It is to be noted that σ MO has no nodal plane, a π MO has one nodal plane and a δ MO has two nodal planes. The cross sections of end-view of the three types of molecular orbitals are given in Fig. 2—27.
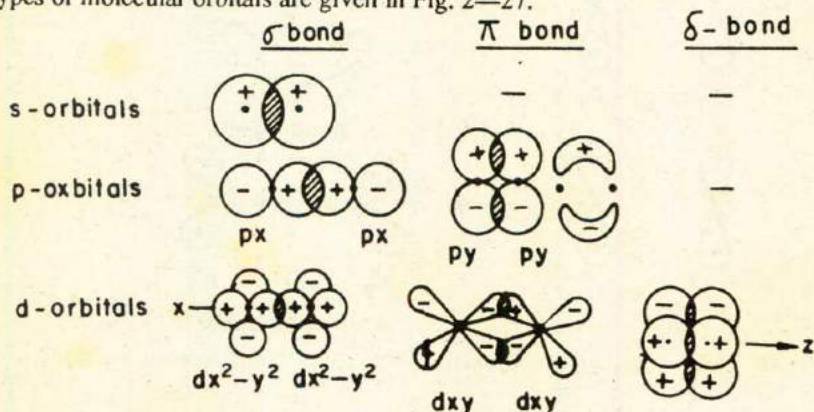
Fig. 2—27 Nodal planes in (a) σ MO, (b) π MO and (c) δ MO.

It may be noted that both the valence bond theory and molecular orbital theory distinguish σ and π types of bonds.

σ and π Bonds:

As a result of the difference in the symmetry of electron distribution, two different kinds of bonds may also be distinguished. In the single bonds, direct or head-on overlap of atomic orbitals produces electron density symmetrical to the bond direction in the molecule. This type of bond is called a *sigma bond* (σ bond). Almost all single bonds have the maximum electron densities between two atoms and are, therefore, σ bond.

The lateral or sideways overlap of orbitals produces an electron cloud having the plane of symmetry in the bond direction and lying above and below the molecular axis. Such bonds are known as *pi-bonds* (π bond).

The head-on overlap of s orbitals of hydrogen with that of p orbitals of oxygen in H_2O produces two σ bonds in H $\underline{\sigma}$O $\underline{\sigma}$H. (Fig. 2—8 page 76).

Similarly, three σ bonds are formed in NH_3 molecules between N and H as shown in Fig. 2—8.

In ethylene, however, the hydrogen atoms are bonded by σ bonds and carbon atoms by a σ and a π bond as shown in Fig. 2—28
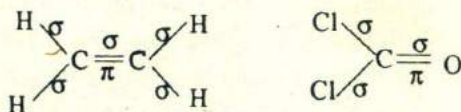

Fig. 2—28. Overlap of p_z orbitals in C_2H_4. The horizontal double lines indicate (C—C) one σ bond and one π bond. The four hydrogen are bonded by 4(C—H) σ bonds. $COCl_2$ also has 2 O—Cl σ bonds, one C—O σ bond and one C—O π bond.

The overlap of π orbitals of two nitrogen atoms to form a molecule of N_2 may be shown as in Fig. 2—29 giving a σ bond and two π bonds.

Some Properties of Covalent Bond

Molecules formed by covalent bonds have come into existence by sharing electron pair or pairs. The total distribution of electricity with each atom is, therefore, unchanged. As each atom remains electrically neutral, the molecule has
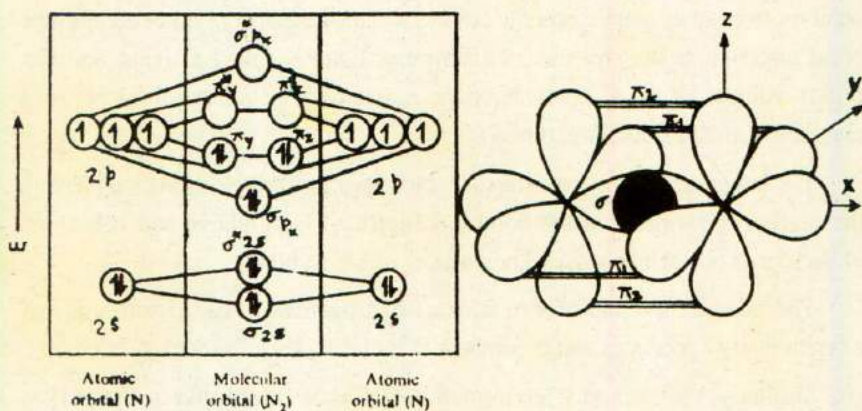
Fig. 2—29   Formation of N_2 molecule. A σ bond is shown by black shading at the centre and the horizontal double lines indicate formation of two π bonds.

no external field of force and covalent compounds are consequently either gases or liquids and solids which have low melting points and are easily vapourized. Covalent bond produces directed bonds and the crystals are made up of atoms held together by definite chemical bonds. Organic compounds provide ample examples.

Covalent compounds do not generally conduct electricity and do not exhibit isomorphism. Due to the factors such as atomic size and electronegativity of the constituent atoms, a covalent compound may tend to be polar in character and shows high dipole moments and dielectric constants. Hence a polar liquid, such as water, is a good ionizing solvent and when associated, it possesses co-ordination characteristics and although shows little tendency to ionize itself, it can dissolve most of the ionic compounds. Water has a dielectric constant of about 80 as compared to about 2 of benzene and paraffins which are non-polar and do not allow dissociation of ionic solids to take place.

Polar molecules have a tendency to exhibit dipole association as mentioned in the case of water. On account of the attractions of opposite poles in a polar

molecule abnormal behaviours are shown in liquids. The more polar the substance the greater is the intermolecular attractions. This point has also been discussed in connection with hydrogen bond. Thus polar compounds have higher melting points and boiling points as compared to non-polar covalent compounds. It has already been mentioned that ionic compounds have very high melting and boiling points due to considerable amount of work which must be done to separate the lattices.

Covalent compounds are usually stable and reactions between covalent molecules usually take place by way of unstable intermediaries. Covalent compounds are normally soluble in non-polar solvents. These are usually sparingly soluble in water. Some covalent compounds dissolve freely in water because they react with it chemically :

$$HCl + H_2O = [H_3O]^+ + Cl^-$$
$$NH_3 + H_2O = [NH_4]^+ + OH^-$$
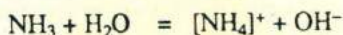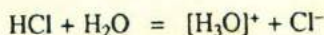
Ethyl alcohol and sucrose dissolve in water due to hydrogen bonding.

One special feature of covalent bonds is that they are directed in space and their relative positions are almost fixed. It is quite possible to have the same groups arranged round an atom in more than one way. In other words, structural and stereoisomerism are possible among groups whose constituent atoms are held together by covalent linkages. This particular aspect gives rise to stereoisomerism and optical isomerism in organic compounds and also in inorganic complexes.

Distinction between ionic and covalent bonds :

In general, the following points of distinctions may be noted regarding the properties associated with the two extreme types of bonds—polar and non-polar.
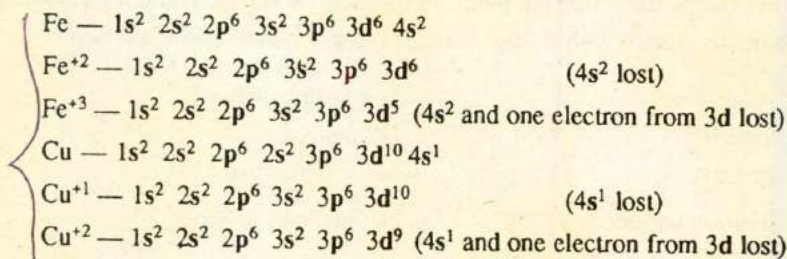
	Polar (ionic)	Non-polar (covalent)
1.	Ionized	Not ionized
2.	Reactive	Not very reactive
3.	Ionizing solvents	Not ionizing solvents

—7

4.	High dielectric constant	Low dielectric constant
5.	Associated molecules	Not associated
6.	Isomorphism	Isomerism
7.	High melting point	Low melting point
8.	High boiling point	Low boiling point
9.	Abnormal liquids	Normal liquids

Variable Oxidation States

The behaviour of the elements to show variable oxidation states is dependent mainly on valence electrons and the presence or the availability of certain electron orbitals. Alkali and alkaline earth metals normally do not show any variable oxidation states because of only s^1 and s^2 electrons in the outermost energy levels respectively. But since it is understood that the difference in energy between 3p and 4s energy levels is less than that between 2p and 2s, a transfer of electron from 3p to 4s is possible giving an excited state with corresponding increase in bonding orbitals in compound formation. In addition, the 3d levels are also available which permit an increase in bond formation. For example, the behaviour of fluorine and chlorine are quite different as regards compound formation. Fluorine is always monovalent, whereas chlorine gives a series of compounds with oxygen, such as Cl_2O, Cl_2O_3, ClO_2 etc. The variable oxidation states of chlorine occurs due to the excitation of 3p electrons to 3d and 4s energy levels. This situation does not exist for fluorine. Similarly, oxygen is always divalent whereas sulphur has variable oxidation of -2, $+4$, $+6$, as in H_2S, SO_2 and SO_3 or SF_6 respectively.

In the case of the transition elements such as Fe (26) and Cu (29), the variable oxidation numbers arise due to the loss of electrons from the 4s as well as 3d levels. Thus—

Fe — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

Fe^{+2} — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$ ($4s^2$ lost)

Fe^{+3} — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$ ($4s^2$ and one electron from 3d lost)

Cu — $1s^2\ 2s^2\ 2p^6\ 2s^2\ 3p^6\ 3d^{10}\ 4s^1$

Cu^{+1} — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ ($4s^1$ lost)

Cu^{+2} — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$ ($4s^1$ and one electron from 3d lost)

If electronic excitation, involving the unpairing and increase in the number of unpaired electrons, requires an expenditure of energy which is less than the bond energies, a variable oxidation states is possible. If, on the other hand, the endothermic electronic excitation energy is greater than the exothermic combination of the atoms, the element will show a single oxidation state.

Other Types of Chemical Bond

The Metallic Bond : The properties of metals and alloys, such as lustre, hardness, tensile strength, malleability, electrical conductivity, heat conductivity etc. are to be explained in terms of a special type of bond known as *metallic bond.*

A number of theories have been put forward to explain the structure and bond systems in metals and alloys. Most metals form crystals in which each atom is surrounded by as many neighbours as is geometrically possible, usually 8 and 12. A number of geometrical shapes of crystals arise due to the various ways of packing. The atoms of metals consist of electrons and positive nuclei. There are not enough valence electrons to create electron-pair bonds between the atoms, since each atom is surrounded by eight or twelve neighbours. It is assumed that the valence electrons are free to pass from one atom to the other and is not associated with a single atom. These mobile electrons serve to hold the atoms together and constitute what is known as *"metallic bond."*

The metallic bond thus appears to be a modified form of covalent bond in which the freely moving electrons resonate between the atoms throughout the crystal lattice. The characteristic properties of metals, such as high lustre, high electrical and thermal conductivity etc. are due to these mobile valence electrons.

The electron-sea model : In metals the electrons are not tied down to a particular pair of atoms as in covalent bond, but are spread out over a relatively larger regions in the crystal lattice. This gives rise to the electron-sea model of metallic bond. The metal thus consists of positive nuclei immersed in a sea of mobile electrons. The metal ions are thus held together by a sort of electron glue. An schematic diagram of electron-sea model of Cs and Ba are shown in Fig. 2—30.
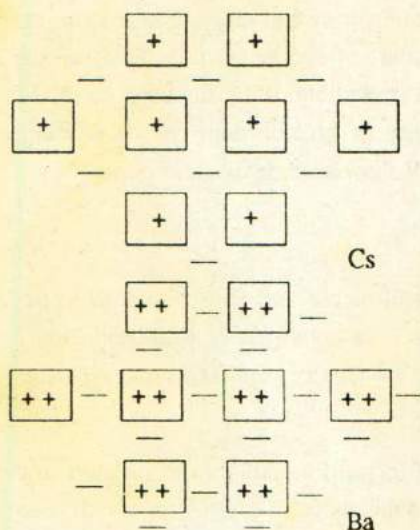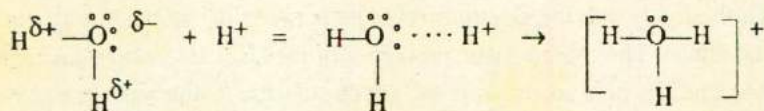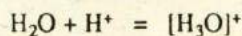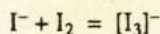
Fig. 2—30. Schematic diagram of electron sea model of Cs and Ba.

Dipole Bond : In some molecules the bond is partly covalent and partly ionic. Thus H_2O and HCl have appreciably polar character due to charge displacement in their molecules. This displacement or separation of charge in a molecule is known as "dipole moment" and is defined as the charge on one of the atoms multiplied by the distance (d) between the charges. Thus in HCl, the dipole moment (μ) is given by equation, $\mu = d.\delta^+$. The origin of the dipole moment lies in the difference in electronegativity of the two atoms forming the bond as explained later.

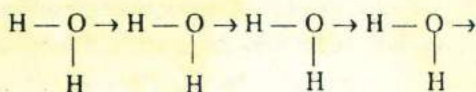$$H^{\delta+}\underline{\qquad d \qquad} Cl^{\delta-} \qquad \mu = d.\delta^+$$
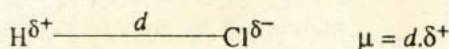
Such molecules have tendency to form bonds with ions or diploes of opposite electrical charges and are known as dipole bonds. Thus—

$$H_2O + H^+ = [H_3O]^+$$

$$H^{\delta+}-\overset{\bullet\bullet}{\underset{\bullet}{O}}{:}^{\delta-} + H^+ = H-\overset{\bullet\bullet}{\underset{|}{O}}{:}\cdots H^+ \rightarrow \left[H-\overset{\bullet\bullet}{\underset{|}{O}}-H\right]^+$$
$$\underset{H^{\delta+}}{|} \qquad\qquad\qquad \underset{H}{} \qquad\qquad\qquad \underset{H}{}$$

Similarly,

$$I^- + I_2 = [I_3]^-$$

The Hydrogen Bond : When hydrogen forms a bridge between two electronegative atoms of adjoining molecules, it is said to form a "hydrogen bond". Thus the familiar example of water molecules which are polar in character have hydrogen bonds indicated by arrows :—

$$H-\underset{\underset{H}{|}}{O}\rightarrow H-\underset{\underset{H}{|}}{O}\rightarrow H-\underset{\underset{H}{|}}{O}\rightarrow H-\underset{\underset{H}{|}}{O}\rightarrow$$

Similarly, in HF, the small electronegative F atoms are joined by hydrogen bonds. The broken lines indicate hydrogen bonds.
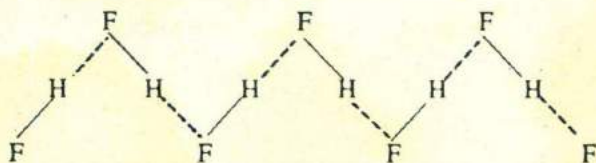
The hydrogen bond is primarily electrostatic in nature. It can not be regarded as a covalent bond since H has only one electron in its orbital and hence cannot give rise to electron-pair bond.

Hydrogen bond exists only between highly electronegative atoms, such as F, O, N etc. involving H atom.

The presence of hydrogen bond confers unusual properties to molecules. Thus the boiling points of H_2O and HF are abnormally high because of hydrogen bonding as compared to other members of each series given in Table 2.3.

Table 2.3. Boiling points of some related compounds (°C).

Group V		Group VI		Group VII	
NH_3	−33	H_2O	+100	HF	+19
PH_3	−85	H_2S	−60	HCl	−85
AsH_3	−55	H_2Se	−42	HBr	−67
SbH_3	−17	H_2Te	−2	HI	−35

Association of the polar molecules is responsible for the abnormally high boiling points in HF and H_2O. This behaviour is due to the fact that energy is required to overcome the hydrogen bonds holding the atoms together in the associated molecules. The abnormally high dielectric constant of H_2O is again due to association of large number of polar molecules and has the dissolving

power for many ionic substances and also some organic substances containing OH groups, such as alcohol, sugar and some acids. The dissolution of these organic substances in water is primarily due to the hydrogen bonding. Hydrogen bond also occurs in many organic substances as in acetic acid which is dimerized.
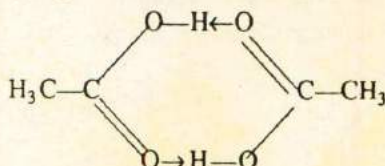
Hydrogen bond is a relatively weak bond and measures approximately to only 5—10% of a covalent bond in strength. The hydrogen bond arises due to the attraction of positively charged proton by the negative electrons of two different atoms which are very electronegative. Intramolecular H-bonds occur in many molecules such as ortho-nitrophenol etc.

Van der Waal's Forces : All molecules and atoms when in close contact exert an attraction for one another. This attraction is very weak and has its origin in electrostatic attraction of the positive nuclei of one molecule for the electron cloud of another molecule in contact with each other. In the case of molecules having symmetrical charge distribution, some amount of inter-molecular attraction arises due to induced dipoles. The attraction of molecules or atoms for one another produces the van der Waal's forces which is electrostatic in nature.

Van der Waal's forces are very weak forces. Crystals having this inter-molecular forces are soft and melt at a very low temperature. The magnitude of the van der Waal's attraction increases with increase in the number of electrons per molecule. The van der Waal's forces cause the inert gases and halogen to become liquid and solid when the temperature is lowered considerably to bring the atoms and molecules of gases very close to each other.

QUESTIONS AND PROBLEMS

1.   Write a note on the Electronic Theory of chemical bonds giving suitable examples.
2.   Write short notes on:—
    (a) Covalent bond.
    (b) Dependence of physical and chemical properties on bond types.

(c) Variable oxidation states.

(d) Electrovalent and covalent compounds.

(e) Coordination bond.

(f) Difference between 'ionic' and 'covalent' bonding.

3.   Give a brief account of the modern concept of chemical bonds. How are the properties of substances dependent on the bonds operating between their atoms ?

4.   Write a concise account of what you understand by the electronic theory of chemical bond. Illustrate your answer with specific examples.

5.   Discuss the connections of the electronic structures of positive and negative ions to that of the inert gases.

6.   What is the physical and chemical differences between an atom of iron and ferrous and ferric ions.

7.   When is the formation of coordination bond possible ? Give an example.

8.   Show the electron distribution in the structural formula of the following molecules (write the Lewis structure):—

(a) $POCl_3$; (b) H_2SO_4; (c) HNO_3; (d) N_2O_4; (e) BF_3; (f) NH_4OH; (g) N_2; (h) $HClO_3$; (i) $HClO_4$; (j) $HClO_2$; (k) $HClO$; (l) O_2.

9.   Write notes on :—

(a) Hybrid bonds; (b) σ and π bonds; (c) Directed bonds; (d) Molecular orbital theory; (e) Limitation of ionic and covalent bonds.

10. Discuss the bonding character of the elements N and P with special reference to their positions in the Periodic Table and to their oxides and hydrides.

11. What types of chemical bonds are recognized in modern electronic concept ? Give examples illustrating each type and write down their electronic formula.

12. (a) Explain the electron distribution in the compounds: magnesium iodide and lithium chloride.

(b) Show that methane, carbon tetrachloride and water contain covalent linkages among their respective atoms.

(c) Prove that hypochlorous acid and phosphorus oxychloride contain coordinate bonds in their molecules.

13. Mention how the distribution (of electrons in atoms) contributes towards the nature of bonding.

Explain the bonding in NaF, CO and $Co(NH_3)_6Cl_3$.

14. How far the knowledge of the electronic configuration of atoms of rare gases has helped in explaining the formations of chemical bonds ?

15.   Indicate the different types of bonds that are present in the following compounds :—

(a) NaCl; (b) $(H_2O)_x$; (c) $[Cu(NH_3)_4]Cl_2$.

Discuss the modes of formation of any two types of bonds.

16.   Write a brief notes on:—

(a) Coordination bond, (b) Variable oxidation states.

17.   (a) Discuss the different types of bonding that are recognised in modern chemistry. Illustrate your answer with suitable examples.

(b) Explain the terms "electronegativity of elements" and "variable oxidation state"

18.   (a) Enumerate the fundamental ideas of the electronic theory of chemical bonds and different bond types.

(b) Explain hybridization of orbitals, bond strength and bond angle.

19.   Discuss the different types of bonding that are commonly encountered in chemical compounds. Illustrate your answer with examples.

What is meant by hydrogen bond?

20.   Discuss the bonding and properties of water.

21.   Write short note on electronegativity of elements.

22.   What are σ– and π- bond ?

23.   What do you understand by bond order. Calculate the bond order in the following molecules N_2, O_2, He_2, NOF_2

24.   Indicate the relationship of bond order with the properties of the molecules.

25.   Discuss bond hybridizations in the compounds of non-transition elements giving examples of inorganic species only.

26.   Compare the Valence Bond and Molecular Orbital Theroires of the chemical bonds.

CHAPTER 3
THE SIZES OF ATOMS AND IONS

The sizes of atoms, ions and molecules have important relationships with their chemical behaviour.

Atomic sizes are expressed in Angstrom unit ($1 \text{ Å} = 10^{-8}$ cm). We can get some idea of the range of atomic size by noticing one of the smallest atoms, F, having radius of 0.72 Å), while one of the largest, Cs, has a radius of 2.35 Å. It may be noted that since an atom is made up of a compact nucleus and a diffuse electron cloud, the size of an atom may be considered primarily as the space occupied by its electron cloud. Hence it is the electronic structure which actually governs the sizes of atoms and ions.

Sizes of Atoms

Atomic and covalent radii : The size of an atom depends upon two factors : (1) The positive charge on the nucleus and (2) the number of occupied electron levels about the nucleus. By keeping these two factors in mind we can easily visualize the relative sizes of the atoms of the various elements. Thus it may be inferred that the size of an atom is determined by the cloud of 1 to 105 electrons from H to Ha which occupy a space whose diameter is of the order of 50,000 to 100,000 times greater than the diameter of the nucleus. The probability of finding an electron at a given distance from the nucleus is maximum at a definite distance which is characteristic of the energy level occupied by the electron. At any given time, however, the electron may be further from the nucleus or closer to it. Hence the size of an isolated atom cannot be expressed in any precise way. Therefore, we measure the distance between two nuclei when two atoms approach each other and then calculate the atomic sizes of the two atoms from the inter-nuclear distances. Thus the size of the isolated

atoms and those obtained in purely covalent compounds of the same atoms are supposed to be identical, Therefore, the *atomic radii* and *covalent radii* of elements have the same definition.

Bond Length

The inter-nuclear (or inter-atomic) distance between two bounded atoms of the same kind is called the Bond Length. This is considered to be the sum of two lengths, called the Covalent Radii of the atoms. The bond length in Cl_2 or Cl–Cl has been determined to be 1.98 Å. One half of this value in chlorine molecule can be attributed to each chlorine atom. Thus the covalent radius of each chlorine atom is 0.99 Å. In diamond crystal, each carbon atom is bound covalently to four other C atoms having inter-nuclear distance of 1.54 Å between two C atoms. In the elementary silicon which also has the diamond structure, the Si—Si distance is 2.34 Å. Thus the covalent radius of carbon is 1.54/2=0.77 Å and for silicon 2.34/2 = 1.17 Å. From these figures it is possible to calculate correctly the bond lengths in compounds containing carbon and silicon. Thus C—Si distance in tetramethyl silane, $(CH_3)_4$ Si, is calculated to be 0.77+ 1.17 = 1.94 Å which agrees very well with the experimental value of 1.93Å. The following methods are generally used for determining the atomic or covalent radii: (1) X-ray diffraction, (2) Electron diffraction, (3) Neutron diffraction and (4) Absorption spectra etc.

The covalent radius of an atom varies from element to element, but the radius also depends on the number of electrons shared in a covalent bond. Thus, the inter-nuclear distance and the covalent radii are largest for a single bond, smaller for double bond and smallest for triple bond. Table 3.1 shows the values of covalent radii of some atoms forming single, double and triple bonds.

We can summarise the relationship between atomic size and the Periodic Table as follows:

1. The size of an atom decreases with increasing atomic number within any one periodic series. It will be noted that this decrease is due to two factors which control the atomic size, namely, (i) the positive charge on the nucleus and (ii) the number of occupied electron level about the nucleus. Hence the atoms in the first series of the Periodic Table will be of small size because there is one electron level. The smallest atom will also be

that one in the first series that has the greatest nuclear charge. This is He which has nuclear charge +2 and only one occupied electron level. The largest atom will have the small nuclear charge but with the greatest number of occupied electron level. Cs is the largest atom because it meets these requirements.

Table 3.1. Normal covalent radii of some atoms in Å units.

Elements	Single bond	Double bond	Triple bond
H	0.30	—	—
B	0.88	0.76	0.68
C	0.77	0.67	0.60
N	0.74	0.62	0.55
O	0.73	0.55	—
F	0.64	—	—
Si	1.17	1.07	1.00
P	1.10	1.00	0.98
S	1:04	0.94	—
Cl	0.99	—	—
Ge	1.22	1.12	—
As	1.21	1.11	—
Se	1.17	1.07	—
Br	1.14	—	—
Sn	1.40	1.30	—
Sb	1.41	1.31	—
Te	1.37	1.27	—
I	1.33	—	—

2. Just after the inert gas structure, the extra electron goes into a new quantum level and hence the alkali metals have much greater atomic radii than the inert gases.

3. The transition elements in which the **d** and **f** levels are gradually filled, the atomic and ionic radii decrease with the increase in the atomic number in the same series. This is because the additional electron goes to the inner energy level closer to the nucleus which exerts greater attraction.

4. The electron cloud around an atomic nucleus "shields" or "screens" the nucleus and cancels the nuclear charge. All the electrons in an atom do not possess the same effect for shielding the nucleus. The fraction of the nuclear charge that in effect is cancelled by an electron is called the screening constant. Effective nuclear charge *of an element is obtained by* subtracting the sum of the screening values of the individual electrons in the cloud from the actual charge on the nucleus. Progressive increase in the atomic number across the Periodic Table leads to progressively greater effective nuclear charge. This gives rise to the decrease in the atomic size (atomic radius).

Ionic Radii and Energy Relationship

Formation of positive and negative ions from neutral atoms involves energy. It may easily be visualized that the size of an atom decreases when one or more electrons are removed from the electron cloud of the atom to form a positive ion. In order to remove the electron from an atom, energy will be required and the quantity of this energy depends upon two factors : (1) the size of the atom from which the positive ion is formed and (2) the number of electrons that must be removed to form the positive ion.

On the other hand, in order to form a negative ion, one or more electrons must be added to the electron cloud of an atom. When a neutral atom gains one electron to form a negative ion, a definite amount of energy is released. It may be easily visualized that the size of an atom increases when one or more electrons are added to it to form a negative ion. The same factors that influence the readiness of atoms to form positive ions, also influence the formation of negative ions.

The closer an electron is to the nucleus, more strongly it is attracted. This means that less energy is required to remove electrons from the outer energy level of a large atom than from a small atom. It is easier to form positive ions from a large atom than from a small atom. In the case of the formation of negative ions, a small atom accepts electron more readily than a large atom. Hence the smaller atoms form negative ions more readily than the larger atoms.

Ionization Energy (Potential) and Electron Affinity

In this connection we come across the terms Ionization Energy (Ionization Potential) and Electron Affinity.

Ionization Potential : Ionization energy of an element is the energy required to remove one electron from the electron cloud of an isolated atom obviously from the outermost energy level. The ionization energy is measured in the units of electron volts (ev) or kilocalories per gramme atom (Kcal/g. atom). An electron volt has been defined as the energy required to raise an electron through a potential difference of 1 volt, or the energy released when an electron drops through a potential difference of 1 volt.

The ionization potential is also a fundamental property of an atom. For each successive electron that is removed, a progressively greater amount of energy is required. In the formation of a singly charged positive ion, the ionization energy is simply the energy required to remove the most loosely held electron from the outermost electron level of the atom. This is referred to as the first ionization energy (potential). For the removal of the second electron from the singly charged positive ion, additional energy is required and this is known as the second ionization potential. It is easily seen that the second ionization energy will be greater than the first ionization energy and that there is a limit to the removal of electrons for the formation of positive ions.

To remove electrons from atoms or ions having inert gas structure considerable amount of energy is required to pull the electron out of a filled energy level. This is the reason why dipositive ions of alkali metal do not exist in nature.

In general, as the number of electrons that must be removed continue to increase, the formation of positive ion becomes progressively more difficult.

Table 3.2 gives the values of first ionization potential both in ev and Kcal/g. atom of alkali metals (1 ev $= 23.06$ Kcal/mole or 6.02×10^{23} ev $= 23.06$ Kcal).

Table 3.2. Ionization potentials of alkali metals.

Elements	Ionization Energy (potential) ev	Kcal/g. atom
Li	5.4	124
Na	5.1	118
K	4.3	100
Rb	4.2	95
Cs	3.9	89

The ionization energies of alkali metals decrease as the size of atoms increases. The successive increase in the amount of energy required to remove more than one electron from an atom is given in Table 3.3 in Kcal/g. atom of Mg, Al and Cu.

Table 3.3. Ionization potential (Kcal/g. atom).

Elements	First Ionization Potential		Second Ionization Potential		Third Ionization Potential	
Mg	Mg^+	176	Mg^{+2}	246		
Al	Al^+	138	Al^{+2}	434	Al^{+3}	656
Cu	Cu^+	178	Cu^{+2}	468		

When the first ionization energy of all the elements are plotted against the atomic numbers, a curve is obtained which shows the periodic variations in this fundamental property with atomic numbers. A part of the curve is shown in Fig. 3—1.

The peaks of the curve showing the maximum amount of ionization energies are occupied by the inert gases, the alkali metals naturally occur at the bottom troughs of the curve. It may be noted that the ionization potential as indicated in the curve increases somewhat irregularly in proceeding along a series

of elements in the Periodic Table. The irregular increase may be attributed to the following main factors : —(1) nuclear charge, (2) number of outermost electrons
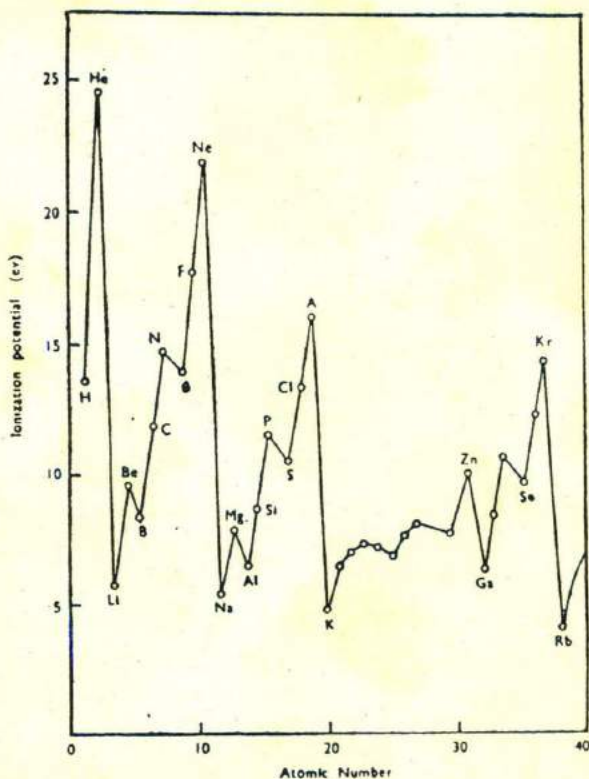

Fig. 3—1. The first ionization potentials of elements from H
to Rb.

and (3) the atomic radii. Table 3.4 gives the values of the first ionization potential of the elements of the first series (row) of the Periodic Table.

Notice the decrease in ionization potential of boron which is due to the presence of a single (unpaired) electron in 2p level. Less amount of energy is required to

Table 3.4. Ionization potential of the first period. (ev)

Elements	Nuclear charge	Electrons configuration	No. of electrons in the outermost level	Atomic Radii Å	First Ionization Potential (ev)
Li	3	$1s^2\,2s^1$	1	1.52	5.39
Be	4	$1s^2\,2s^2$	2	1.07	9.32
B	5	$1s^2\,2s^2\,2p^1$	3	0.89	8.30
C	6	$1s^2\,2s^2\,2p^2$	4	0.77	11.26
N	7	$1s^2\,2s^2\,2p^3$	5	0.70	14.54
O	8	$1s^2\,2s^2\,2p^4$	6	0.66	13.64
F	9	$1s^2\,2s^2\,2p^5$	7	0.64	17.42
Ne	10	$1s^2\,2s^2\,2p^6$	8	1.12	21.56

remove one electron from $2p^1$ of B atom as compared to the removal of an electron from paired-up $2s^2$ of Be or $2p^2$ of C. The first ionization potential of B shows a decrease in value (Fig . 3—1). Since a half-filled $2p^3$ level of N is more stable than $2p^4$ of oxygen, the removal of one electron from $2p^4$ requires less energy. Hence the ionization potential of oxygen is less than that of nitrogen. Similar drops in ionization potential occur for other elements (Fig. 3—1).

Electron Affinity: Electron affinity of an atom may be defined as the energy released when a neutral isolated atom in the ground state takes up 1 electron to form a negative ion.

The readiness of atoms to form negative ions also depends upon two factors: (1) the size of the original atom and (2) the number of electrons involved in ion formation. The smaller the atom and smaller the negative charge on the resulting ion, the more readily a negative ion is formed. The fundamental causes of this behaviour of atoms are probably very complex. It can be easily visualized that the nucleus of the smaller atom exercises a greater attraction on available electrons than does the nucleus of the larger atom.

Taking the formation of halide ions from halogens, it is known that atoms o the halogen family increase in size from fluorine to iodine. The smallest fluorine

takes up one electron most readily, the largest iodine takes up least readily. Thus the tendency of the formation of negative ions decreases markedly from fluorine to iodine. Similarly, this is the case in the series O, S, Se and Te.

Once a halogen has accepted an electron to form a negatively charged ion, it will show reluctance to accept further electrons.

It is also noticed that a singly charged negative ion forms more readily than a doubly charged negative ion. Taking the examples of Na, Mg, Al, Si, P, S and Cl, it is known that only the last two, namely, S and Cl, form negative ions readily. Sulphur takes up 2 electrons in its outer energy level to produce the electronic configuration of argon. Chlorine takes up only one electron for the same reason but much more readily than sulphur atom. The formation of phosphide ion P^{-3} takes place less readily. In fact, *simple* negative ions with a charge greater than -2 are very unusual.

In each case the negative ions are always larger than the neutral atoms from which they are formed.

Ionic Radii

The size of an atom decreases when one or more electrons are removed from its electron cloud to form a positive ion and increases when electrons are taken up by the atom. Hence it is possible to frame a general rule to the effect that the ionic radius of any cation is smaller than the radius of the neutral atom, whereas the radius of the anion is always greater. The change in the size of atoms after removing one or more electrons are shown below in Å.

Fe — 1.26	Fe^{+2} — 0.75	Fe^{+3} — 0.60
Mn— 1.29	Mn^{+2} — 0.80	Mn^{+4} — 0.52
Pb — 1.75	Pb^{+2} — 1.21	Pb^{+4} — 0.84

By X-ray methods it has been possible to determine the distance between the nuclei of two oppositely charged adjacent ions in an ionic compound. The distance between the neighbouring positive and negative ions in contact with each other in a crystal is called the inter-ionic distance. It has been assumed that ions act as spheres of almost constant radii and the measured inter-ionic distance

R is the sum of the radii of two spheres, r^+ and r^-, in contact with each other as shown in Fig. 3—2.
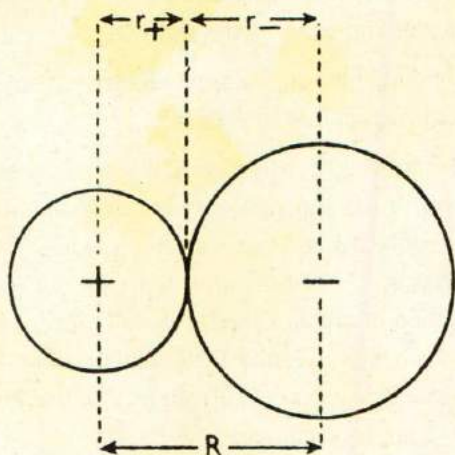

Fig. 3—2. Inter-ionic distance and ionic radii.

If R is measured, say, by X-ray diffraction method and either the radius of the positive ion r^+, or the radius of the negative ion r^- is known, the unknown radius can be easily calculated from,

$$R = r^+ + r^-$$

The ionic radii of elements exhibit periodicity or periodic variations as in the case of atomic radii.

The size of the ions is a physical property but this property is closely connected with the chemical properties of the elements. The chemical bonds among the elements are mostly dependent upon or related to the sizes of ions. The acid or alkali behaviours of cations in aqueous solutions are related to their ionic sizes. Similarity and dissimilarity of properties among groups of elements are influenced by ionic size and so on. Substitution of one ion by another in a crystal depends on the ionic radii of the species concerned. As a matter of fact, the ionic size is one of the most important factors which determines the structure and properties of substances.

Radius-Ratio Effect in Ionic Crystals : The geometrical shape of a crystalline solid is largely determined by the ratio of the ionic radii of the

positive and negative ions. This ratio also determines the coordination number of the central ion. In ionic crystals each ion tends to surround itself with as many oppositely charged ions as possible from geometrical considerations, and the number of the nearest neighbours is the coordination number of the central ion in the crystal.

Crystal Coordination Number : Thus the crystal coordination number of a positive ion in a crystal may be defined as the number of negative ions arranged in a symmetrical manner around the positive ion and in contact with it.

It has been assumed that ions are perfect spheres, and it is possible to calculate the minimum radius of an ion around which other ions of unit radius can be arranged. For instance, the ratio r^+/r^- having a value of about 0.15 indicates that only two anions can be arranged about a cation so that the three ions are in contact with each other. Similarly, the ratio r^+/r^- having values from 0.15 to 0.22 indicates that three anions could be in contact with each other enclosing a central cation giving a 3-fold symmetrical coordination. Fig. 3—3 shows some of the arrangements. Notice the different sizes of the central cations (black spheres).
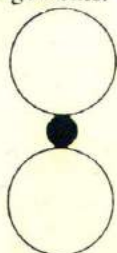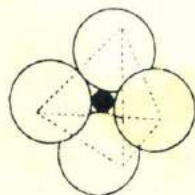

Two-fold coordination
(Linear)
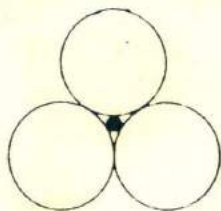
Three-fold coordination
(Triangular)
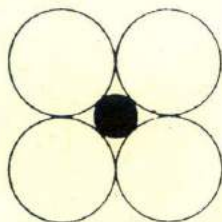
Four-fold coordination
(Planar)

Four-fold coordination
(Tetrahedral)

Fig. 3—3. Relative sizes of the ions and coordination number.

Table 3.5 shows the dependence of coordination number and geometrical shapes on the radius-ratio r^+/r^- in general.

Crystal Lattice : A crystal lattice is made up of an infinite repetitions of a small group of ions in three-dimensional pattern.

Solid ionic compounds consist of crystal lattice which is built up by the combination of a regular array of ions in which each ion is surrounded by a definite number of ions of opposite charges. Thus in the ionic lattice of sodium fluoride, the Na—F distance is 2.31 Å and of this 0.95 Å is the radius of the fluoride ion. The radius ratio, $\dfrac{rNa}{rF}$, is 0.69, and hence the crystal lattice possesses octahedral or 6-fold coordination in which each sodium ion is surrounded by six fluoride ions and each fluoride ion is surrounded by six sodium ions. NaCl has the same crystal structure.

Table 3.5. Radius-ratio effect.

Ratio $\dfrac{r^+}{r^-}$	Coordination Number	Geometrical shape
Upto 0.15	2	Linear
0.15 — 0.22	3	Triangular
0.22 — 0.41	4	Tetrahedral
0.41 — 0.73	4	Planar
0.41 — 0.73	6	Octahedral
0.73 and above	8	Cubic

The small group of ions which is repeated in a crystal lattice in three-dimensional pattern is known as a *unit cell*. The unit cell is thus the smallest portion of the crystal lattice which has all the various kinds of symmetry which characterise the crystal. A unit cell cannot exist singly since all the unit cells in a crystal lattice have common boundaries.

Lattice Energy : The lattice energy of an ionic compound is defined as the energy released when the crystal lattice is formed by combination of requisite number of free gaseous positive and negative ions in an ionic crystal to give one mole of the compound. Conversely, it may also be defined as the energy required