First Year
Paper II - Inorganic Chemistry I

UNIT I
BONDING AND STEREOCHEMISTRY

Electronic configuration of elements – significance of quantum numbers – Polyelectronic atom – Pauli's principle – Aufbau principle – qualitative treatment of VB and MO theory – and P bonds – Hybridization and resonance – applications of VB and MO theory – the electron deficient molecule – boronhydrides and metal alkyis.

Bond order – Bond energy – bond length – bond polarity – partial ionic character – electro negativity and different scales of Pauling, Mulliken, Aldrich and Rochow and Sanderson scales – Conversion to Pauling scale – Periodicity of electro negativity, electron affinity and ionic radius – lattice energy Born – Haber cycle and numerical problems involving it for the calculation of electron affinity or lattice energy – Covalent character in ionic compounds – different types of electrostatic interaction – Hydrogen bonding.

Stereochemistry – VSEPRA, Walash diagrams (tri and penta atomic molecules) d_π □ P_π bonds – bent's rule and energetic hybridization – uses of Bent's rule "apicophilicity".

UNIT II
SOLID STATE CHEMISTRY

Elements of crystallography - space lattices - Unit cells - crystal systems - X - ray diffraction, Bragg's equation - Bragg's method -rotation method and powder method of X-ray diffraction - structure of typical lattices such as calcite, Zinc blende, Wurtzite, Rutile, Fluorite, antifluorite, Pervoskite.

Crystal defects in solids - line and plane defects - non-stoichiometry - schottky and Frenkel defects and colour centres; solid elecrolytes

Free electron and band theory - semiconductors - types and properties of semiconductors - Hall effect - Photovoltaic and solar energy conversion - superconductivity - high temperature super conductors -cooper electrons - Meissner effect and leviation.

UNIT III
NUCLEAR CHEMISTRY

Radioactivity and modes of decay α, β and γ – Different types of nuclear reactions with natural and artificial particles - Q value, corss section, spallation, fission and fusion characteristics of fission reactions, product distribution and for fission, of liquid drop fuel, fissile and fertile isotopes; nuclear fusion and stellar energy. Transmutation of elements and chemical effect on transmutation, Isotopes and their applications. Radioactive analysis and counting techniques Geiger - Muller, Ionisation, proportional and Scintillation counters.

Radioanalytical Method :

Neutron activation analysis - Isotopic dilution methods - Radiometric titrations.

Coordination chemistry and Magnetism: Bonding in Coordination Compound

Nature of metal-ligand bond: VB theory - electroneutrality principle and back bonding - crystal field effects for octahedral, tetragonal, square planar and tetrahedral symmetries, applications of CFT - Site preferences; spectrochemical series and nephelauxeticeffect; MO theory for octahedral complexes - pi bonding and MOT; - Static and dynamic Jahn - Teller behaviour.

Magnetic behaviour - dia, para, ferro, ferri. and antiferro magnetisms; magnetic moment determination by Guoy and Faraday methods; Spin only value and its deviation - Quenching of orbital angular moments and spin - orbit coupling. Determination of geometry of Co and Ni complexes from magnetic data. Spin Crossover phenomenon; magnetic properties oflanthanides and actinides.

Unit V

Metallurgy and Inorganic polymers:

Occurrence, isolation, purification, properties and uses of the following metals and their important compounds: Zr, Ge, Pu, Th, U and Os.

Silicates:

Various silicate structure - property correlation - silicones - polyacids - structure of heteropoly and isopolyacids - polymeric sulphur nitride - borazines - phosphonitrilic compounds - boranes and carboranes.

1. Jame E. Huheey, Inorganic Chemistry: Principles of structure and Reactivity (Harper Collins)
2. K.F. Parcel and J.C. Kotz, Advanced Inorganic Chemistry (Saunders Golden)
3. G.C. Demitrass et.all, Inorganic Chemistry, (prentice Hall)
4. B.E. Douglas, D.H.Mc. Daniel and J.J. Alexander, concepts and Models of Inorganic chemistry.
5. H.J. Emeleus and A.G. Sharpe, Modem Aspects of Inorganic chemistry, ELBS.
6. M.C. Day Jr. and J. Selbin, Theoretical Inorganic Chemistry, East West Press.
7. F.A Cotton and Wilkinson, Advanced Inorganic Chemistry, John Wiley.
8. N.N. Greenwood and A Eamshow, Chemistry of Elements, Pergamon.
9. L. Araroff, Introduction to Solids, Tata Mc Graw-Hill.
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14. D.K.Chakrabarthy, Solid state chemistry Ne Age International.
15. S.Glasstone, Source Book on Atomic Energy, East west Press.
16. H.J. Amiker, Essential of Nuclear Chemistry, Wiley Eastern.
17. G.Fridlander, J.W.Kenedy E.s.Macias and J.M.Miller. Nuclear and Radiochemistry, John Wiley and Sons.

MANONMANIAM SUNDARANAR UNIVERSITY

DIRECTORATE OF DISTANCE AND CONTINUING EDUCATION

M.Sc CHEMISTRY

INORGANIC CHEMISTRY - I

Introduction

Inorganic chemistry deals with the theoretical aspects of bonding and structure of inorganic molecules, crystals and Coordination compounds. The subject is divided into 5 units. At the end of each unit some important questions are given.

The First unit discusses the bonding and structure with various aspects like Pauli's exclusion principle, Aufbau principle, Bond length, Electronegativity, Resonance and Hybridization. It also discusses elaborately the shape of molecules using VSEPR theory.

The Second unit discusses the Solid-state chemistry of Ionic crystals. The Theory of conductors, Semiconductors formation and Solar energy conversation into electrical energy and the Principles of super conductivity are also dealt with in thisunit.

In the Third unit, the Nuclear chemistry describes the emission of Alpha, Beta and Gamma radiations from the nucleus, the Liquid drop model for Fission reaction and the various nuclear reactions with a number of examples. Finally the applications of traces elements are given. Some worked out examples are also presented.

The Fourth unit deals with Coordination chemistry. The theories of Coordination bond and their magnetic properties are explicitly given.

Finally the Fifth unit discusses about the Metallurgy of some trans- uranium elements and inorganic polymers.

The following text - bbiks are useful as reference material for this paper.

1. James E.Huheey, Inorganic Chemistry: **Principles structure and Reactivity** Harper Collins, London.

2. K.F.Purcel and J.C.Kotz, **Advanced Inorganic Chemistry**, Saunders Golden.

3. G.C.Demitrass et.al., **Inorganic Chemistry** Prentice Hall.

4. B.E.Douglas, D.H.McDancil, J.Alexander **Concepts and Models of Inorganic Chemistry,** Third Edition, John Wiley & Sons, New York.

5. H.J.Emeleus and A.G.Sharpe, **Modern "Aspects of Inorganic Chemistry,** ELBS, London.

6 M.C.Day Jr and J.Selbin, **Theoretical Inorganic Chemistry,** East west press, Chennai.

7. F.A Cotton and J.Wilkinson **Advanced Inorganic Chemistry,** John Wiley, New York.

8. C.Kittel, **Introduction to solid state Physics,** Wiley Eastern.

9. A.F.Weils, **Structural Inorganic Chemistry,** ELBS.

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UNIT -I
BONDING AND STEREOCHEMISTRY

SYLLABUS

Electronic configuration of elements - significance of quantum numbers Poly electronic atom - Pauli's principle - Aufbau principle - qualitative treatment of VB and MO theory - a and n bonds - Hybridization and resonance - applications of VB and MO theory - the electron deficient molecule - boron hydrides and metal alkyls.

Bond order - Bond energy - bond length - bond polarity - Partial ionic character - electro negativity and different scales of Pauling, Mulliken, Aldrich and Rochow and Sanderson scales - Conversion to Pauling scale - Periodicity negativity, electron affinity and ionic radius - lattice energy Born - Haber numerical problems involving it for" the calculation of elegon affinity r lattice energy - Covalent character in ionic compounds - different types of e lectrostatic interaction - Hydrogen bonding.

Stereochemistry - VSEPR, Walsh diagrams (tri and penta atomic molecules) $d_\pi - p_\pi$ bonds - Bent's rule and energetic hybridization uses of Bent's rule "apicophilicity".

I. Introduction

Electronic configuration of elements

In 1926, Schrodinger proposed an equation that specified no discrete orbits, but instead described the wave associated with the electron "particle". This equation, given below, provided the basis for wave mechanics.

$$\frac{h^2}{8\pi^2 m}\left(\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}+\frac{d^2\psi}{dz^2}\right)+v\psi = E\psi \qquad \text{........ (1)}$$

In this equation, Ψ is the amplitude of the wave function associated with the electron E is the total energy of system, V is the potential energy of the system (equal to $-e^2/r$ for hydrogen), m is the mass of electron, h is Planck's constant, and x, y and z are the Cartesian coordinates. The frequency of the wave describing the electron is related to its energy by $E = \frac{hv}{\mu}$

The Schrodinger equation is generally written in operator from.

$$\underbrace{\tilde{H}}_{\text{(Hamiltonian) Operator}}\ \underbrace{\psi}_{\text{Eigenfunction (or operand, or trial wave function)}} = \underbrace{E}_{\text{Eigenvalue (a constant; the energy or other observable)}}\psi \qquad \text{........ (2)}$$

The equation is known as the time-independent Schrodinger wave equation, and the solution obtained are to be multiplied by a phase factor e.

$\tilde{H}$ is an operator - that is, it gives directions for an operation (such as taking a derivative) to be performed on the function that follows it. If the result of performing this operation is a constant times the original trial function, the trial function is termed an eigenfunction of the operator and the constant is called an eigenvalue. The Hamiltonian operator is the one associated with energy. Other operators are associated with other observables such as angular momentum. In equation (2), the Hamiltonian operator consists of taking the second partial derivatives of the trial function with respect to each of the Cartesian coordinates and of multiplying each by a constant and adding the results to the potential energy V.

Because the probability of finding the electron in a given volume element is proportional to $\Psi^2 d_\tau$ is the size of the volume element, Ψ itself must be a single valued function with respect to the spatial coordinates, must be continuous, and must become zero at infinity. These conditions are imposed as boundary conditions on the solutions to the wave equation.

The transformation from Cartesian coordinates, x,y,z, into polar coordinates facilitates solution of the wave equation. The position variables in polar coordinates are r, θ and φ, where r is the radial distance of a point from the origin, θ is the inclination of the radial line to the z axis, and φ where r is the radial distance of a point from the origin θ is the inclination of the radial line to the z axis, and Ψ is the angle made with the x axis by the projection of the radial line in the xy plane. After this transformation the Schrodinger equation can be factored into two equations, one depending only on r and the other only θ and φ.

. The relationship between the Cartesian and spherical polar coordinates results using the right triangles visible in Fig. 1.

$\cos\theta = z/r,\qquad z = r\cos\theta$ .... (3)

$\cos(90-\theta) = \sin\theta = s/r \qquad s = r\sin\theta$ .... (4)

$\cos\Phi = x/s, \qquad x = s\cos\Phi = r\sin\theta\cos\Phi$. .... (5)

$\sin\Phi = y/s, \qquad y = s\sin\Phi = r\sin\theta\sin\Phi$ .... (6)

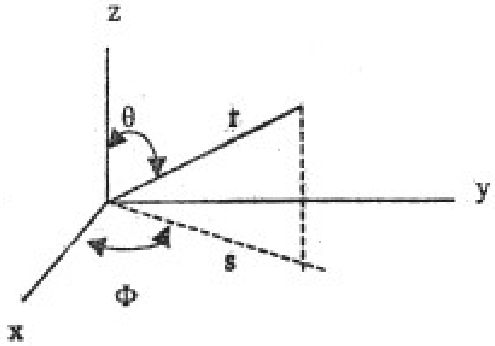


Fig. 1 : Variables of polar coordinates

The solutions for Ψ, called wave functions, may be expressed as the product of three functions, each of which depends on only one spherical polar coordinate:

$$\Psi(r, \theta, \Phi) = R(r)\,\Phi(\theta)\,\Phi(\Phi) \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

The boundary conditions require that certain constants entering into the solution of the wave equation on only certain integral values. These constants, called quantum number, are designed by n,*l*, and m. The principal quantum number, n, may take on the values 1,2,3 .....; I may have the values 0,1,2, ... up to (n-1); man have values ranging from – 1 through 0 to + 1. the wave functions, $\Psi_{n,l,m}$, which are solutions of the Schrodinger equation, are commonly called orbital. Orbital for which l = o, 1,2,3, and 4, are called, respectively, s, p, d, f and g orbital.

II Significance of Quantum Numbers

The extension of Bohr's theory became necessary as a result of more detailed investigation of spectra by using high resolving equipment. It was reported that

(i) Many single lines were found to contain a number of very closely related lines

(ii) When a source was kept in a magnetic field (Zeeman effect) or in a electric field (stark effect) many single lines were found to split up.

The resulting fine structure of spectra is due to the increase in the number of possible orbits in which an electron can reside in an atom. In simple words, there are more possible energy changes within the atom to explain the fine structure of observed spectral lines.

The term quantum number is used to identify the various energy levels that are available to an electron. The word, 'quantum' is used to signify that all the energy levels which are available to an electron are governed by the laws of Quantum Mechanics

1. Principal Quantum Number

This number is designated as 'n' and is identical with the Bohr's integers to describe stationary states in atom.

This gives the number of the principal shell in which the electron is revolving around the nucleus. It designates the average distance of the electron from the nucleus. Hence this quantum number represents the size of the electron orbit.

The principal quantum number not only determines the size of the orbit but also governs the allowed energy levels in an atom.

The principal quantum number, given by Bohr's Theory, can be described mathematically in the equation.

$\mu r \frac{nh}{2\pi}$ where h is the Planck's constant

N always assumes the integral values 1,2,3,4, ... ∞ (not zero).

Thus n = 1 for the K – level, 2 for L – level and so on. The first energy level, n = 1 is the one which is nearest to the nucleus, n = 2 the next energy levels is away from the nucleus, and so on. As the first energy level is nearest to the nucleus, it binds strongly to the nucleus. The next energy level is farther from the nucleus and hence binds to the nucleus with a lesser bending force and so on. Thus the principal quantum number describe roughly.

(i) The size of the electron orbit i.e., distance between the nucleus and the electron.

(ii) The binding force between the nucleus and the electron.

As n increases, the energy of orbit increases until it is zero at n = ∞. Beyond this energy is no longer quantized; the electron is not bound to the nucleus and can have any arbitrary amount of kinetic energy.

Accordingly, the spectrum in this region does not contain lines but is continuous and is called continuum. The difference in energy between $E_{n=1}$ is the energy needed to ionize the atom and is called the ionization energy of the hydrogen atom.

The values of n also fix the number of nodal surfaces. The total number of nodal surfaces in an atom is n including the one ∞. At a nodal surface the wave function Ψ changes phase and Ψ^2 is zero, i.e., an electron is not found at this surface.

2. Azimuthal quantum number

This quantum number is also known as the second, the subsidiary, the lesser, or the orbital quantum number and usually defined by the following mathematical relation.

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

Where l is the azmuthal quantum number which can have values ranging from 0 to n -1 i.e.,

$l = 0, 1, 2 \ldots (n-2), (n-1)$.

From this, it follows that

(i) in $n = 1$, the l can have only one value.equal to zero, $l = 0$

(ii) if $n = 2$, the l can have two value, 0 and $(n=0, n= 1-1)$.

(iii) if $n = 3$, the l can have three values, $l = 0,1,2$

(iv) if $n = 4$, the l values associated with $n = 4$ are 0,1,2 and 3

If any one shell, having the same quantum number, the srbshells corresponding to $l = 0,1,2,3....$ Are denoted by the symbols s, p, d and f which are derived from the names of the spectral lines – sharp, principal, diffuse and fundamental respectively. The s sub – shell is spherical, p the dumb – bell shape, d and f some more complicated shapes. Each shell is made up of sub – shells which differ from one another in their azimuthal quantum number values and hence differ in their shapes. Thus, azimuthal quantum number describes the shape of the orbital in which the electron is present. The greater the value of 'l' the more diffused the sub – level is

In a particular energy level the energies of its sub – shells are in the order:

$S<p<d<f$

Thus, s electrons will shield p electrons from the attraction of the nucleus an p electrons shield d electrons from the nucleus. Therefore, the sequence of filling the various sub – shells is s, p, d, f and so on.

3. Magnetic quantum number

This quantum number was introduced to describe the Zeeman effect (i.e. splitting spectral lines under the influence of an applied magnetic field).

We know that each sub - shell is further sub – divided into various orbitals; the number of these orbitals, being given by n2, thus when n = 2, there are 4 possible orbitals. Each orbital contains two electrons.

When an atom is placed in a magnetic field (Zeeman effect) due to the presence of negatively charged electrons in it, the orbitals orient themselves relative to the magnetic field and their orientation in the magnetic field is determined by the magnetic quantum number (m).

This number is usually designated as 'm' and can have values from + l to – l through zero, i.e.,

$m = +l, (l-1), (l-2) \ldots\ldots\ldots\ldots 0, 1, 2 \ldots\ldots\ldots\ldots - (l-1), -l.$

In other words, the number of m values for a given l value is $2l +$ i.e.,

$m = (2l + 1)$ values through zero.

Examples

For a s electron with $l = 0$ m is zero $(+l = 0, l = 0)$

For a p electron with $l = 1$, m can be – 1, 0 and 1

For a d electron, with $l = 2$, can be -2, -1, 0 + 1, +2.

Every value of m, for a given value of l, corresponds to one orbitals in that sub – shell designed by l. hence we have.

(i) s will have one orbital as m has only one values (m = 0)

(ii) p will have three orbitals as m has three values (-1,0,1)

(iii) d will have five orbitals as m has five values (-2,1,0,1,2)

(iv) f will have seven orbitals as m has seven values (-3,-2,-1,0,1,2,3)

It means that two orbitals in the same sub shell can have identical n and l values but must differ in m values.

Thus, p–sub shell is made up of three identical orbitals, in the absence of a magnetic field. But in a magnetic field the three orbitals of p sub – shell take up different positions with respect to the lines of force of field and thus acquire slightly different energy levels. Therefore, three 2p orbitals can be denoted as 2px, 2py and 2pz. Similarly, in magnetic field, the 3d orbitals can be obtained by $d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{yz}, and d_{xy}.

4. Spin Quantum Number

This quantum number, which is designated as 's' arises from the spectral evidence that an electron in its motions around the nucleus in an orbit also rotates or spins about its own axis. The electron can spin clockwise or counter clockwise. The spin of electron contributes to its overall angular momentum and since it can either be forward (clockwise) or back ward (anticlockwise) relative to the direction of the path of electron it may cause angular momentum to increase or decrease. This leads to two sub – levels of slightly different energy for each value of m, thus corresponding to two possibilities of s. Assuming the total energy difference between these two sub – levels to be one quantum, s level will have values + ½ and – ½. The two values are often conveniently put as

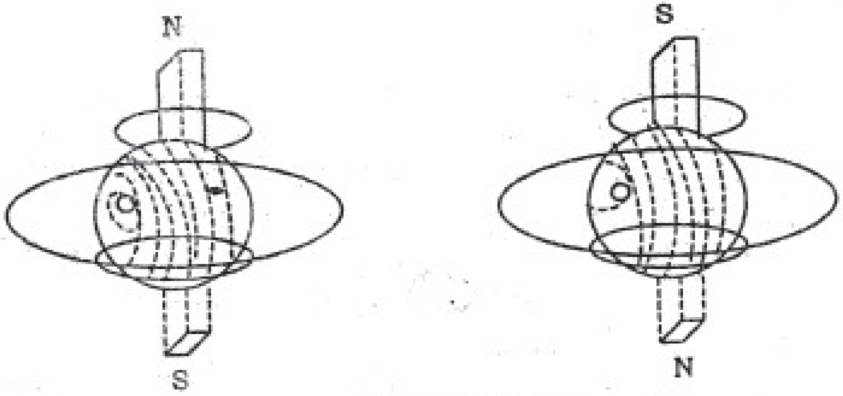
↑ and ↓

Mathematically this quantum number is defined by the equation.

$$\mu r = \frac{h\sqrt{s[s+1]}}{2\pi}$$

Where μr denotes the angular momentum and a may have values of either + ½ and -½.

The concept of electron spin is important in applying the Pauli's principle which limits only two electrons in an orbital provided they have opposite spin. Such electrons are known as paired electrons. When an orbital has only one electron, it is known as odd or unpaired electron.



Spinning electron

The spin quantum number gives rise to magnetic properties of materials. If there are two electrons in any orbital with opposite spins (paired electrons) their magnetic moments will be cancelled. Presence of magnetic properties indicates the presence of one or more unpaired electrons.

Conclusion

To sum up, it may be enunciated that four quantum numbers characterize completely the shape and size of the particular electron cloud surrounding the nucleus in a similar manner to a normal post office address.

Table summarises the various permitted values for the four quantum numbers, describing the state of an electron.

Quantum Number	Symbol	Permitted value
1. Principal	n	1,2,3,4 ..... n
2. Azimuthal	L	0,1,2, ... (n-1) for each value of n
3. Magnetic	M	0, ±1, ±2, ... ±1 for each value of l
4. Spin	S	±1/2 for each value of m

III. Paull Exclusion Principle

Introduction

This is the most important principle, which cannot be derived from any fundamental concept. We know that four quantum numbers are needed to define the energy of an electron in an atom. Wolfgang pauli (1925) Put forward and ingenious principle, which controls the assignment of values of four quantum numbers of an electron. It applies certain restrictions on their values for electrons in an atom and hence the name 'exclusion principle'.

Statements

This principle can be stated in a number of ways such as:

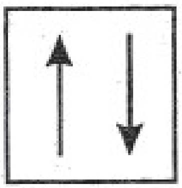
(i) All electrons in any system must be distinguishable

(ii) No two electrons in a single atom can have all their quantum numbers identical.

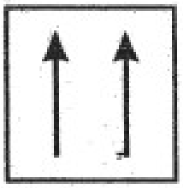
(iii) No two electrons in an atom can exist in the same quantum state.

All the above statements are identical and carry the same meaning that if two electrons posses the same values for n, l and m, they must have different values of s. thus, every electron in any atom differs from every other electron in total energy and therefore there can be as many electrons in a shell as there are possible arrangements of different quantum numbers.

According to Pauli's principle the electrons entering the same orbital (n, *l* and m, values are identical) should have opposite spins. Thus this state (opposite state) gives a lower energy state than when the pairing of electrons with parallel spins. According to the thermodynamics, a system having lower energy is maximum stable. Therefore, the state with the lower energy (opposite spins), is preferred and electrons entering the same orbital must have spins in opposite direction.



Opposite spin Lower Energy More stable



Opposite spin More Energy More stable

From the above discussion, it follows that no orbital can contain more than two electrons. Therefore, pauli's principle can be stated in another way.

"Two electrons can occupy the same orbital only if their spins are opposed".

IV. Aufbau Principle

The word Aufbau is a German expression, which means 'build up' or 'construction'. This Aufbau principle is mainly concerned with the building up process in which the extra nuclear electrons are being added to the various available orbitals so as to balance the nuclear charge. Broadly speaking this principle states that every electron enters the lowest possible energy state available.

Two important rules are

(i) Orbitals with lower n – values are filled up before those with higher n – values.

(ii) For any given principal quantum number n, s-orbitals are lower in energy the p – orbitals and they in turn are lower than d-orbitals and so on. Thus the order for filling up orbitals for same n is s, p, d, f etc

Order of Energy Levels

Since for hydrogen, the energy of the orbital has been found to depend upon the principal quantum number only, the orbital order for the increasing energy (for decreasing stability) has been as follows:

$$Is > 2s = 2p > 3s = 3p = 3d > = 4s = 4p = 4d = 4f \quad 5s = 5p = 5d = 5f = 5g > \ldots\ldots\ldots\ldots$$

For the polycharged nucli, because of the inter electronic repulsions and the shielding effects of the inner electrons, the degenerate states in the hydrogen atom do not remain degenerate. Although the p and d orbitals with a particular principal quantum number become smaller (the most probable radius decreases in the order s > p> d> f for the same value of n), the presence of increasing number of nodes is able to cause the orbitals with a higher number of nodes to get more affected by the nucleus, so that the energies of the orbitals follows the order f> d> p> s. As more and more electrons are fed into the atom, splitting of the energy levels occurs due to increasing nuclear charge. As a result, the ns state atom, splitting of the energy levels occurs due to increasing nuclear charge. As a result, the ns state overlaps the (n-1) d state and becomes more stable. This overlap becomes greater for the f orbitals.

The following order of the orbitals has been found to hold good for elements up to nuclear chare Z = 20 satisfactory, and beyond with slight modifications have to be made in it.

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p$$
$$< 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p < \ldots\ldots\ldots\ldots\ldots \quad [1]$$

With an increasing atomic number, the relative positions of the stabilities or the orbitals tend to change gradually till for the heavy elements (Z > 90), the order of the energy levels as tends to become.

$$Is < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 4d < 4f < 5s$$
$$< 5p < 5d \; <6s \; <6p \; <5f \; < 6d < \ldots\ldots\ldots\ldots \quad [2]$$

The following empirical rules called the (n + *l*) rules can be used to remember the order in Equation (1).

(1) The energy of the orbitals tends to increase with the increasing (n + *l*), values. Thus the energies of the orbitals will be in the order.

$$Is < 2s < 3s < 4s \;\; 3s < 3p < 3d \; 4p < 5d \;\; 6s < 5f$$

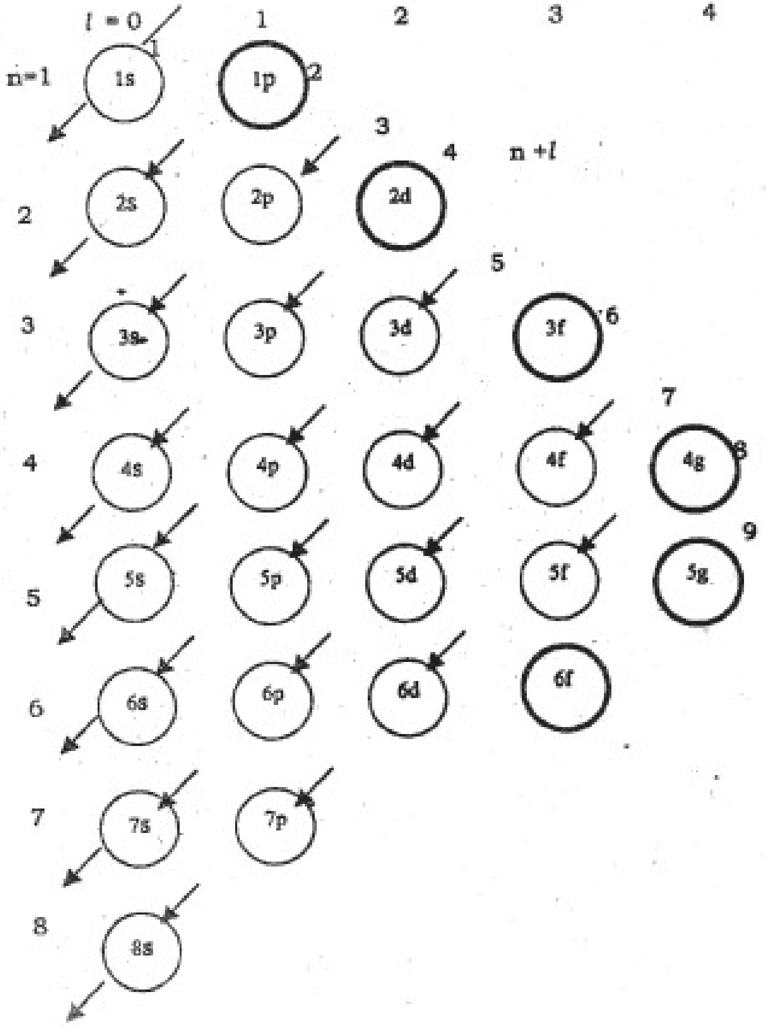
n + 1 l = 1 1 2 3 4 3 4 5 5 7 6 8

(2) For same value of n + *l*, the energy tends to increase with the increasing n value. Thus the order of increasing energies will be.

$3d < 4p < 5s$ and $4d < 5p < 6s$

$n + l = 5$ 5   5   6   6   6

The order of energy levels (E. 1) can be remembered with the help of Fig. 1, by proceedings from top to bottom as indicated by the diagonal arrows.



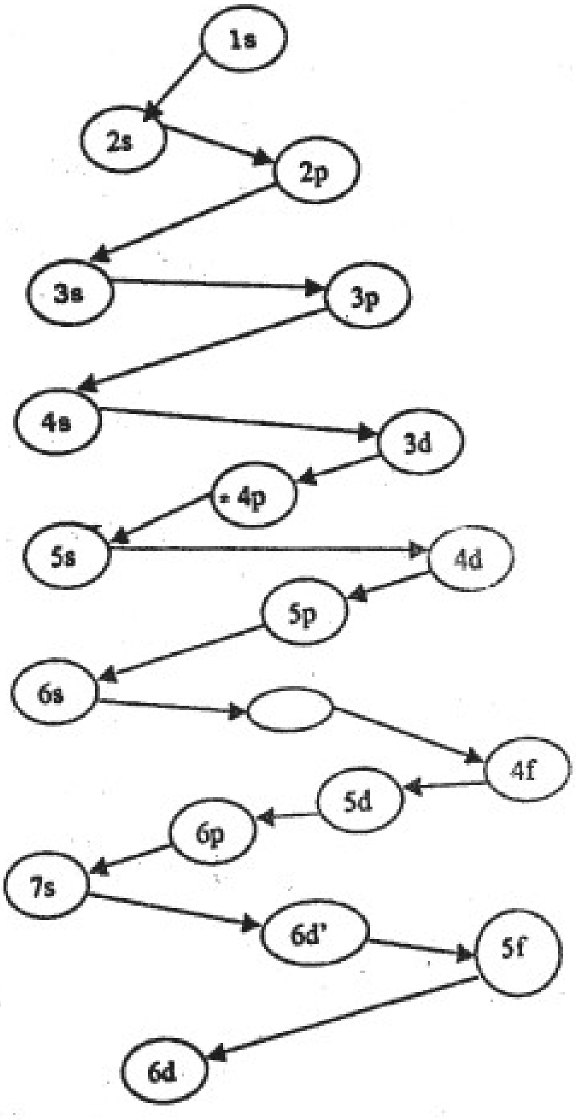
Mnemonic for determining the order of the filling of orbitals (approximate) in elements from the aufbau principle. The orbitals in bold circles are the non-exsistent orbitals.

Degenerate Orbitals

The orbitals, like the three p - orbitals for a given value of p, which give equal energy states, are called degenerate orbitals. As the 2p sub - shell has three equivalent energy orbitals, it means that it has a three - fold degeneracy. Similarly, d will have five fold degeneracy and f, seven fold degeneracy, while filling the orbitals, no differentiation is made between three p, five d or seven f levels.

Screening Rule

The electrons in complete inner shells screen the outer electrons against attraction by the nucleus. This is known as screening effect, it has been observed that this screening effect is less penetrating ones. As a result of the screening effect, every ns orbital is filled earlier than the corresponding (n – 1) d orbital. Thus, 4s is filled earlier than 3d. for similar reasons, 5s, 5p and 6s orbitals are filled before the 4f orbital.



Alternative sequence of filling of various orbitals in lanthanides and actinides

Aufbau principle has been found to be a very useful device to formulate ground state electronic configuration of atoms but this order of filling does not have universal application. Although electron configuration based on Aufbau order of filling have been found to agree mostly with those derived experimentally yet there are quite a few exceptions where errors in Aufbau configuration arise due to one (rarely two) misplaced electron. This happens mostly in those cases where the subshells involved in configuration are exceedingly closely placed and are thus, prone to exchanging positions.

V Valence Bond and Molecular Orbital Theories

Introduction to valence Bond Theory

Heitler and London developed this theory in 1927. Later, Pauling and Slater modified this theory to take into account the directional nature of the covalent bond, which predicts the accurate geometries of molecules. They further postulated that resonance structures should also be considered.

Let us discuss these theories one by one.

Heitler – London Theory

This theory is based upon the pairing and resultant netrualization of opposed electron spins. The fundamental idea about this theory is summarized below:-

(i) In order for an atom to enter into chemical combination, it must possess one or more unpaired electrons. The number of unpaired electrons, which it possesses, thus determines the valency of a species.

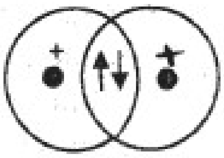
(ii) Although participation in bond formation by paired electrons is formally ruled out, such electrons may be involved if they can be unpaired with the expenditure of excessive energy.

(iii) A chemical bond results in when the two electrons are paired. For a stable bond formation, it is essential that the two electrons must have opposite spins.

Examples :-

In order to understand this theory completely, one has to understand the following simple examples:

(a) Formation of H_2 molecule – when hydrogen atoms are brought sufficiently close together, it is possible that their 1 s charge may interact with each other in one of the two ways :



H- H

Formation of Hydrogen molecule

i) They can overlap or fuse into each other, resulting ir the union of two atoms; or

ii) They can repel each other and thus prevent any union of the two atoms Calculations involving applications of Pauli's exclusion principle reveal that the attraction between to atoms occurs when the electrons are of opposite spins, i.e., when they are paired; electrons of the same spin cause repulsion. Thus, for stable bond formation, the condition is that the electrons should have the opposite spins.

The concept of orbital overlap can be understood in the following manner.

It has been observe that if a mole of H_2 molecule is heated to sufficiently high temperature, the reaction takes places as follows:

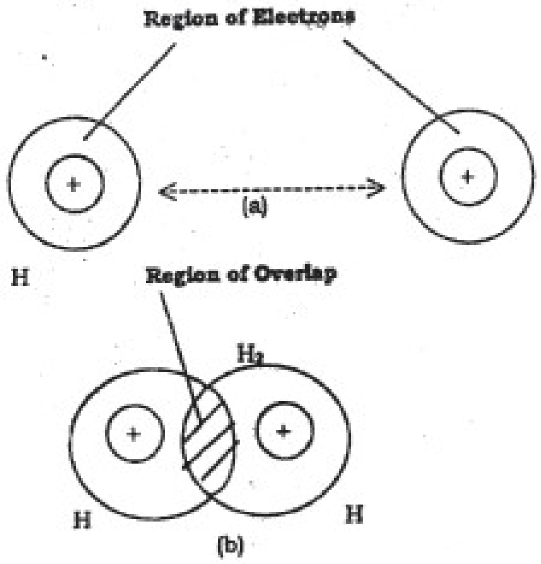
$$H_2(g) + 433KJ \longrightarrow H(g) + H(g)$$

This means that 433 kj of energy is required to dissociate a mole of hydrogen into hydrogen atoms. In otherwords, the formation of a mole of hydrogen atoms given 433 kJ of energy. Thus, the bond formation is accompanied by lowering of the energy of the system. In case of the atoms where electron transfer is not favoured on energy consideration, a chemical bond may be formed in some manner, which may also lead to lowering of the energy of the system. For instance, if one or more electrons of one atom may get so close to the other atom that they may experience attractive interaction with the other nucleus (besides its own) the total energy can be lowered. A nucleus attracts electrons in the region of space defined as orbital. The overlapping of the orbitals of the two atoms is essential for an electron to face simultaneous attractive interactions from the nuclei of the two atoms. This overlap region should be available to electrons of both the atoms. The occupation of the overlapping orbitals by electrons may take place in the following ways.

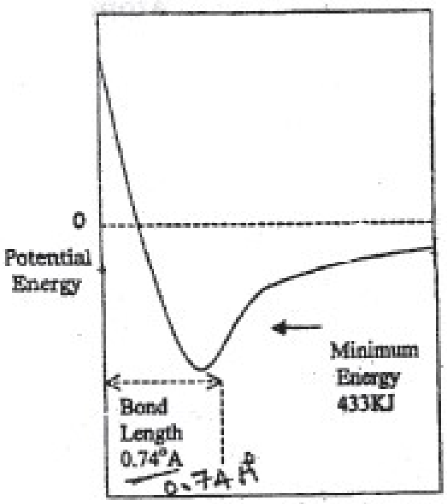
(i) Overlapping of orbitals of the atoms, which contribute one electron each. The bond formed is called covalent bond.

(ii) Overlapping of orbitals of an atom having two electrons (lone pair) an empty orbital of an atom. The bond formed is called co–ordinate bond.

Let us now study orbital concept of covalent bonding, the overlapping of s –orbitals in the case of bonding in hydrogen. It can be seen that during overlapping parts of atomic orbitals of the atoms occupy the same space. The question now arises, 'how much orbital overlapping can take place?' it is known that there are attractive and repulsive interactions present. The repulsive interactions tend to increase the potential energy.



Whereas the attractive interactions tends to decrease the potential energy. Considering the gradual approach of the atoms, at first the attractive interactions increase more rapidly than the repulsive interactions resulting in the decrease of the potential energy of the system. As the energy of the isolated atom is arbitrarily taken as zero, the decrease in the energy of the system is shown as negative. After a certain interatomic distance, the repulsive interactions start increasing more rapidly than the attractive interaction thereby resulting in the increase in potential energy of the system. The position of minimum energy is one where attractive and repulsive forces balance. The more the overlapping of the orbitals, the more will be the decrease in the energy of the system and hence a more stable covalent bond will be formed.



Distance between Hydrogen Nuclei
Fig. Potential Energy Curve for H₂ Molecule formation

According to molecular orbital (MO) theory, atomic valence electrons are influenced by all nuclei and other electrons of the molecule. Inner electrons, of course are localized on one atom or on a small group of atoms. We are concerned only with the valence shell electrons – those that participate in chemical bonding. In order to obtain wave functions for the molecular orbitals, we assume that these are linear combinations of atomic orbitals (LCAO). Atomic orbitals (AOs) that can combine are limited by the symmetry of the molecule and the symmetries of the orbitals. The most effective combinations involve AOs of similar energies as well.

In valence bond theory a chemical bond is considered as resulting form overlap of one AO an each atom. Mos are combinations of all AOs of suitable energy in the molecule consistent with the symmetry of the orbitals.

Consider first the diatomic molecule H_2. The Is AOs give two MOs expressed as linear combinations. The number of MOs is the same as the number of AOs combined – we conserve orbitals. The sum of the AOs (Actually the wave functions are added, $I_{SA} + I_{SB}$) gives a bonding molecular orbital, because the maximum electron density (the square of the sum of the wave functions occurs in the region between the atoms. The other linear combination, $I_{SA}+I_{SB}$) gives a bonding molecular orbital, because the maximum electron density (the square of the sum of the wave functions occurs in the region between the atoms. The other linear combination, $I_{SA} - I_{SB}$, gives cancellation in the region between atoms, resulting in a nodal plane separating the atoms. Because the electron density is depleted between the atoms (zero in the nodal plane), the nuclei are poorly screened from one another and a repulsive interaction results; this is an antibonding orbital. MOs with rotational symmetry about the bond axis ($C\infty$) are called sigma (σ) orbitals. The bonding orbital is designated σ^*. An occupied σ orbital forms a σ bond.

The wave functions for MOs are normalized by multiplying by a normalization constant N such that $\int (N\psi)^2\, dr = 1$ or the probability of finding the electron somewhere outside of the nucleus is unity. For our bonding orbital, the normalization equation is

$$\int (N\,\Psi_{1sA} + \Psi_{1sB})^2\, dr = N^2 \int (\Psi^2_{1sA} + 2\Psi_{1sA}\Psi_{1sB} + \Psi^2_{1sB})\, dr$$

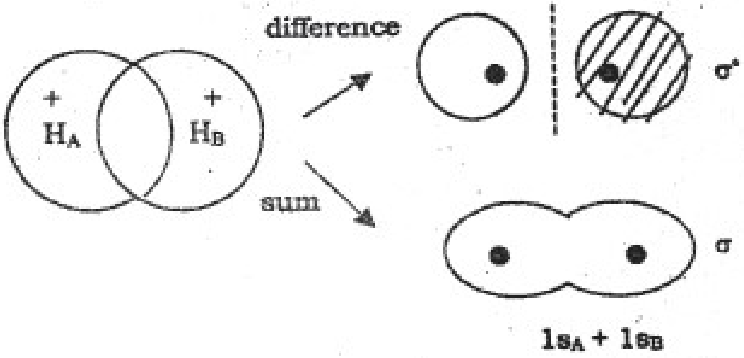
$$= N^2\left(\int \Psi^2_{1sA}\, dr + 2\int \Psi^2_{1sA}\Psi_{1sB}\, dr + \int \Psi^2_{1sB}\, dr\right) = 1$$

As we are using normalized atomic wave functions it reduces to

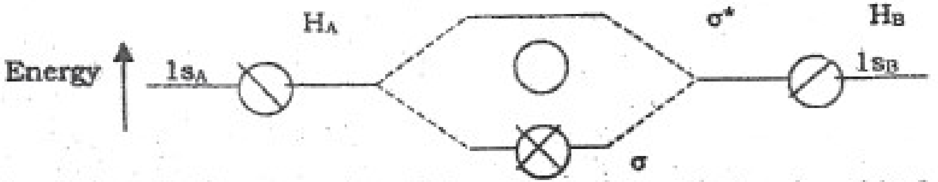
$$1 = N^2\left(2+2\int \Psi_{1sA} + \Psi_{1sB}\, dr\right) \text{ or } N = \pm \frac{1}{\sqrt{2\left(1+\int \psi_{1sA}\ \psi_{1sB}\, dr\right)}}$$

we choose the positive sign to give a positive wave function. The integral $\int \Psi_{1sA} + \Psi_{1sB}\, dr$ called the overlap integral, is usually neglected in the LCAO approximation, giving $N \doteq 1/\sqrt{2}$

Our two MOs are $\Psi_\sigma = \frac{1}{\sqrt{2}}(\Psi_{1sA} + \Psi_{1sB})$ and $\Psi_{\sigma^*} = \frac{1}{\sqrt{2}}(\Psi_{1sA} - \Psi_{1sB})$



The linear combination of atomic orbitals for H_2
The negative lobe for σ^* is shaded



The relative energies of the molecular and atomic orbitals for H_2

Two spin-paired electrons occupy the bonding orbital giving the configuration σ^2. In the more general case the normalization constant N equals 1 divided by the square root of the sum of the squares of the coefficients in the LCAO for all orbitals.

$$\psi=a\psi_1+b\psi_2-c\psi_3.... \text{ and } N=\frac{1}{\sqrt{a^2+b^2+c^2.....}}$$

VI σ and π Bonds

Sigma (σ) Bond

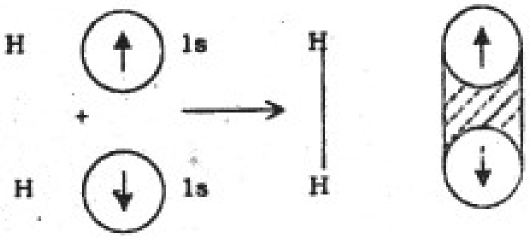
The head on overlapping of half-filled atomic orbitals along te inter-nuclear axex, forms this type of bond. It is a strong bond as the extent of overlapping is maximum.

Types of axial overlap

Various types of axial overlap of s an p electronic orbitals are as follows.

1. s-s orbitals overlapping or s-s sigma bond

This type of sigma bond is obtained when half-filled s-orbitals of two atoms get overlapped. For example, the formation of hydrogen molecule by the overlapping of Is – orbitals of two hydrogen atoms, has been involving this type of bonding.



Hydrogen molecule

2. s-p orbitals overlapping or s-p sigma bond

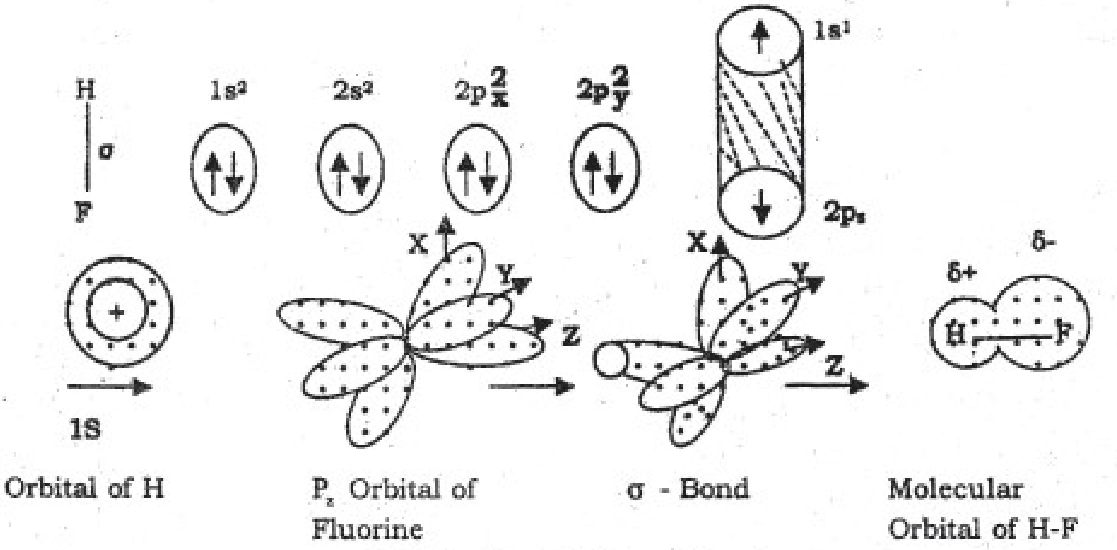
This type of sigma bond is obtained when half filled s-orbital of one atom gets overlapped with half-filled orbital of other atoms. Following examples are given to illustrate this concept.

i. Formation of Hydrogen Fluoride (HF)

$_9F=1s^2\ 2s^2\ 2p\frac{2}{x}\ 2p\frac{2}{y}\ 2p\frac{2}{z}$. It is having one half filled $2p_z$ orbital.

$_1H=1s^1$ It is having one half filled s - orbital.

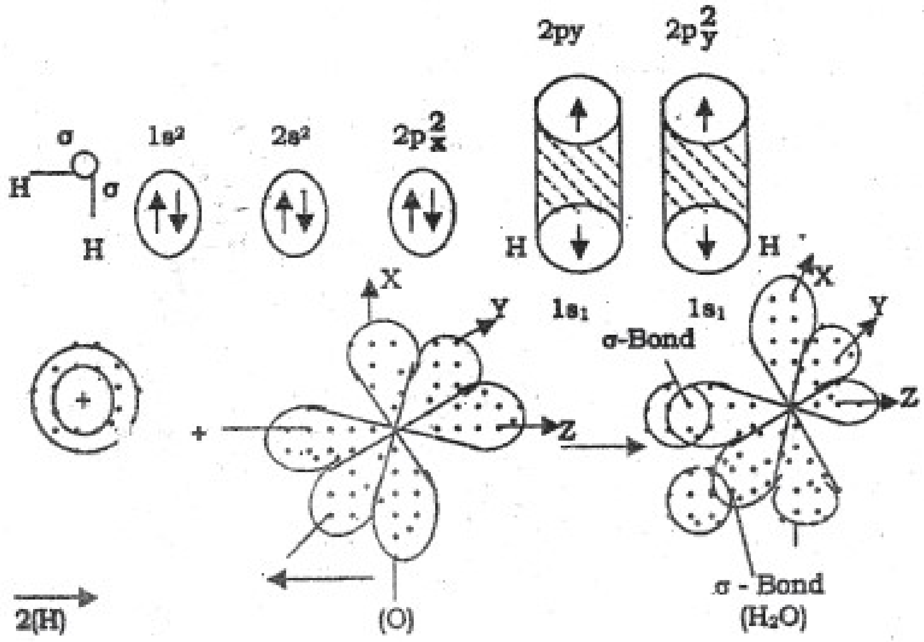
One lobe of half filled 2pz orbital (dumbbell in shape) gets overlapped with s orbital of H – atom along the internuclear axis. Because of this sp – molecular



Formation of HF molecule

Orbital is produced. Due to higher electro negativity of F-atom than that of H – atom, the bond pairs of electrons reside more closely to F-atom. Because of this charge separation occurs.

ii. Formation of water (H_2O molecule)



Formation of water Molecule

O - atom $\left(1s^2 2s^2 2p_x^2\ 2p_y^1\ 2p_z^1\right)$ is having two half filled orbitals while H-atom $(1s^1)$ is having one half filled s - orbitals.

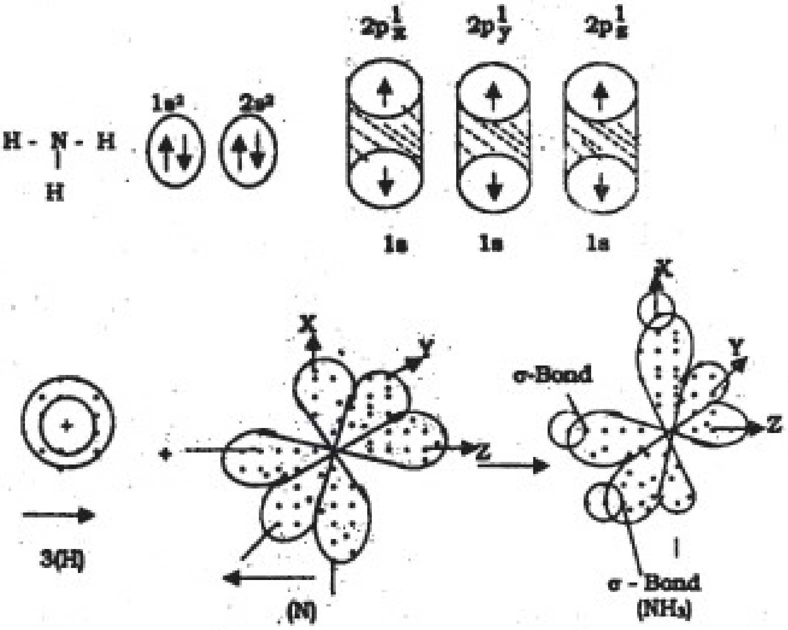
Half filled 2p orbitals of oxygen undergo overlapping with s – orbital of each H – atom to form sp sigma bonds.

The p – orbitals are making an angle of 90° with one another yet the bond angle in water is 150°. It occurs due to the repulsive interaction between lone pairs and also between lone pairs and bond pairs.

iii. Formation of Ammonia NH_3 molecule

N-atom $\left(1s^2 2s^2 2p_x^1\ 2p_y^1\ 2p_z^1\right)$ is having three half filled 2p orbitals. H atom $(1s^1)$ has one half filled s- orbitals.

Half filled 2p - orbitals of nitrogen get overlapped with s - orbital of each H-atom to yield s-p sigma bonds.



Formation of ammonia molecule

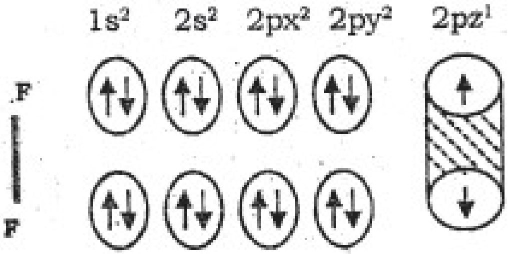
The p – orbitals are making an angle of 90° with one another. But the bond angle in NH_3 is 108°. It is attributed to the repulsive interaction between lone pair – bond pair and also between bond pair – bond pair.

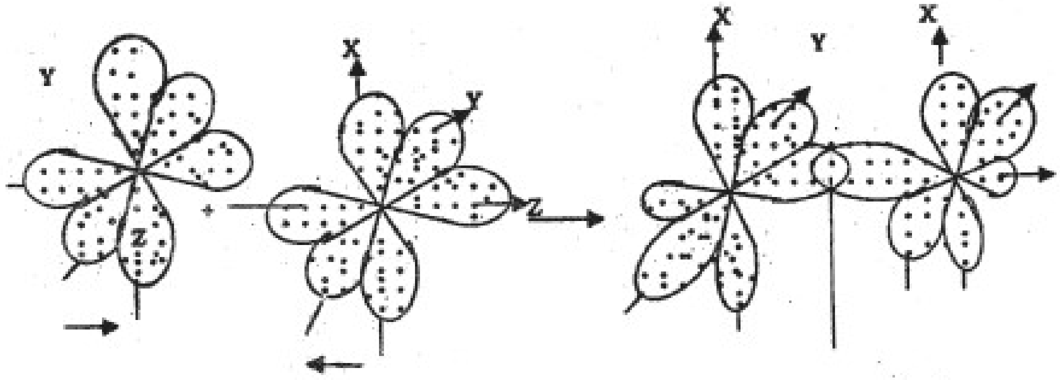
3. p-p orbitals overlapping or p-p sigma bond

This type of sigma bond is obtained when half filed p orbital of one atom gets overlapped with half filled p – orbitals of other atom. Following example is given for illustration:

Formation of Fluorine molecule

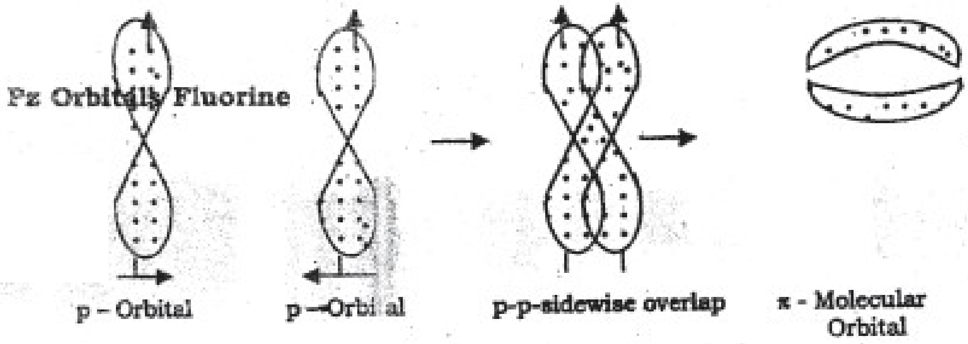
($_9$F = $1s^2\ 2s^2\ 2px^2\ 2py^2\ 2pz^1$). One lobe of half filled 2p – orbital of one F – atom is overlapping with one lobe of half filled $2p_z$ - orbital of second F – atom along the inter nuclear axis. Because of this p-p (σ) molecular orbital is obtained.





Atom σ-Bond

Formation of F_2 molecules



Formation of F_2 Molecule

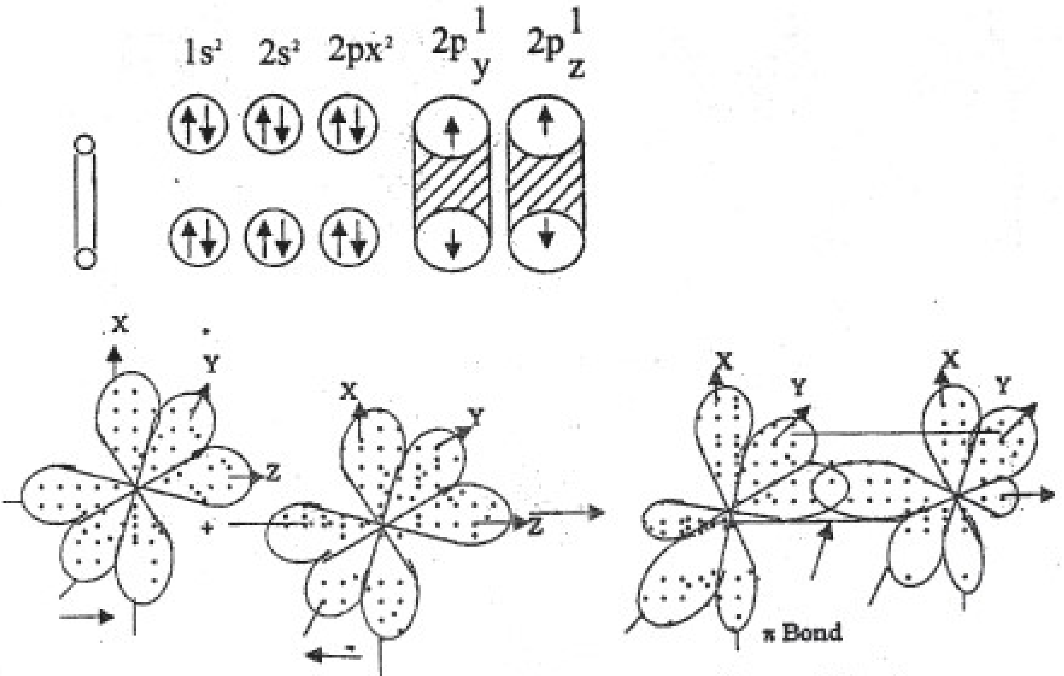
4. pi (π) bond

This type of bond is obtained by the sidewise overlapping of half filled atomic orbitals in a direction, which is perpendicular to the inter-nuclear axes. It is a weak bond as the extent of overlapping of atomic orbitals has been somewhat small

Type of sideways or lateral overlap

The only type of side wise overlapping has been the p-p atomic orbital overlapping which is perpendicular to the inter nuclear axes. Following figure reveals that the two p – orbitals have been perpendicular to the inter nuclear axes. On coming closer, these slightly overlap laterally. The upper lobes of the two orbitals tend to overlap above and lower lobes of the two orbitals tend to overlap above and lower lobes below the inter – nuclear axes. Pi-molecular orbital is having electron cloud above and below the internuclear axis. Following examples are given for illustration.

i) Formation of oxygen (O_2) Molecule



p – Orbitals of Oxygen Atom

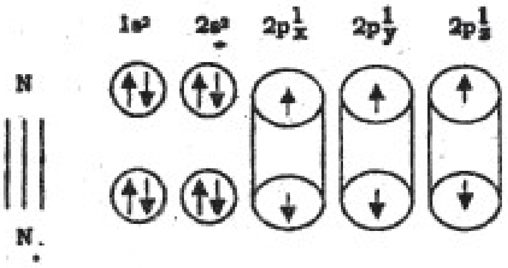
Oxygen Molecule

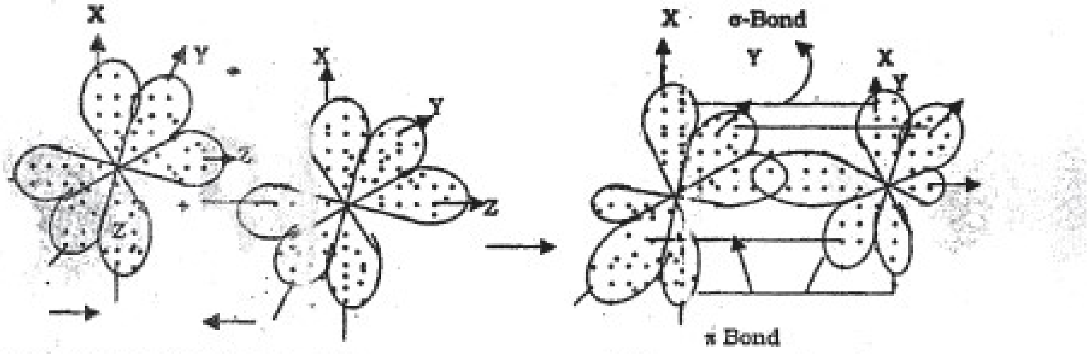
Formation of O_2 molecule

O- atoms $\left(1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1\right)$ is having two half filled p – orbitals. One half – filled 2p – orbital of one O – atom is overlapping with one half – filled 2p – orbital of another O – atom along inter – nuclear axis to form σ - bond. Second half – filled 2p orbital of one O – atom is overlapping side wise with second half – filled 2p – orbital of another O – atom to yield π - bond. The Molecule is a double bond, which consists of one sigma and one π - bond. The covalence of oxygen would be two.

ii) Formation of nitrogen (N_2) molecule

N- atoms $\left(1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1\right)$ is having three filled 2p-orbitals. One of these half-filled p-orbitals of one N – atom would overlap with one half-filled 2p orbital of another N – atom along inter – nuclear axis to yield σ bond. Other two half – filled 2p orbitals of one N – atom would be overlapping sideways with each half-filled 2p – orbitals of another N – atom to yield two π - bonds. The molecule has a triple bond consisting of one sigma and two π - bonds. The covalency of nitrogen would be three.





p-Orbitals of nitrogen atoms Nitrogen molecule

Formation of N_2 molecule

Characteristics of Sigma (σ) and Pi (π) bonds

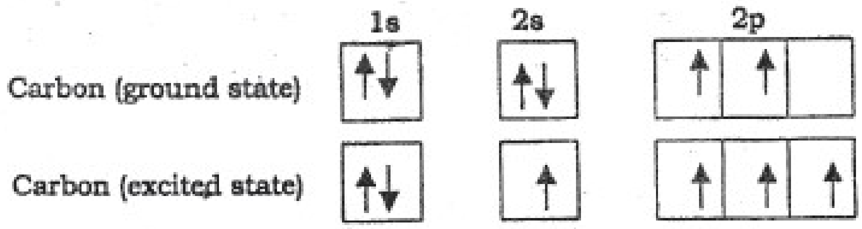
The characteristic of sigma and Pi bond are given below.

COMPARISON OF SIGMA (σ) AND PI (π) BOND

Sigma (σ) bond)	Pi (π) bond
(i) It is a strong bond as orbitals overlap to greater extent.	(i) It is weak bond as orbitals overlap to less extent.
(ii) s-orbitals are involved in the formation of a sigma bond.	(ii) S – orbitals are not involved in formation of pi bond.
(iii) One lobe of p-orbital involving in σ - bond formation stretches whereas the other lobe reduces in size.	(iii) Bothe lobes of p- orbitals involving in a π - bond formation remain of the same size.
(iv) This bond is formed by overlap of orbitals along their inter – nuclear axis, i.e. end to overlapping	(iv) Pi bond is formed by side to side overlapping or orbitals (Lateral overlapping).
(v) Sigma bond is a strong bond	(v) Pi bond is a weak bond
(vi) Electron cloud of a sigma bond is symmetrical about the line joining two nuclei concerned.	(vi) Electron cloud of pi bond is asymmetrical.
(vii) There can be free rotation of atoms around the sigma bond	(vii) As the electron clouds overlap above and below the plane of the atoms, free rotation is not possible around a pibond.
(viii) It determines the direction and extent of internuclear distance	(viii) it has no primary effect on the direction of bond but shortens the inter nuclear distance.

VII. Hybridization and Resonance

In order to understand the concept of hybridization, consider the case of carbon. Its atomic number is 6 with electronic configuration $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$



In the ground state, carbon has two unpaired electrons and therefore it is bivalent. But in almost all its compounds, it shows tetravalency. It order to explain the tetravelency of carbon it is assumed that one of the 2s electrons becomes unpaired and gets excited to the vacant $2p_z$ orbitals resulting in the configuration, $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$. Now carbon contains four unpaired electrons and, therefore it is capable of forming four bonds. If these four electrons now form four bonds, three bonds (involving the electrons $2p_x$, $2p_y$, and $2p_z$) would be of one type and at right angle to each other and fourth bond (involving the electron of 2s orbital) would be different with new directional properties. But it is known with certainty that four bonds formed by the carbon atom are equivalent.

In order to get four equivalent bonds, it is assumed that one of 2s electrons becomes unpaired, gets excited to the $2p_z$ orbitals and then four orbitals (2_s, $2p_x$, 2py and $2p_z$) get mixed up and finally redistribution of energy takes place between them, resulting in the formation of four equivalent hybrids.

This phenomenon of mixing of the atomic orbitals and the formation of new orbitals of equal energy is known as hybridization and the new orbitals formed are known as hybrid orbitals. The bonds formed by such orbitals are called hybrid bonds. The compounds, which are formed from these bonds, are known as hybrids.

Conditions for Hybridization

Following are the rules for hybridization.

Rule 1

Only orbitals of similar energies belonging to the same atom or ion can undergo hybridization.

Rule 2

Number of hybrid orbitals produced is equal to the number of orbitals mixed. Hybrid bonds are stronger than the single non-hybridised bonds of comparable energy

Rule 3

Most of the hybrid orbitals are similar but they are not necessarily identical in shape. They differ from one another in orientation in space.

Rule 4

For equivalent hybrids, the orientation in space is determined by:

(i) The number of orbitals mixed and consequently the number of hybrids obtained, and

(ii) Which of x, y and z directions are preferred by the orbitals when pure.

Rule 5

Once an orbital has been used to build a hybrid it is then no longer available to hold electron in its pure form.

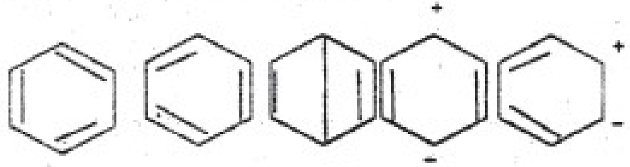
Rule 6

The type of hybridization indicates the geometry of molecules. From the type of hybridization one can tell about the bond angles and structure.

Shape of molecule	Hybrid type	Bond angle	Examples
Linear	sp	180°	$BeCl_2$, $HgCl_2$
Planar	Sp^2	120°	BF_3, BCl_3, CO_3^{2-}, NO_3^-
Tetrahedral	Sp^3	109°18'	CH_4, NH_4^+, BH_4^-
Square planar	dsp^2	99°	$(Ni(CN)_4)^{2-}$, $(PtCl_4)^{2-}$
Trigonal bipyramidal	dsp^3	90°,120°	PF_5(g)
Octahedral	sp^3d^2 and d^2sp^3	90°	$(CrF_6)^{3-}$, SF_6, $Co(NH_3)_6)^{3+}$ $(Fe(CN)_6)^{4-}$

Resonance

The tern resonance refers to the fact that many molecules cannot be represented by any single valency bond structure, but must be considered as intermediate between two or more such structures such molecules are called resonance hybrids. This term does not imply the molecule resonances (in the physical sense) between the structures; the molecule is not well represented by one structure during part of its life time, by another during another part; rather the structure is unique, but is most conveniently described by the mathematical expedient called resonance. Thus benzene, for example, cannot be represented by any of the structures I to V alone but intermediate between all of them, and many others resembling structures given below.



I II III IV V

The canonical forms have no physical significance because these are merely a convenient way of picturing a molecule in terms of familiar Lewis structures.

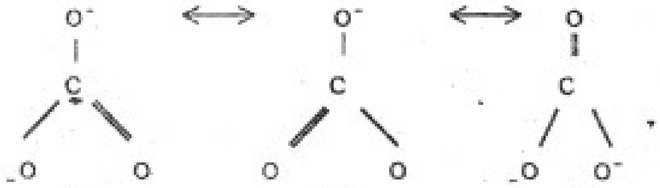
Mathematically this is expressed by saying that the wave function describing the molecule, ψ_a, is a linear combination of the wave functions, Ψ_1, Ψ_2, Ψ_3..... describing the various structure.

$$\psi_G = C1\ \psi_1 + C2\ \psi_2 + ...$$

The classic difficulty over the concept of resonance is the disposition to regard the molecule as oscillating from one to another of the assigned forms. The fault is not with the molecule but rather with the human inability to describe properly this hybrid by single structural formula that characterizes it.

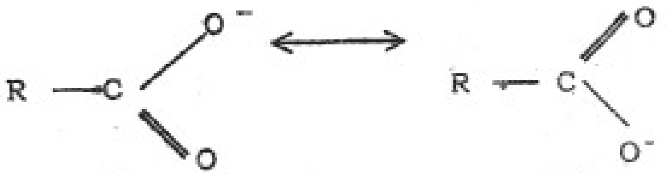
Bond Order for Resonance Systems

It is very easy to calculate the bond order for molecules or irons. (i.e. CO_3^{2-}, NO_3^- etc) having symmetrical canonical structures. For example, the C-O bond order in CO_3^{2-} comes out to be $1\frac{1}{3}$ because its various canonical forms (a) to (c) are contributing equally and each oxygen atom is carrying a negative charge of 2/3 units.



(a) (b) (c)

Similarly, the C-O bond order in a carboxylate ion comes out to be $1\frac{1}{2}$ and each oxygen carrying a negative charge of $\frac{1}{2}$ unit.



(a) (b)

The C–O bond order in CO_2 has been found to be greater than 2 because of the non- equivalence of its various canonical forms.

$$O = C = O \leftrightarrow \overset{-}{O} - C = \overset{+}{O} \leftrightarrow \overset{+}{O} = C - \overset{-}{O}$$

(a) (b)

Conditions Necessary for Reasonance

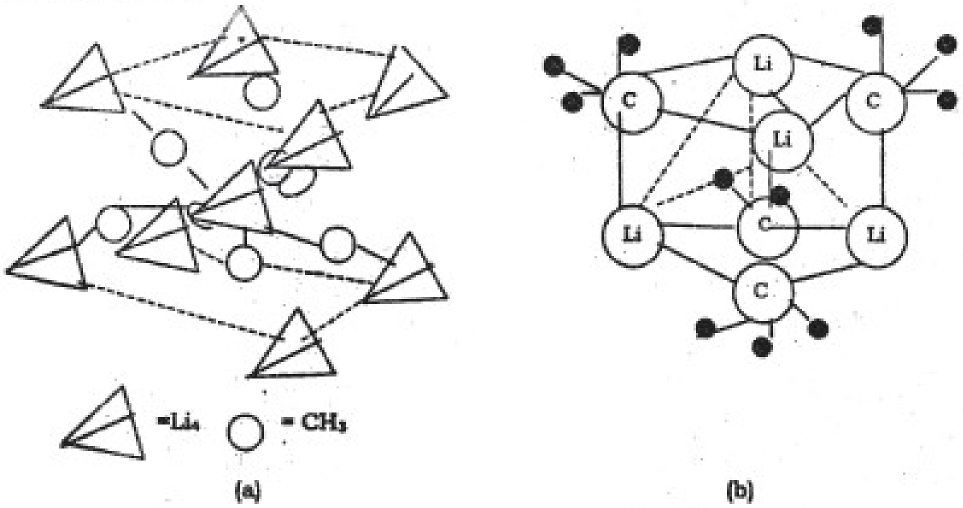
If $\psi_1, \psi_2, \psi_3 ....$ are the various wave functions of the possible structures (i.e., the resonance forms) of a molecule contributing to its resonance hybrid (i.e., the actual structure), the important ones will be those for which the C is large in the following expression:

$$\psi = N\,(C_1, \psi_1 + C_2, \psi_2 + C_3, \psi_3 + ...)$$

Where ψ represents the wave function of the actual structure of the molecule. It must be emphasized that ψ represents a wave function which is the sum of the wave functions $\psi_1, \psi_2, \psi_{3...}$ These various wave functions are included in the resultant (ψ) but they are not individually recongnisable.

VIII. Electron Deficient Molecules

Organometallic compounds of the smallest and most electropositive main-group metals (Li, Be, Mg, A and to some extent, B and Zn) have a structural chemistry and reactivity strongly influenced by their having too few electrons and too many valence orbitals to obey the octet rule as monomers. They form aggregate in the solid state in which the "sigma" electrons are delocalized in multicentered bonds. The tendency toward aggregation increases with metal electropositivity; it decreases as the steric requirements of the alkyl group increase. LiMe(s) is a tetramer whose unit cell contains a body – centered packing of Li_4 tetrahedra. A methyl caps each triangular face. Each C in the $(LiMe)_4$ unit interacts with an adjacent Li_4, providing bonding throughout the solid lattice which accounts for the low solubility of LiMe in poorly solvating media. NaMe(s) has a similar structure. Alkyls of other alkali metals are best considered as ionic compounds. (KMe has the NiAs structure with methyl carbanions). They are intractable white solids that decomposes on heating and are insoluble in virtually all solvents. Extremely bulky R groups can lead to monomers; for example, Li $(2,4,6\text{-}Ph_3C_6H_2)$ is a monomer with three coordinate Li.

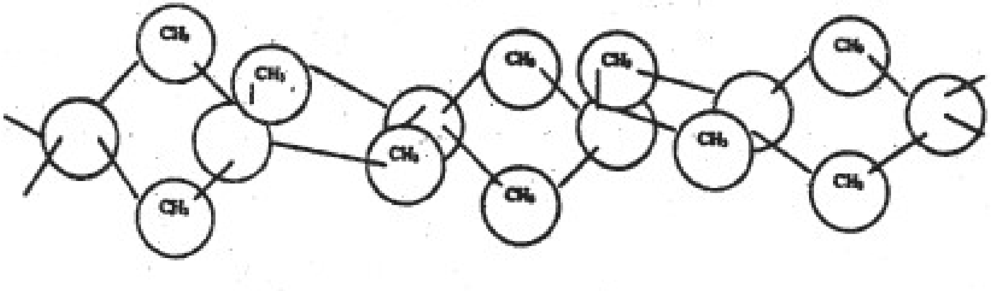


(a) Unit cell of LiMe(s).

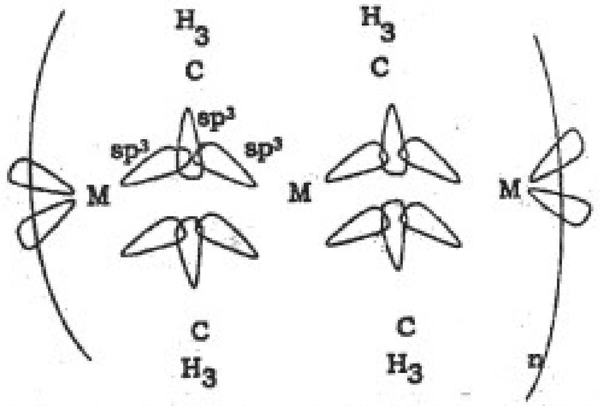
(After E Weiss and E.A.C. Lucken, J.Organomet. Chem. 1964,2,197.

(b) Schematic drawing of $(LiMe)_4$ unit.

$BeMe_2$ (s) amd $MgMe_2$ (s) are long – chain polymers having metals tetrahedrally coordinated by μ - Me. The bridging entails three – center bonding in which each metal contributes two empty sp^3 orbitals while each Me contributes one sp3 hybrid filled with two electrons. In contrast, more electronegative Zn, Cd and Hg form alkyls R_2M, which are linear volatile monomers. However, ph_2Zn crystallizes as a PhZn $(\mu\text{-Ph})_2$ ZnPh dimmer.



Chain structure of Mme_2 (M = Be, Mg).
(the chlorides also have this structure)

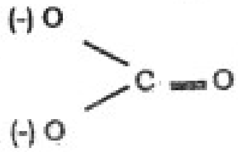


Three – Center bonding with bridging methyls

IX. Bond Order

The Bond order is defined as one – half of the number of net bonding electrons (number of bonding electrons) giving 1 for H_2 and ½ for H_2^+. population of the antibonding orbital weakens the bond, weakens the bond, since the net number of bonding electrons is reduced to one and the Bond order is ½ for H_2^- and zero for unstable H_2^{2-}.

Some molecules or ions cannot be represented adequately by a single valence bond formula. The rules of combination lead to the representation.



for the carbonate ion, but the oxygen atoms are known to be equivalent and the bond angles are all 120° in the planar ion. The difficulty arises simply because, in reality, electrons are not restricted to particular positions.

The "fourth" electron pair, which forms a double bond wherever it is written, is not localized in any one of the three bonds, but rather is delocalized over all three bonds. Three are three equivalent bond, each of which is something between a single and a double bond. Here the "fourth" bond can be written in any one of the three positions, so that each bond is described as having a bond order of $1\frac{1}{3}$. The bond order (B.O) of a single bond is 1; of a double bond, 2 and of a triple bond, 3.

X. Bond Energy and Bond length

The process of bond formation involves release of energy, because the bonded atoms possess lesser energy than the individual atoms. It, therefore, follows that an equivalent amount of energy will have to be absorbed by the molecule for breaking the bond. The amount of energy required to break a mole of bond and separate the bonded atoms in a gaseous sate is known as the bond energy.

Bond energy is a measure of the strength of the bond.

Bond energy is expressed in kJ or Keal per mole.

For an diatomic molecule like hydrogen, the bond energy is the same as that of bond dissociation energy because the breaking of one bond disrupts the whole molecule

$H2(g) \rightarrow 2H(g)$ Bond energy = 435.1 kJ mol^{-1}

For polyatomic molecules, the bond energy is not equal to bond dissociation energy because in a polyatomic molecule, the energy necessary to rupture a given bond will depend to some extent on the nature of the remainder molecule. Therefore, the bond energy for a particular bond in polyatomic molecules will vary from compound to compound.

Calculations

One can calculate bond energies in the same way as that of bond length; for example, the energy of HI bond would be the sum of bond energy contribution of hydrogen and iodine atoms.

$$E_{H-I} = \frac{1}{2} E_{H-H} + E_{I-I}$$

Thus,

$$= \frac{435.4}{2} + \frac{150.6}{2} = 293.3 \text{kJ mol}^{-1}$$

The calculated value of 29.3 kJ mol^{-1} is quite near to the experimental value of 297.0 kJ mol^{-1}

We can apply the above method of calculating bond energies to such molecules, which have similar types of bonds. The strength of the bond is indicated by the stability of the bond, energy. Thus, the strength of F-F bond is lower than that of Cl – Cl bond. Consequently, fluorine is more reactive than chlorine.

The bond energies of some diatomic molecules are given in the following Table.

Bond	Bond Energy kJ/mol	Bond	Bond Energy kJ/mol
H-H	435.4	C-C	347.8
O-O	497.9	C-C	606.7
N-N	945.6	C-C	803.3
F-F	154.8	C-O	334.7
CI – CI	242.7	C-O	694.5
I – CI	209.2	C-S	272.0

Factors Affecting Bond Energy

(i) Bond Length

Shorter the bond length, greater would be value of bond energy

(ii) Size of bonded atoms

Shorter the size of bonded atoms, greater would be the value of their bond energy.

(iii) Electro negativity

Greater the electro negativity difference between bonded atoms, greater would be the value of their bond energy.

Importance

Its value has been regarded a measure of bond strength. Greater the bond energy greater would be the strength of the bond.

XI. Electro negativity

1. Pauling's Method

Pauling introduced the concept of electro negativity of atoms and described its quantitative aspect as a measure of he tendency of an atom in a molecule to attract electrons to it. He used the idea to account for the fact that the energy of a heteropolar bond A- B which may be symbolized by $E_{(A-B)}$ is generally higher than either the average arithmetic or average geometric mean value of the homopolar bond energies of the molecules A-A and B-B. For the case of the arithmetic mean we can write.

$$E_{AB} = \frac{1}{2} (E_{AA} + E_{BB} + A_{AB}$$

Where Δ_{AB} is called the Ionic resonance energy. For considering a hypothetical molecule A – B with geometrical mean of the bond energies, the ionic resonance energy can be evaluated as

$$\Delta_{AB} = E_{AB} - \sqrt{E_{A-A} \, X E_{B-B}}$$

Ionic resonance energy Δ_{AB} is a measure of partial ionic character of a covalent bond. However, the difference in electro negativities between the bonded atoms is also related to the ionic character of the bond. It can be interpreated that the difference in electro negativities between the two bonded atoms is proportional to Δ_{A-B}. Since Δ_{A-B} is not additive but it is only $\sqrt{AB}$ is additive, we have $\chi_B-\chi_A \alpha \sqrt{\Delta AB}$ (x=Chi) or $\chi_B - \chi_A \alpha \sqrt{\Delta AB}$ where χ_A and χ_B are the electro negativity values of atoms A and B respectively. Pauling Proposed that $\sqrt{\Delta AB}$ expressed in electron volts would give a good representation of the difference in electro negativity of B and A. This can be expressed as

$\chi_B-\chi_A = 0.18 \sqrt{\Delta AB}$ where the value of the constant is 0.18.

2. Mulliken's Method

Mulliken defined the electro negativity of atom as the arithmetic mean of its ionization energy and electron affinity.

$$X_A = \frac{1}{2}(\text{I.P.}+\text{E.A.})$$

Mulliken gave another formula for calculating the electro negativity

$$X_A = \frac{\text{Ionisation potential - Electron affinity}}{5.6} \text{ -------- } (1)$$

Where X_A is the electro negativity value of atom A on Mulliken's scale and 5.6 is scale – adjustment factor with the help of which the electro negativity of atom A on Mulliken's scale approximate that on Pauling's scale.

In equation (1), the factor 1/5.6 is used when ionization potential and electron affinity are expressed in electron volts. If the ionization potential and electron affinity are expressed in kcal/mole, equation (1) becomes as follows.

$$X_A = \frac{\text{Ionisation potential - Electron affinity}}{2 \times 62.5} = \frac{\text{IP-EA}}{2 \times 62.5}$$

On the basis of Mulliken's scale, the conditions for the formation of purely covalent A –B bond and ionic $A^- - B^+$ or $A^+ - B^-$ bond may be written as follows :

(i) when there is the formation of purely covalent A- B bond, then

$$\frac{(IP)_A - (EA)_A}{5.6} = \frac{(IP)_B-(EA)_B}{5.6} \text{ and hence } X_A = X_B$$

ii) When there is the formation of A^{-}-B^{+} bond, then

$$\frac{(IP)_A-(EA)_A^{*}}{5.6} > \frac{(IP)_B-(EA)_B}{5.6} \text{ and hence } X_A > X_B$$

iii) When there is the formation of A^{+}-B^{-} bond then

$$\frac{(IP)_A-(EA)_A}{5.6} > \frac{(IP)_B-(EA)_B}{5.6} \text{ and hence } X_A > X_B$$

The Mulliken's scale has the advantage that it can account for the different hybridizations of the element in chemical compounds.

The value of electro negativity obtained by Mulliken's method is in consistent with those obtained by other methods but the method has limitations due to the following reasons.

(i) The accuracy of electron affinities is only available for a limited number of elements.

(ii) During the formation of bond the transference of electron between two atomic orbitals occurs whose exact constitution may not be known.

3. Allred – Rochow Electrostatic Approach

According to them, electro negativity is defined as the electrostatic force exerted by the nucleus on the valence electrons. They assumed that an electron in a bond is attracted by one of the two nuclei according to Coulomb's law, i.e.,

$$X_A = F_{ES} = \frac{e^2(Z^*)_A}{(r_A)^2} \quad \ldots\ldots \quad (1)$$

Where X_A is ther electro negativity value of atom A on Allred – Rochow's scale, e is the charge on the electron. Z* is the effective nuclear charge on atom defined by equation (2) ant r_A is the covalent radius in Angstrom unites, and F_{ES} is the force of attraction in dynes.

$$(Z^*)_A = Z_A - \sigma_A \quad \ldots\ldots \quad (2)$$

Here Z_A is the actual nuclear charge of the atom A and σ_A, the screening constant for atom A. on substituting the value of e (8 x 10-^{10} esu) in equation (1), we get

$$X_A = F_{ES} = \frac{e^2(Z^*)_A}{(r_A)^2}$$

4. Sanderson's Method

Sanderson suggested that electro negativity of an atom is stability ratio (S.R), which may be defined as the ratio of the average electron density of an atom to that of a hypothetical inert atom.

$$i.e.\ S.R = \frac{D}{Di} \quad \ldots\ldots (1)$$

Where D is the average electron density and is a measure of the comparative compactness of the atom, and Di is the density of a hypothetical inert atom. The following relation calculated the value of D as

$$D = \frac{\text{Atomic Number}}{\text{Atomic Volume}}$$

$$= \frac{Z}{4\pi r^3} = \frac{3Z}{4\pi r^3} = \frac{Z}{4.19 r^3} \quad \ldots. (2)$$

In the above equation r is the non-polar covalent radius. In order to calculate Di, the electron densities of inert gas atoms are plotted against atomic numbers and the value for a particular atomic number is found by interpolation.

The Sanderson (S.R.) and Pauling values (χ) are related by the expression

$$\sqrt{x} = 0.21\ \text{S.R} + 2.77$$

The two scales agree quite closely except for germanium, arsenic and antimony, where the Sanderson values are appreciably higher than the corresponding Pauling electro negativities. A high value for germanium is also obtained on an electro negativity scale given by Allred and Rochow, Sanderson, Allred and Rochow claim that here is a great deal of evidence in favour of the high value for germanium.

Pauling describes electro negativity as the power f an atom in a molecule to attract electrons to it. Further more he state that this property differs from the electrode potential and electron affinity, although is related to these properties in a general way. From heats of formation of the most common elements in some of their compounds Pauling has set up an arbitrary electro negativity scale for atoms of these elements.

Certain conclusions may be drawn from the relative negativities and electro negativity differences. These values indicate that the bonds between alkali metals and non-metal are more than 50 per cent ionic. Magnesium and alkaline earth metals form essentially ionic bonds with the more electronegative atoms. The bonds formed by A1, Be and B and Si, vary widely in their ionic character, ranging from less than 1 per cent for the B-H bond to more than 70 per cent for the A1-F bond. The most ionic carbon bond is C-F with 43 percent ionic character and the bonds from fluorine and oxygen to all metals are essentially ionic. In nonmetallic oxides, and fluorides the bonds have an appreciable ionic character.

Since electro negativity scale is derived from heats of formation for certain univalent elements, it would seem that electro negativity values could also be used to determine heats of formation. However, the agreement between the predicated and observed heat of formation is only approximate. Numerical values of percentage ionic character of bonds are roughly qualitative, never quantitative Moreover, the application of this method to multiple bonds is more difficult and so far less successful.

Periodic Trend

Along the group, moving down a group as the nuclear charge increases the electro negativity of a lower element should be more than that of upper element. Consequently due to nuclear radii and shielding effects a lower element of a group is less electronegative than the upper element of the same group. In general, small atoms of a group attract more electrons than bigger ones.

Along the period, as we move from left to right across a period the values of electro negativity increases gradually. This is due to gradual decrease in atomic size and additional electrons are held tight.

XII. Electron Affinity and Lattice Energy

Electron affinity is defined as an element on capturing an electron liberates energy and it is known as positive electron affinity.

$$A(g)+e(g) \rightarrow A^-_{(g)}$$

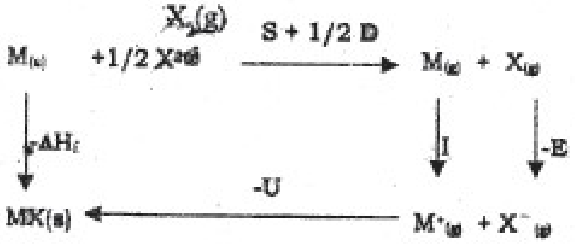
Electro negativity of an atom is defined as a measure of its tendency to attract electrons towards itself in a molecule. The numerical value of this property depends upon the ionization potential and the electron affinity of the atom concerned. Higher values of ionization potential indicate that it is difficult to remove an electron from an atom or in other words, the atom has greater electron affinity. Thus greater value of ionization potential and greater electron affinity both indicate grater electro negativity.

Electron affinity is the amount of energy liberated when a neutral atom captures an electron to produce an anion.

$$A(g)+e^{-}_{(g)} \rightarrow A^{-}_{(g)}$$

A direct experimental determination can be made of the electron affinity. But it is more common to determine it in an indirect way by the Born – Haber cycle. The cycle devised by Born and Haber in 1919 relates to the lattice energy of a crystal to other thermo chemical data. With the help of this cycle the value of electron affinity of an element, say chlorine can be evaluated if the other quantities such as heat of formation of NaCI (ΔH_f), sublimation energy (S) of sodium, dissociation energy (D) of chlorine, ionization energy (I) of sodium and lattice energy (u) of NaCI crystals crystals are known. Using the equation.

$\Delta H_f = S + ½D + I - E - U$ electron affinity may be evaluated.



Metal atoms have small electron affinities and do not form negative ions easily. Non – metals do, however, form negative ions readily as expected from their high electron affinities. Alkali metals are electropositive and they do not form negative ions due to electron affinity. Hence the electron affinity is not significant for alkali metals. This is high in the case of halogens.

Periodic Trend

Along a group moving down, the size of atom decreases significantly and therefore the effective electron attraction decreases and electron affinity decreases.

In case of halogens the electron affinity is decreasing from CI to I in the halogens. But fluorine being a small atom gains an electron producing high electron – electron repulsion giving lower electron affinity than that of chlorine.

Along a period if we move across, the size of atoms decreases and nuclear charge increases. Both these factors favour increase in force of attraction exerted by the nucleus on the electrons. Consequently, the atom will possess a greater tendency to attract the additional electron (i.e.) its electron affinity would increase as we from left to right. Due to this reason electron – affinity of non-metals are high than those of metals.

Element	Ionisation Energy K Cal /g atom	Electron Affinity K Cal / g atom
F	429.0	98.5
Cl	298.0	86.5
Br	272.1	81.5
I	240.8	74.2
H	312.0	16.5
Li	123.8	Assumed zero
Na	117.9	Assumed zero
K	99.7	Assumed zero
Rb	95.9	Assumed zero
Cs	89.4	Assumed zero

XIII. Hydrogen Bonding

Many compounds are known in which the hydrogen atom exists simultaneously between two strongly electronegative atoms and thus acts as a bridge between them. In this situation, the hydrogen atom is involved in two bonds; one is natural covalent bond and the second is known as hydrogen bond. The hydrogen bonding is illustrated below for the association of several molecules of hydrogen fluoride.

$$\overset{+\delta}{H} - \overset{-\delta}{F} \;.......\; \overset{+\delta}{H} - \overset{-\delta}{F} \;.........\; \overset{+\delta}{H} - \overset{-\delta}{F}$$

The hydrogen bond is generally represented by a dotted line as shown above. The solid line represents the original covalent bond.

Causes of Formation of Hydrogen Bond

A hydrogen atom contains one proton and one electron. When the hydrogen atom is attached to a strongly electronegative atom (say, F), the electrons of the covalent bond are displaced towards the electronegative atom F. this consequently results in the developments of a fractional positive charge on the hydrogen atom, and the fractional negative charge on the electronegative atom F.

$$\overset{+\delta}{H} - \overset{-\delta}{F}$$

When two H – F molecules approach each other the H will exert a strong electrostatic force and so can attract F of other molecule. The attractive force between hydrogen and F leads to the formation of a weak bond called Hydrogen Bridge or hydrogen bond.

$$\overset{+\delta}{H} - \overset{-\delta}{F} \cdots\cdots \overset{+\delta}{H} - \overset{-\delta}{F} \cdots\cdots \overset{+\delta}{H} - \overset{-\delta}{F} \cdots\cdots \overset{+\delta}{H} - \overset{-\delta}{F} \cdots\cdots$$

Hydrogen bond is formed with such electronegative atoms, which are having small cationic radii. Fluorine, oxygen, and nitrogen are of this character.

Atoms bigger in size than, N, O or F is not able to form H – bond. The reason for this may be put as follows.

Atoms bigger in size than N,O and F are not able to attract covalent electrons effectively. It occurs due to the screening effect of electrons between valence electrons and nucleus. Thus, the covalent bond between hydrogen and other atom would be less polar. The electrostatic force of attraction becomes very weak in them. Therefore, H – bond **does not get formed**, e.g. H – bonding in HCl or HBr would not be due to big size of Cl and Br – atoms. Hence, the factors favouring the H – bond include:

Types of Hydrogen Bonds

There are two types of hydrogen bonds

(a) Intra – molecular Hydrogen Bonding

(b) Inter – molecular H – Bonding

Intra – molecular H bond arises due to the electrostatic forces of attraction between hydrogen and an electronegative element present in the same molecule.

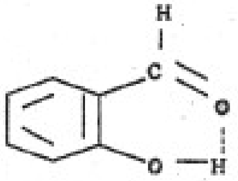
For example,

i) The compound salicyladehyde contains a hydroxyl and aldehyde group adjacent to each other there by permitting the formation of a hydrogen bond between two groups.

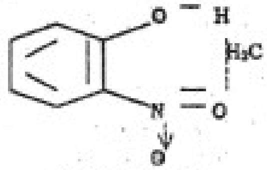
ii) Other compounds in which such intramolecular hydrogen bonding takes place are o – hydroxybenzoic acid, enolic acid, enolic form of acetoacetic ester. The enolic – from of acetoacetic ester-has lower boiling point than the keto form. This is probably due to intra – molar hydrogen bonding in the enol form, which prevents intermolecular bonding and thus prevents association, which raises the boiling point.

Conditions for intra – molecular hydrogen bonding

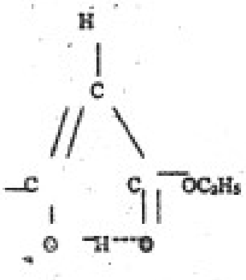
In case of intermolecular hydrogen bonding, the most important condition is that the molecules must contain one hydrogen atom linked to one highly electronegative atom.



Salicylaldehyde



o – Nitrophenol



Acetoacetic ester

In case of intermolecular hydrogen bonding the following conditions are favourable for hydrogen bonding.

(i) The molecule should contain two groups so that one group contains H – atoms linked to highly electronegative atom and the other group should also contain a highly electronegative atom linked to a lesser electronegative atom.

(ii) The molecule should be planar

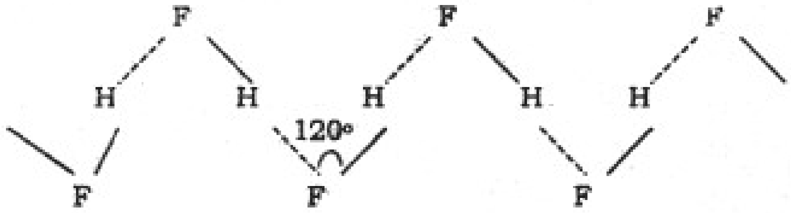
(iii) the hydrogen bonding should lead to the formation of atleast a six – member ring including the H – atom.

Inter molecular Hydrogen Bonding

When the hydrogen bond is formed between the different molecules, the bonding is known as inter – molecular hydrogen bonding. Some examples are;

(i) Crystalline hydrogen fluoride consists of infinite chains of the type as shown with an H-F-H angle of 120°. These chains persist to a large extent in the liquid and gaseous phases.

As might be expected each hydrogen atom lies closer to the more firmly attached, covalently – bonded fluorine atom than to the hydrogen – bonded fluorine atom. Heating progressively shortens the length of the chains until above the boiling point, the associated units, (HF), become quiet small; x can be any integer up to 6. In aqueous solution hydrogen fluoride ionizes to yield not the simple F ion, but the bifluoride ion, HF_2^- (giving salts of the type KHF_2).

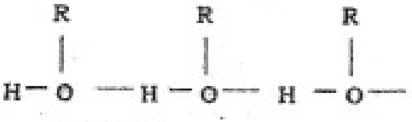


The HF_2^- ion is a resonance hybrid for which the following resonance structures can be written as follows:

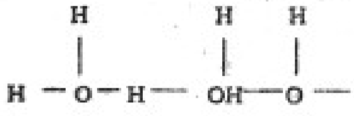
$$^-F - H - F \leftrightarrow F - H - F^-.$$

A consequence of this resonance is that the hydrogen atom is equidistant from the two fluorine nuclei. This is exceptional for hydrogen bonding.

(ii) Alcohols forms associated molecules like water molecules.



Alcohols



Water

The hydrogen bonding or the association of molecules may extend to several molecules.

(iii) The formation of hydrogen bonds between molecules of HCN is made possible by the triple bond, which enhances the electro negativity of the nitrogen atom and f the carbon just as the triple bond in acetylene enhances the electro negativity of the two carbon atoms. Hence polymerization occurs.

$H - C = N$ ..... $H - C = N$...... $H - C = N$ .....

The various characteristics are

(a) Nature

The hydrogen bond is formed due to the electrostatic forces, which exist between the positive, and negative ends (dipoles) of the same molecule or of different molecules of the same species. In simple words, it is a case of van der Wall's forces. For example while the bond energy of van der Wall's attraction is approximately 4.2 KJ per mole that of hydrogen bond has been found to vary between 14.6 - 42kJ per mole. Therefore, it is wrong to consider the hydrogen bonding as van der Waal's attraction.

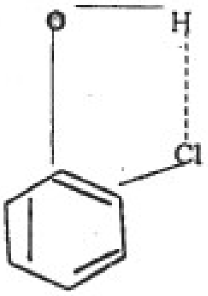
The bond energy of ordinary covalent bond is 3360 – 4200 KJ per mole. Thus, hydrogen bond is quite different from a covalent bond.

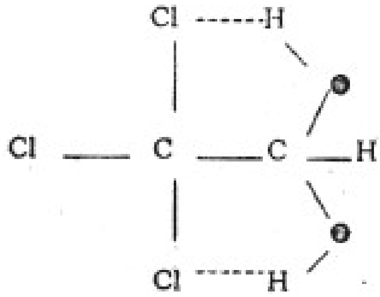
Also, the formation of a hydrogen of a hydrogen bond does not involve any sharing of electron pairs. Therefore, it is quite different from a covalent bond.

(b) Electro negativity

Hydrogen bond can form a bridge only between two atoms both of which are small in size, and highly electronegative. For example, hydrogen bonds are formed by elements like N, F and O.

Recent infra-red studies have shown that hydrogen bonding can also occur between any polar $X^- – H^+$ group and a highly polarizable atom or molecule. For example, the molecule of O^- chlorophend shows hydrogen bonding. Similarly, it may be mentioned that the stabilization of chloral hydrate is to be explained by the formation of an intra – molecular hydrogen bond.





(c) Bond Length

Some research workers have suggested that the distance between two hydrogen bonded atoms may be – 2.45A. But others have suggested that the bond length depends upon the electro negativity of two atoms forming hydrogen bond. Some values are given below.

Compound	Bond	Bond Length of Hydrogen Bond A
$(HF)_n$	F-H... F	2.55
HCOOH	O-H... O	2.67
H_2O(S)	O – H... O	2.76
B $(OH)_3$	O – H...O	2.74

There is evidence that for bond lengths of less than 2.44 A° the hydrogen bond is symmetrical, and that as the bond length increases, the arrangement X-H.... X becomes less symmetrical. Electron diffraction analysis has shown that the three atoms in the boric acid are not collinear.

(d) Position of Proton

Normally the proton does not lie in the middle of two electronegative atoms in the hydrogen bond. In hydrofluoric acid, the proton is situated midway between the two fluorine atoms whereas in ice, the proton is not at the mid point between two oxygen atoms.

(e) Physico – chemical properties

The effect of hydrogen bond formation on the properties of a compound may be seen as follows:

(i) Melting points and boiling points

It is found that HF, $H2_0$ and NH_3 have high values of the melting and boiling points as compared to the hydrides of the other elements in the respective subgroup. This can be explained on the basis of association of their molecules due to hydrogen bonding, which therefore, requires more energy than usual to rupture the hydrogen bonds to set the molecules free to melt or vaporize.

(ii) Dielectric constants

Compounds, which undergo polymerization by hydrogen bond formation, have abnormally high dielectric constants. A curve may be drawn showing the relation between the dielectric constants of certain liquids at 20°C and their dipole moments when the substances concerned are either in non – polar solvents or in gaseous state, so as to avoid dipole association. From the curve it follows that if the polymer is linear as in HCN, the dipole moment will be three times that of the monomer. This is roughly in agreement with the observed value. But if polymerization leads to zig-zag chain or a ring structure, the dipole moment of the polymer may be less that of the monomer.

XIV. Valence Shell Electron Pair Repulsion Theory (VSEPR Theory)

Gillespie and Nyholm developed this theory. According to this theory. The geometry of a molecule depends upon the number of bonding and non – bonding electron – pairs (lone pairs) in the central atom which arrange themselves in such a way that thaer is a minimum repulsion between them so that the molecule has minimum energy and maximum energy and maximum stability. Such there can only be one orientation of orbitals corresponding to minim energy a molecule of a given substance has invariably a definite shape i.e. a definite geometry.

Gillespie has proposed the following rules for explaining the shapes of molecules and ions.

Rule 1

When the central atom in a molecule is surrounded only by bonded electron pairs but not by lone pairs, the molecule will have a regular geometry of shape. This geometry depends on the number of bonded electron pairs as given in the Table.

Number of electron pairs	Geometry	Bond angle	Examples
1.	Linear	180°	$BeCl_2$, $HgCl_2$, CdI^2
2.	Trigonal Plane	120°	BF_3, BI_3, GAI_3,
3.	Tetrahedral	109° 28'	CH_4, $SnCl_4$, $SnBr_4$, BF_4^{-1}
4.	Trigonal bipyramid	90° and 110°	PCl_5, $SbCl_5VO_3^{-1}$,
5.	Octahedral	90°	SF_6, $(SiF_6)^{2-}$, $(PbCl_6)^-$
6.	Pentagonal bipyramid	72° and 90°	IF_7,

Rule 2

Some molecules may have distorted or irregular geometry if the electron pairs surrounding the central atom are not equivalent, i.e. some are bonded while remaining are lone pairs. Lone pair electrons repel adjacent electron pair more strongly than do bonding electron pairs. Also, the repulsion is expected to increase in the following order:

Bond pair – bond pair < bond pair – lone pair < lone pair – lone pair

Rule 3

The greater the number of lone pairs of electrons on the central atom, the greater, in general will be the tendency of bond angles to contract and hence, greater will be the distortion in the geometry of the molecule. The rule is understood by considering the following series.

$No_2^+, 110^0; \dot{N}O_2, 104^0; \ddot{N}O_2^-, 115^0$

Rule 4

The smaller the electro negativity of the central atom, the smaller is the bond angle and hence, smaller is the distortion in the regular shape of molecules, For example,

(i) $PI_3, 102^0 > PBr_3, 101.5^0 > PCl_3, 100^0$

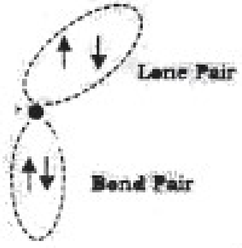
(ii) $AsI_3, 101.4^0 > AsBr_3, 100.5^0 > AsCl_3, 98.4^0$

Rule 5

Bond angles involving multiple bonds are generally larger than those involving only single bonds. However, multiple bonds do not affect the geometry of a molecule.

Rule 6

Repulsion between electron pairs in filled shell is greater than that in incomplete shell. For example, the bond angle decreases.



$OH_2 \geq SH_2 > SeH_2 > TeH_2$

Reason – Lone pair of electrons may be defined as that pair which is found in the valence shell of the central atom. It is not involving in bonding (except when required) and gets influenced by the nucleus of the central atom only.

Due to the attractive influence of two nuclei the electron cloud of the shared pair "contracts" and would be occupying a smaller volume. On the other bond the electron cloud of the lone pair is under the attractive influence of only one nucleus, "spreads out" and would be occupying a larger volume. Hence, lone pairs due to their larger electron clouds become more nearer to other lone pairs. This gives rise to maximum repulsion between lone pairs. Due to the small size of the electron cloud of bond pairs, the repulsive force between the two bond pairs would be the least. The repulsion between a lone pair and bond pair would be somewhat in between the two extreme cases.

Applications of VSEPR theory

By applying these rules of VSEPR theory, one can deduce the regular geometry as well as the distortion in its regular shape in different molecules.

1. Regular Geometry

According to this theory, a molecule will have a regular geometry if the central atom is surrounded only by orbitals containing shared pairs of electrons (i.e. the bond pairs) and there are no orbitals containing lone pairs (non – bonding) in the valency shell. Gillespie and Nyholm calculated theoretically (with the help of some geometry) the regular geometries of molecules containing two to eight pairs of bonding electrons in the valency shell of a central atom.

(a) Two bonding electron pairs

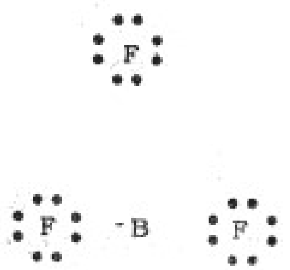
If there are two bonding pairs of electrons in a molecule, the only way to keep them to the maximum extent is to arrange them at 180° to each other. It yield a linear molecule with a bond angle of 180° . example is the molecule of beryllium fluoride.

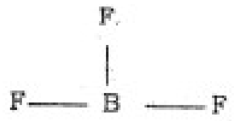
F – Be – F

(b) Three bonding electron pairs

If there are three orbitals around the central atom in a molecule, the molecule in this case will be planar triangle and in this case the bond angle be 120°. this is the case with boron trifluoride. Here B, the central atom has the electronic configuration: Is^2, $2s^2$, $2P^1$, or 2,3 i.e., it has three electrons in its valency shell. These three valency electrons form three covalent bonds with three fluorine atoms.

The molecule has the shape of an equilateral triangle with boron atom lying at the centre and the three atoms lying at he corners of the triangle. This shape is also known as trigonal plane. The bond angle F – B – F is 120°





(c) For bonding electron – Pairs

If there are four orbitals around the central atom in a molecule, the only way to keep them farthest apart is to have them directed towards the four corners of a regular tetrahedron. Thus, the molecule will be tetrahedral in shape and the bond anle In thus case will be 109.5° An example for this is methane. Here the central atom c, has electronic configuration: Is^2, $2s^2$, $2p^2$ outer orbit has four electrons in its valency shell. These electrons form four equivalent covalent bonds with 4 hydrogen atoms.

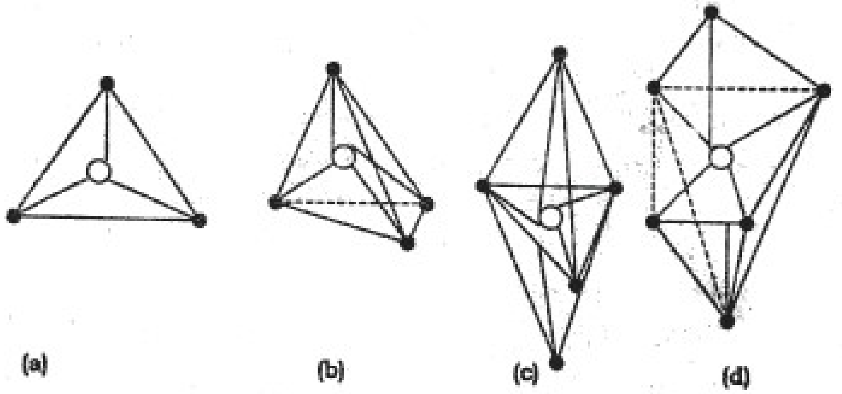


Fig : Shapes of molecules containing 2,4,5 and 6 bonding orbitals

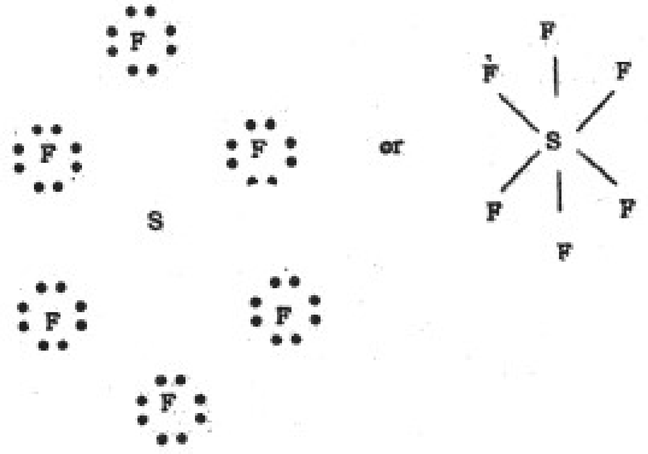
As all the four bond pairs are equivalent, the molecule has a regular geometry of tetrahedron with a bond angle H-C-H as 109°28.

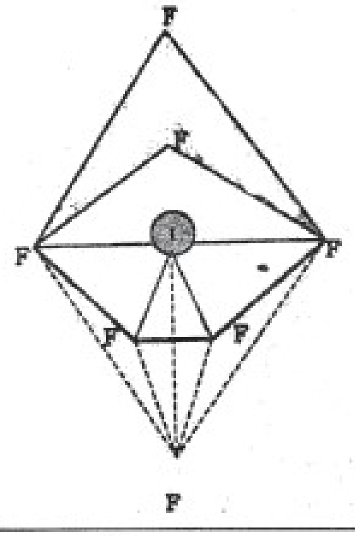
(d) Five bonding electron pairs

If there are five bonding electron pairs, the only way to keep them farthest apart is to have an arrangement of the type, trigonal bipyramidal. Examples are PCl_5 (g) and PF_5.

(e) Six bonding electron – pairs

If there are six bonding electron pairs in a molecule, the molecule will be octahedral in shape and the bond angle will be 90°. An example of this is SF_6. the central atom, S has six valence electrons. These are used in bond formation with 6 fluorine atoms. Since all the six bond pairs are equivalent and no valency electron is left unused, the molecule has a regular geometry of an octahedron.

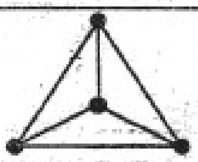
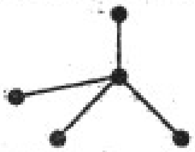
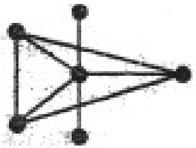
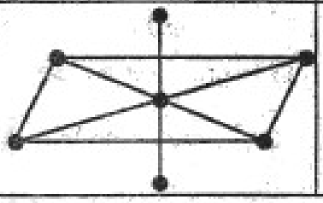




(f) Seven bonding electron pairs

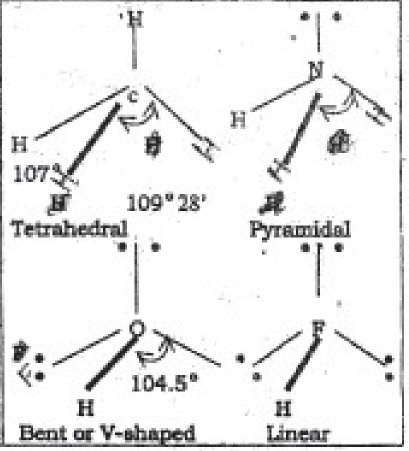
If there are seven bonding electron pairs, the molecule will be pentagonal bipyramid. An example of this is IF_7 the structure of this molecule can be better understood if we visualize two pyramids placed in such a way that their bases touch one another congruently. The base of the pyramid is a pentagon.

TABLE – 1 GEOMETRY OF VARIOUS MOLECULES

Number of electron pairs around central atom	Geometry of Molecules	Bond Angles	Examples
2	Linear 	180°	$BeCl_2$,$MgCl_2$
3	Planar Triangular or Trigonal Planar 	120°	BF_3,$AlCl_3$
4	Tetrahedral 	109° 28' or 109.5°	CH_4,$SiCl_4$
5	Trigonal biopyramidal 	120° and 90°	PF_5, $SbCl_5$
6	Octahedral 	90°	SF_6,TeF_6

In terms of VSEPR theory, a pair of electrons in the valence, shell, either bonding or lone pair, have been under the influence the structure of the molecule. These electron pairs are termed as stereo active as they are effective in ascertaining the stereo or structural arrangement of atoms in a molecule. However, the lone pair of electrons due to their more diffuse (spread out) electron clouds bring about larger repulsions. Because of this, bond pairs move away from them and come closer to each other. This causes the decreases in bond angle from the normal expected values (Table-1). The effect of the lone pairs on molecular geometry in case of the hybrids of the second row non-metals (having lower steroactive electron pairs) is shown in Table – 2.

TABLE – 2 EFFECTS OF LONE PAIRS ON GEOMETRY

Compound	Number of shared pairs	Number of unshared pairs	Structure
CH_4	4	0	
NH_3	3	1	
H_2O	2	2	
HF	1	3	

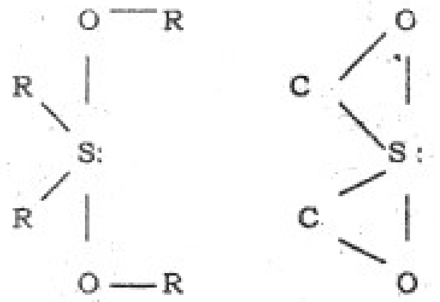
XV. Bent's Rule

This rule may be stated as follows:

More electronegative substituents "prefer" hybrid orbitals having less s character and more electropositive substituents "prefer" hybrid orbital having more s character. Although proposedas an empirical rule, in the chlorofluorides of phosphorus, it is substantiated by molecular orbital calculations.

An example of Bent's rule is provided by the fluoromethanes. In Ch_2 F_2 the F- C- F bond angle is less than $109\frac{1}{2}$, indicating less than 25% s character, but the H-C-H bond angle is larger and the character. The bond angles in the other fluoromethanes yield similar results.

The tendency of more electronegative substituents to seek out the low electro negativity $p_z d_z^2$ apical orbital in TBP structures is often termed "apicophilicity". It is well illustrated in a series of oxysulfuranes of the type prepared by Martin and Coworkers. These as well as related phosphorances provide interesting insight into certain molecular rearrangements.



Bent's rule is also consistent with and may provide alternative rationalization r Gilespie's VSEPR model. Thus the Bent's rule prediction that highly lectronegative substituents will "attract" p character and reduce bond angles in ompatible with the reduction in angular volume of the bonding pair when held ghtly by an electronegative substitutent. Strong s – rich covalent bonds require larger volume in which to bond. Thus double bonded oxygen, despite the high lectro negativity of oxygen, seeks s – rich orbitals because of the shortness and etter overlap of the double bond. Again, the explanation, whether in purely s – haracter terms (Bent's rule) or in larger angular volume for a double bond SEPR) predicts the correct structure.

uestions

1. write the significance of quantum numbers.
2. Write briefly on Pauli exclusion principle
3. What is the significance of Aufbau principle?
4. Differentiate σ and π bonds.
5. Discuss the salient features of valence Bond Theory and Molecular Orbital Theory.
6. Write a short not on (i) Electron deficient molecules (ii) Bond – order (iii) Bond – energy
7. Discuss the usefulness of Pauling is electro negativity scale.
8. How it is different from that of Sanderson scale.
9. Discuss the various methods of evaluating electro negativities.
10. Discuss the Pauling's method of electro negativity scale and how it differs. When we move along a period and along a group.
11. Discuss the bonding in boron hydriaes.
12. Define electron affinity how is it useful in determining lattice energy.
13. Discuss the Born – Haber cycle and its significance
14. what do not mean by hydrogen bonding. Discuss its types and its effect on molecular characteristics.
15. Discuss briefly VSEPR theory.
16. what will be the shape of the molecule O – Be – O with an angle of 180o ? Explain the reasons.
17. what are the various types of interactions changing the molecular shape?
18. Discuss the sigñificance of Bent's rule and apicophilicity.

UNIT – II
SOLID STATE CHEMISTRY

SYLLABUS

Elements of crystallography – spacelattices – unit cells – crystal systems – X – ray Diffraction – Bragg's equation – Bragg's method – rotating and Powder method of X – ray diffraction – Structure of typical lattices such as Calcite, Zinc blende, wurtzite, rutile, Fluorite, antifluorite, pervoskite.

Crystal defects in solids – line and plane defects – non – stoichiometry - Schottky and Frenkel defects and colour centres; solid electrolytes.

Free electron and band theory – Semi conductors. Types and properties of semiconductors – Hall effect – Photovoltaic and solar energy conversion – Super conductivity – High temperature super conductors – Cooper electrons – Meissenner effect – levitation.

I. Introduction - Elements of Crystallography

1. Solids

These are the substances, which maintain their definite shapes against mild distorting forces. Examples of solids are NaCl, KCl, etc. A true solid possesses the following characteristics;

(i) A sharp melting point

(ii) A characteristic heat of fusion

(iii) General incompressibility

(iv) A definite three – dimensional arrangement

2. Crystalline and Amorphous Solids

(a) Amorphous Solids

These are such solids, which have incompressibility and rigidity but they do not have a geometrical shape. In amorphous solids, though the atoms or molecules are strongly bonded yet there is no geometrical regularity or periodicity in the way in which atoms are arranged in space. Examples of amorphous solids are glass, fused silica, rubber and polymers of high molecular masses.

(b) Crystalline solids

Some solids have incompressibility and rigidity but they posses a definite geometrical shape. These solids are known as crystalline solids. A crystalline solid possesses a definite and regular geometry due to definite and orderly arrangement of molecules, atoms or ions in a three dimensional space. A crystalline solid has same geometry irrespective of the source from which it is obtained. Some examples of crystalline solids are NaCl, KCl etc.

3.Symmetry of Crystals

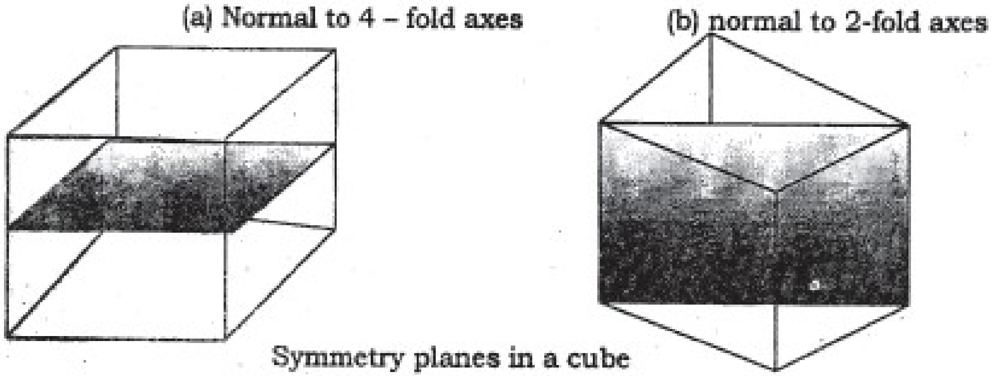
In order to understand symmetry, we shall first consider the kinds of symmetry elements a molecule may possess and the symmetry operations generated by symmetry elements.

i) Symmetry elements

A symmetry element is a geometrical entity such as a line (or axis), a plane or a point with respect to which one or more symmetry operations may be carried out. The various types of elements are as follows;

(a) Plane of Symmetry

A crystal is said to possess a plane of symmetry when an imaginary plane passing through the centre of crystal can divide it into two parts such that one is the exact mirror image of the other. The standard rotation for a plane of symmetry is indicated by σ .

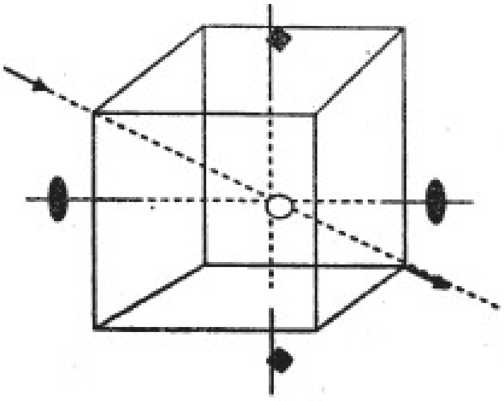


Symmetry planes in a cube

(b) Axis of Symmetry

It is a line about which the crystal may be rotated so that it represents the same appearance more than once during a complete revolution. If equivalent configuration occurs twice, thrice, four and six times i.e after rotation of 180°, 120°, 90° and 60°, the axes of rotation are known as two fold (diad), three-fold (triad), four-fold (tetrad) and six – fold (hexad), axes of symmetry, respectively. C indicates the axes of symmetry. If it is two fold it is indicated by C_2. Similarly three-fold and six-fold axes of symmetry are indicated by C_3 and C_6, respectively.

In general if the same appearance of a crystal is repeated on rotating it through an angle of 360° around an imaginary axis it is known as n – fold axis.



● 2 fold rotation axis (there are 6 in all)

▲ 2 fold rotation axis (there are 4 in all)

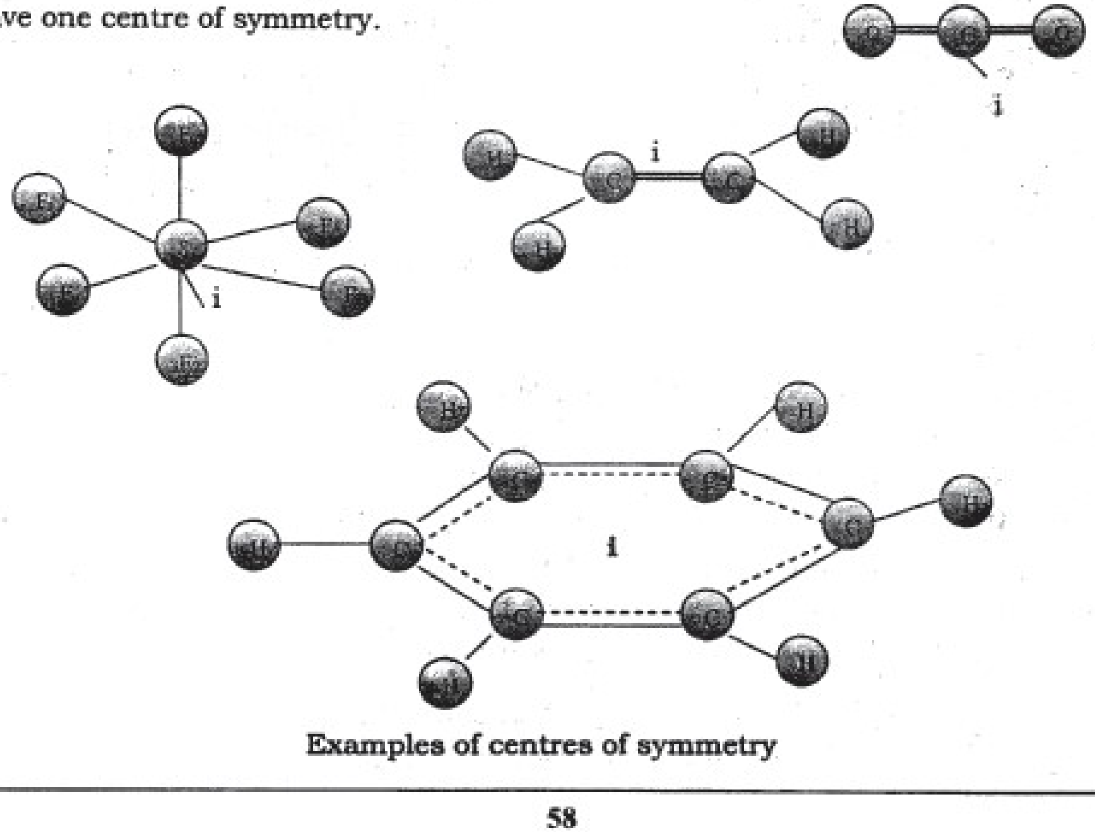
◆ 4 fold rotation axis (there are 3 in all)

○ centre of symmetry

Symmetry axes in a cube

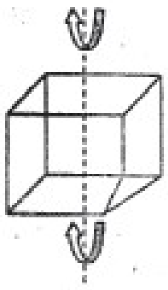
(c) Centre of symmetry

It is a point that any line drawn through it will meet the surface of the crystal at equal distance on either side. It is important to mention here that a crystal may possess a number of planes or axes of symmetry but it can only have one centre of symmetry.



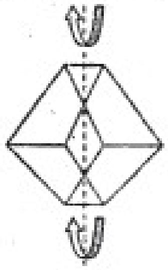
Examples of centres of symmetry

Fourfold



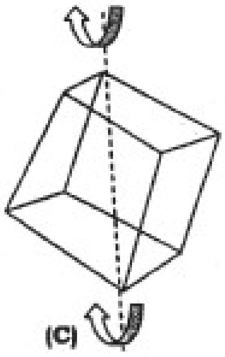
(A)

Two Fold Axis



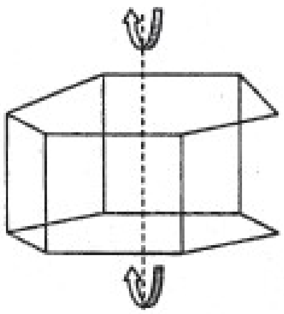
(B)

Three Fold Axis



(C)

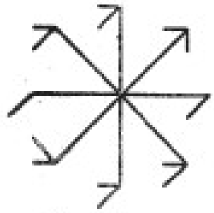
6 Fold Axis



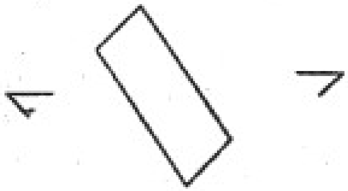
(D)

ii) Symmetry Operation

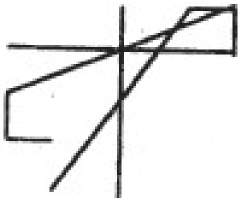
A symmetry operation is a movement of a body, such that, after the movement has been carried out, every point of the body is coincident with an equivalent point (or perhaps the same point) of the body in its original orientation. There are four principal operations for repeating a figure (a) Translation operation (b) Rotation operation (c) Reflection operation across a line in two dimensions or plane in three dimensions and (d) Inversion through a point.



Rotation



Reflection



Inversion

4.Symmetry Elements of a Cubic Crystals

A cube has thirteen axes of symmetry (three four-fold, four three fold, six two-fold), nine planes of symmetry and one centre of symmetry i.e 23 elements the symmetry altogether. This will be understood from the discussion given below;

(a) Rectangular planes of symmetry;

In Fig. (a) one rectangular plane of symmetry : been shown. Besides, this, there are two more such planes not shown in (a). Each of these two planes is at right angle to the plane. Hence, total number of rectangular planes will be three.

(b) Diagonal plane of symmetry

In Fig. (b) one plane passing diagonally through the cube has been shown. Similar to this, there are five more such planes passing diagonally through the cube. Hence, the total number of planes passing diagonally through the cube will be six.

(c) Centre of symmetry

Only one centre of symmetry is possible, which is lying at the centre of cube. It is shown in Fig. (c).

(d) Axes of two- fold symmetry

In Fig. (d) one axis of two - fold symmetry emerging from opposite edges has been shown. Evidently, there will be a total of six such axes of two-fold symmetry.

(e) Axes of three - fold symmetry

In Fig. (e) one axis of three-fold symmetry passing through opposite corners has been shown. Evidently, there will be a total of four such axes.

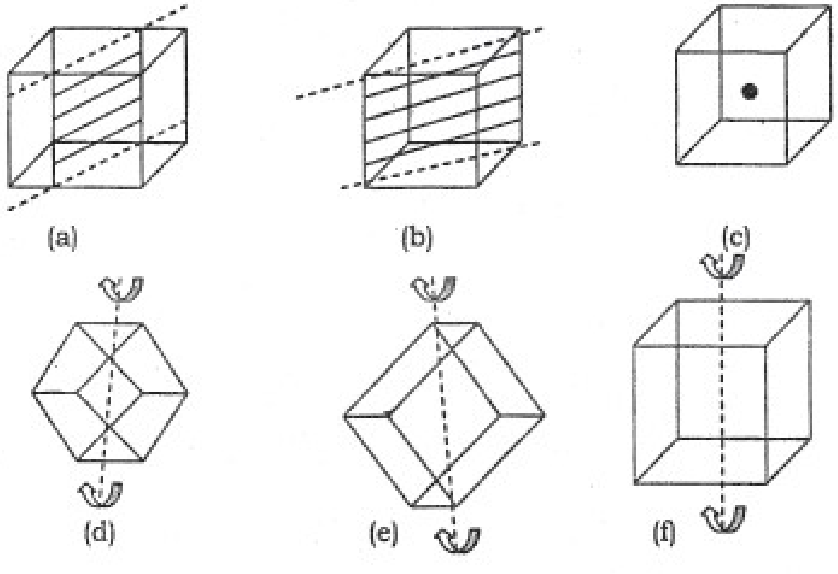
(f) Axes of four-fold symmetry

In Fig. (f) one axis of four - fold symmetry has been shown. Evidently, there will be a total of three such four-fold axes at right angles to one another.

From the above discussion the number of symmetry elements of various types in a cube would be 23.

Centre of symmetry = 1
Planes of symmetry = 3 + 6 = 9
Axes of symmetry = 3 + 4 + 6 = 13

∴ Total number of elements will be 1 + 9 + 13 or 23.


(a) (b) (c)
(d) (e) (f)

Various elements of symmetry in a Cube

II. Space Lattice and Unit Cell

Point groups

From geometrical considerations, it may be assumed that 32 different combinations of elements of symmetry of a crystal are possible theoretically. These are known as 32-point groups or 32 systems. But some of these could be grouped together. Therefore, these 32 systems could be grouped together in seven different categories, which are known as the seven basic crystal systems. These seven systems are cubic or regular, tetragonal, hexagonal, orthorhombic or rhombic, monoclinic, triclinic and rhombohedral or trigonal. All these systems with the maximum number of planes and axes of symmetry and examples of elements are given in the following Table.

System	Symmetry	Examples
1. Cubic or Regular	Nine planes Thirteen axis	NaCl, KCl, CaF_2, Cu_2O, ZnS, Pb, Ag, Au, Hg, alums, diamond
2. Tetragonal	Five planes Five axis	KH_2PO_4, SnO_2, TiO_2, $PbWO_3$
3. Hexagonal	Seven planes Seven axis	ZnO, CdS, HgS, Graphite, Ice, PbI_2, Beryl, Mg, Zn, Cd
4. Orthorhombic or rhombic	Three planes Three axis	$PbCO_3$, $BaSO_4$, K_2SO_4, Rhombic sulphur, Mg_2SiO_4
5. Monoclinic	One plane One axis	$Na_2B_4O_7$, $10H_2O$, Na_2SO_4. $10H_2O$ Monoclinic sulphur, $CaSO_4$, $2H_2O$
6. Triclinic	No planes No axis	$CuSO_4$. $5H_2O$, H_2BO_3
7. Rhombohedral (or Trigonal)	Seven planes Seven axis	$NaNO_3$, ICl, Magnesite, As, Sb, Bi, Quartz

1.Space lattice or Crystal lattice

It is the regular pattern of points which describes the three dimensional arrangement of particles (atoms, molecules or ions) in a crystal structure. Thus, a space the environment about any particular point is in every way the same.

For example, in Fig .A there is an array of points in one dimension. But in this figure environment about any two points are the same. Hence, Fig.A represents a lattice.

In Fig .B there is an array of points in two dimensions. In this case the environments about any two points are the same. Hence, Fig.B represents a lattice.

In Fig.(C), a three-dimensional space lattice has been shown in which each point is representing an identical atom or group of atoms.

It is important to remember that it is the arrangement of the points, which are a lattice and not the lines, which are joining them.

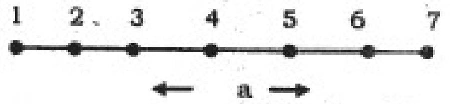


FIG.A – One-dimensional lattice

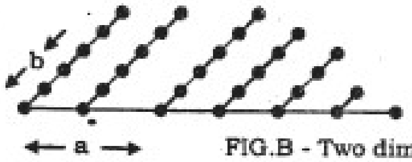


FIG.B - Two dimensional lattice

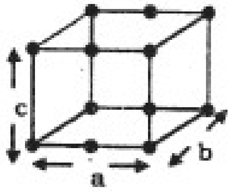


FIG.C - Three-dimensional lattice

Unit Cell

It is the smallest portion of a space – lattice, which on moving equal distance in various directions reproduces the whole crystal structure. The conditions for choosing the unit cell are;

(i) The unit cell should have the same symmetry as the crystal itself.

(ii) Where more than one simple arrangement are possible, the one with the smaller number of atoms or particles is chosen.

In Fig (a) a two – dimensional geometric pattern is shown. In this there are three possible unit cell marked A, B and C. It is possible to generate space lattice by placing any one of these unit cells side by side in space. But a single unit cell is to be chosen which may be found out by considering;

(i) the symmetry of each of these three-unit cells and (ii) volume per unitcell.

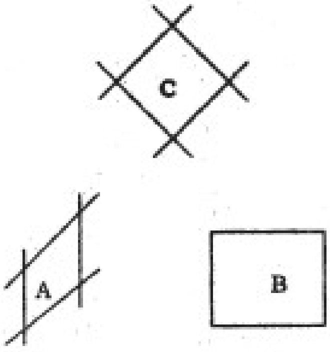
Unit cell A is having 2 – fold symmetry and is having two dots and one cross per unit cell. Unit cell B is having 4 – fold symmetry and is having four dots and two crosses. However, it is larger than A. Unit cell C is also having maximum symmetry of 4 – fold axis of rotation and is having two dots and one cross per unit cell. On the basis of minimum volume, cell B could be rejected.

Out of cell A an (both are having the same volume), unit cell A has been rejected (in favour of B) because it is having low symmetry.

In order to describe a unit cell, one has to know;

i] The distance a, b and c which give the length of the edges of the unit cell and

ii] The angles α, β and γ, which give the angles between the three imaginary axes OX, OY and OZ (Fig. b).



(a) Lattice and a unit cell

(b) Description of a unit cell

2.Bravais Lattice

From geometrical considerations A. Bravais showed it in 1848 that all possible three-dimensional space lattices are of fourteen distinct types. These are known as Bravais lattices and are derived from seven crystal systems. All crystalline solids can be represented by one of these lattice structures. The unit cells for these fourteen Bravais lattice are shown in Figures in the next page with the parameters of unit cell, i.e. the intercepts a, b and c, interfacial ?, α, β and γ are shown.

Three types of unit cells for cubic crystals are as follows;

(a) Simple cubic lattice

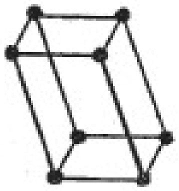
When one unit is situated only at each corner of the cubic cell, it is known as simple cubic lattice. In other words, it contains eight points, which are situated at eight corners of a cube. There is no lattice point inside the cube.

(b) The body centered cubic bcc lattice

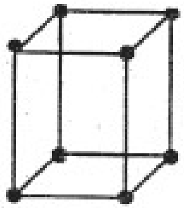
When one unit is situated at each corner and one at the centre of a cube, it is known as body centered cubic lattice. In all bcc lattice consists of nine points.

(c) Face centered cubic fcc lattice

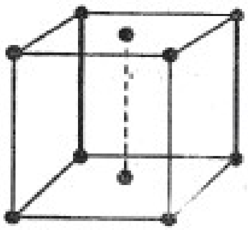
When one unit is situated at each corner and one at the centre of each of the faces, it is known as face centered cubic lattice. In all fcc lattice will consist of fourteen points.



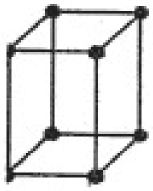
1. Triclinic



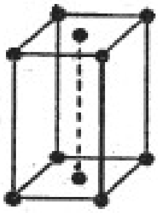
2. Simple Monoclinic



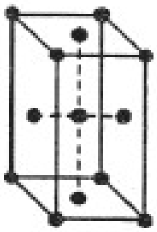
3. Side-centered Monoclinic



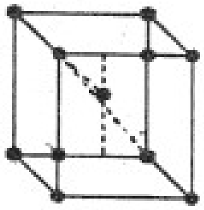
4.Simple Orthorohombic



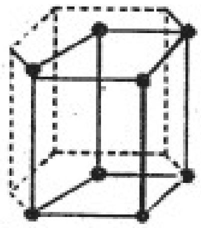
5.End-centered Orthorohombic



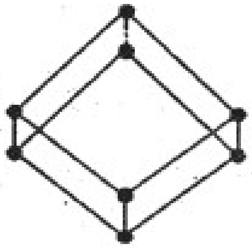
6.Face-centered Orthorohombic



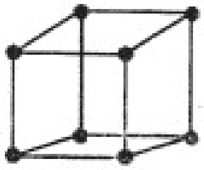
7. Body centered Orthorohombic



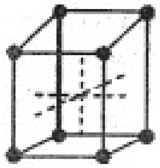
8. Hexagonal



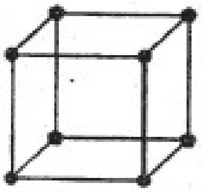
9.Rhombohedral



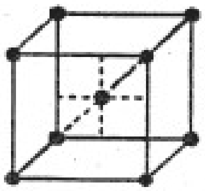
10. Simple Tetragonal



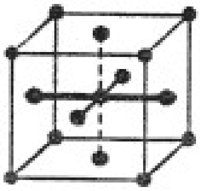
11. Body Centered Tetragonal



12.Simple cubic



13. Body centered cubic



14. Face centered cubic

We have already described that a maximum of 32 elements of symmetry (point groups) would be possible. On combining these with 14 Bravais lattices, 230 different arrangements known as space groups are possible.

III Crystal Systems

1.Classification of Crystals on the Basis of their shapes

Theoretically, 230 crystal forms are possible. Practically, all have been observed. On the basis of their symmetry, these 230 crystal forms have been divided into 32 classes and these in turn have been further classified into seven crystal systems. The shapes of these are shown in figure and their characteristics are given in the Table.

(i) I column is giving the name of the crystal system

(ii) II column is giving the number and types of space lattices present in the given crystal system.

(iii) III column is giving axial distances

(iv) IV column is giving axial angles

(v) V column is giving examples

Crystal System (I)	Types of Lattices (II)	Axial distances (III)	Axial angles (IV)	Examples (V)
1. Cubic	Primitive, Face centered, Body centered = 3	$a = b = c$	$\alpha=\beta=\gamma=90^\circ$	Copper, KC*l* and Zinc blende
2. Tetragonal	Primitive Body Centered = 2	$a = b \neq c$	$\alpha=\beta=\gamma=90^\circ$	White tin, SnO_2
3.Orthorhombic	Primitive Face centered, Body centered, End centered = 4	$a \neq b \neq c$	$\alpha=\gamma=90^\circ$ $\beta \neq 90^\circ$	Rhombic sulphur
4.Rhombohedral	Primitive = 1	$a = b = c$	$\alpha=\gamma=90^\circ$ $\beta \neq 90^\circ$	Calcite
5. Monoclinic	Primitive End centered = 2	$a \neq b \neq c$	$\alpha=\gamma=90^\circ$, $\beta \neq 90^\circ$	Monoclinic sulphur
6. Triclinic	Primitive = 1	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma = 90^\circ$	Potassium dichromate
7. Hexagonal	Primitive = 1	$a = b \neq c$	$\alpha=\beta=90^\circ$, $\gamma=120^\circ$	Graphite

2.Classification of Crystals on the Basis of Bond Type

On the basis of units, types of binding forces and their properties, the crystals can be divided into four categories, viz. Ionic crystals, Molecular crystals, Covalent crystals and Metallic crystals.

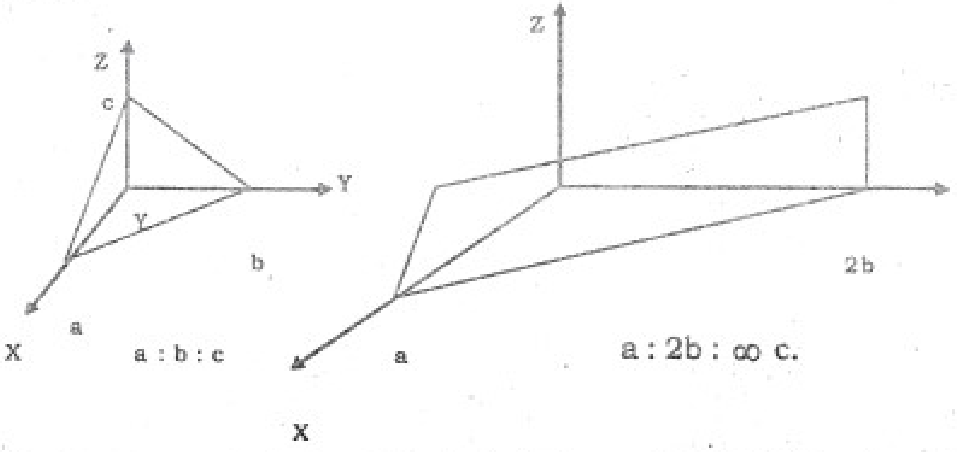
Ionic crystals

The forces, which hold the ions together within the ionic crystal, are the strong electrostatic coulombic forces. The type of lattice with which the ionic compound crystallizes depends on two factors;

i) The size of the ions and ii) The necessity for the preservation of electrical neutrality. Thus, the lattices in ionic crystals consist of alternate positive and negative ions in equivalent amounts.

3. Miller Indices

The law of rotational indices states that the intercepts of the planes of the various faces of a crystal on a suitable set of axes can be expressed by small integral multiples of three unit distances. The relative orientation of crystal or lattice planes is of great importance in crystal structure analysis. The important planes of a crystal lattice can be described in terms of intercepts that are multiples of the unit cell dimensions. Since crystal planes are similarly oriented they can be similarly described. In this way Weiss indices are used; and planes are described by their relative intercepts as the x, y and z axes in a : b : c (or) a : 2b : ∞ c.



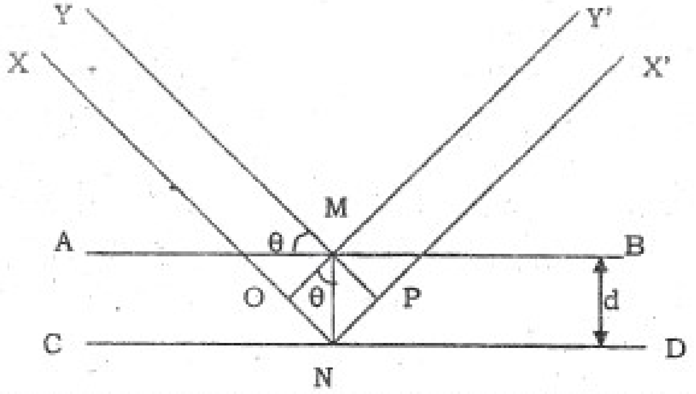
a : b : c

a : 2b : ∞ c.

Much more convenient, particularly in the analysis of diffraction data, are sets of numbers called 'Miller indices'. These are obtained by taking the reciprocals of the coefficients of the Weiss indices. These three reciprocals are then cleared of the fraction and reduced to the smallest set of integers.

The plane a : b : c becomes a (111) plane, the a : 2b : c plane becomes a (212) plane. The a : b : ∞ c plane becomes a (110) plane. The Miller indices, in general are referred to as (h k *l*) describe the relative directions of the crystal planes. The directions of the special planes that pass through many lattice points can be described by Miller indices.

IV. X – ray Diffraction : Bragg Equation



The important fact that a crystal can be used as a diffraction grating led to the use of X – rays for studying crystal structure by using the crystal as a reflection grating for homogenous X – rays i.e. X – rays of uniform wave length. When X – rays fall on the surface of a crystal, they are reflected by atoms on the surface as well as those lying in the successive lattice planes parallel to the face of the crystal.

AB and CD represent two lattice planes of a crystal. The distance between them is 'd'. YM and MY' are, respectively the incident and reflected rays which make an angle θ with plane AB. Similarly XN and NX' are, respectively, the incident and reflected rays on the plane CD. If MO and MP are drawn perpendicular to XN and NX' the path difference between the two rays is equal to NO + NP = 2 NO. Since the angles AMN and YMO are 90° each, the angle YMA is equal to the angle OMN i.e. < OMN = Q

$$\frac{NO}{NM} = \sin\theta$$

$\therefore$ NO = NM Sin θ

$\therefore$ Path difference = 2NO = 2 d sin θ

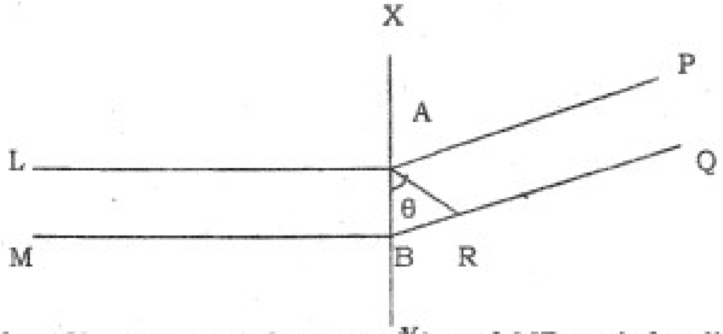
This is an integral multiple of the wavelength of the x- rays.

$N\lambda = 2d \sin\theta$

This is the Bragg equation when n is an integer n = 1,2,3 representing the order of reflection. The intensity of X-rays decreases with increasing order of reflection.

V. Rotating Crystal Method

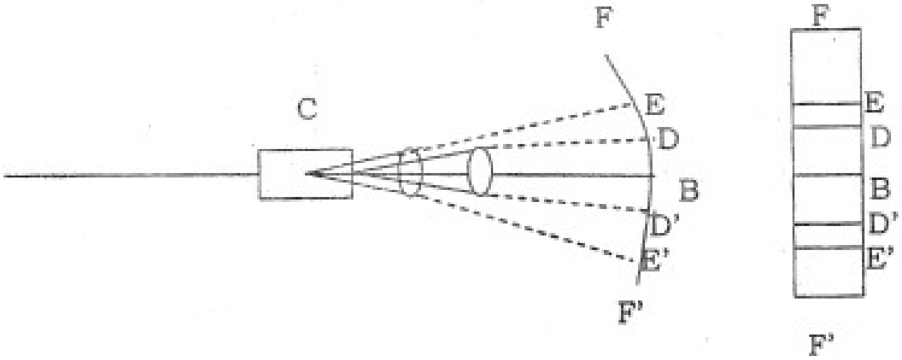
The method of using a rotating crystal for X-ray analysis was interpreted by M.Polanyi (1921). This method is probably used more for structure determination. A crystal, which should be small enough not to absorb all the radiation in which it is bathed, is rotated round an axis parallel to one of the crystal axes and exposed to a beam of homogenous X-rays from a direction at right angles. For any particular position of the crystal there may be no diffraction, but as it rotates various planes come successively into suitable positions for diffraction to occur and corresponding spots are produced on a photographic plate. The conditions for diffraction are shown in the figure, in which XY is the axis of rotation and A and B represents points in two successive lattice planes.



The incident X – rays are shown at LA and MB and the diffracted rays at AP and BQ. For diffraction maximum to occur the difference in the path AP and BQ that is BR must be equal to n λ (i.e.) a whole number of wavelengths. The value of n will depend on the angle BAR (θ) and a series of directions of diffraction will be obtained for increasing values in θ as n increases from zero upward. All lattice planes having the same spacing (AB) in the direction parallel to the axis of rotation will produce diffraction spots lying on a more or less horizontal line, such lines are known as layer lines and a series is obtained corresponding to different values of n.

From the vertical distance between layer lines and that from the crystal to the photographic plate, it is possible to calculate θ providing the wave length of X – rays spacing between the planes. In addition to the layer lines it is seen that the spots fall on a set of curves in a transverse direction; these are called row lines; and their positions are of importance in the interpretation of the results. By taking three photographs, with the crystal rotating about each of three axes, the lattice spacing and the size of the unit cell can be readily deduced. The exact identification of the spots with various orders of spectra from different planes is not always a simple matter, but graphical devices have been introduced to expedite the work.

VI. Powder Method



Here a narrow beam of X - rays falls on the finely powdered substance to be examined and the diffracted rays are passed on to a strip of the film, which almost surrounds the specimen. In the fine powder, the crystals are oriented in all possible directions and so a large number of lattice planes will be in the correct orientation for the Bragg equation. Suppose θ is the glancing angle necessary for the first order reflection in (100) plane all crystalline particles whose (100) plane make an angle θ with the incident beam will therefore produce reflections. Since this condition can be satisfied by a series of orientations parallel to a common axis, the diffracted rays will lie on a circular cone as shown above.

AB is the direction of incident X – rays, C is the powder and DCD' represents the case of rays for the first order diffraction from (100) planes of a large number of crystals. Similarly some crystals will be oriented in such a way to give a circular cone of X – rays ECE' as second order reflection from the 100 planes and so on for the other planes. If a strip of photographic film is placed at FF' it will cut the cone in such a way to produce two arcs. Each pair gives the position of reflections of a definite order from a particular plane.

The magnitude of the glancing angle can be calculated if the distance from the crystal to the photographic film is known for the semi vertical angle of the cone is 2 θ. If the indices of the various diffraction arcs are determined the lattice spacing can be calculated, provided the wavelength of X – rays is known.

θ = S/r where θ is glancing angle in terms of radian

S = distance of the arc from the spot

r = distance from capillary to film

For e.g.

$$X - \text{ray of } 0.12 \text{ radian gives } \theta = 0.12 \times \frac{180}{x} = 69^\circ \text{ as radian} = \frac{180}{x}$$

Using the Bragg equation,

d = distance between the lattice planes can be calculated giving

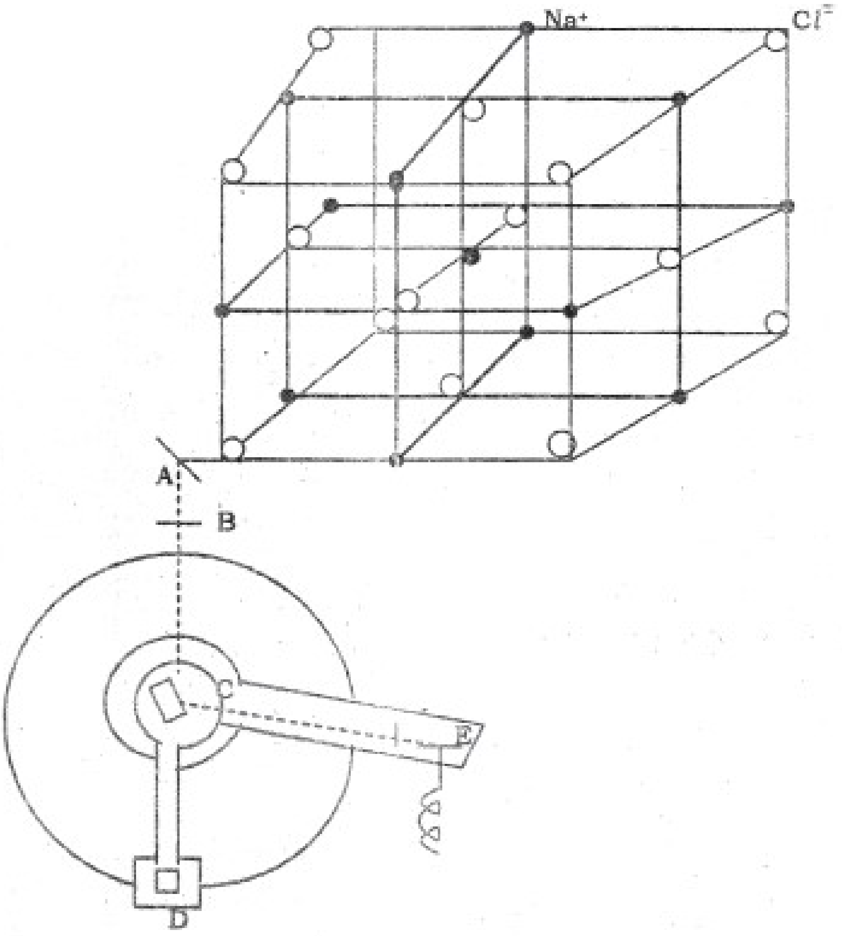
$$d = \frac{\lambda}{2\sin\theta} \text{ assuming to be first order reflection } (n = 1)$$

VII. Crystal Structures

A beam of X – rays of definite wave length from the anticathode of an X -ray tube passes through slit B and then falls upon a face of the crystal C mounted on a rotating Table, the position of which can be read on the scale D. The X- rays reflected from the crystal pass through [illegible] detector (ionization chamber). The response of the detector is proportional to the intensity of the X – rays reflected. Starting with a small glancing angle between the incidents X – rays on the surface of the crystal the value is increased in stages by rotating the Table. The apparatus is so designed that the reflected X – rays always enters the detector chamber and the intensity of reflected X – rays for various angles are thus determined.

If θ is the angle of incidence when the intensity of reflected ray is maximum (1st order reflection) and λ is the wavelength of the X – rays the distance d between the two planes can be found out.

$$d = \frac{n\lambda}{2\sin\theta} = \frac{\lambda}{2\sin\theta} (n = 1)$$



X – ray spectrometer (Bragg)

The first order reflection from (100) (110) and (111) faces of the sodium chloride using palladium anti – cathode were observed to be 5.9°, 8.4° and 5.2° respectively, so that the ratio of the spacing parallel to the three principal planes are;

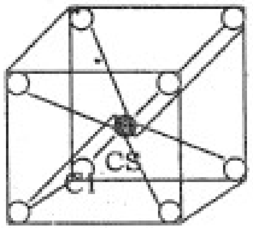
$$d_{100} : d_{110} : d_{111} = \frac{1}{\sin 5.9^\circ} : \frac{1}{\sin 8.4^\circ} : \frac{1}{\sin 5.2^\circ}$$

$$= 9.731 : 6.844 : 11.04 \text{ Divide with } 9.731$$

$$= 1 : 0.704 : 1.136$$

The ratio is identical with $1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}$

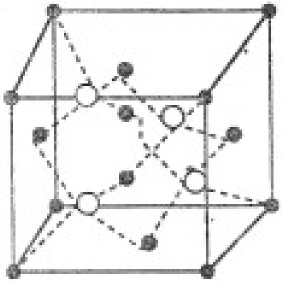
It gives the relative spacing in the unit cell of a face centered cubic lattice.



Cesium chloride

According to radius ratio calculation value of cesium chloride is 0.93, which is above 0.732 showing 8 coordination. This is also surrounded by 8 chloride ions.

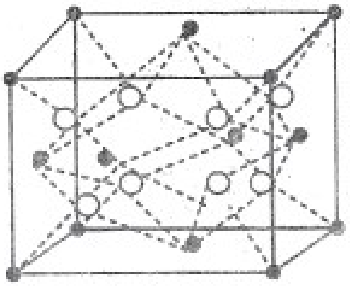
1.Zinc Blende



(a)

● - Sulphide

○ - Zinc



(b) Structure fluorite

● - Calcium

○ - Fluoride

Zinc blende is a structural form of ZnS. It has 4: 4 coordination. The cubic ZnS is shown in the figure. The zinc blende structure is face centered cubic array of sulphide ions. There is a tetrahedrally coordinated hole at each corner of the cube; the Zinc ions occupy four of the eight tetrahedral holes.

2.Fluorite

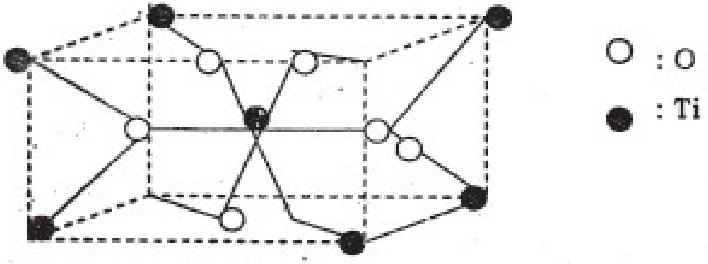
For compounds of 1 – 2 valence types, the typical structures are the cubic fluorite CaF_2 and tetragonal rutile (TiO_2).

In fluorite, the Ca^{2+} ions are in a face-centered cubic arrangement. This lattice has in addition to the octahedral holes, holes that are tetrahedrally coordinated. The tetrahedral holes of the face centered cubic structure are occupied by F^- ions in fluorite. Each fluoride ion is tetrahedrally coordinated to Ca^{2+} ions. Figure b shows that the Ca^{2+} ions on the top face are connected to four fluoride ions (not shown in the figure) lying above it. The coordination of the Ca^{2+} ion is eight and the fluorite structure is described as having 8 – 4 coordination. Fluorite may be considered as a face centered cubic array of calcium ions interpenetrated by a simple cubic array of fluoride ions.

3.Rutile Structure TiO_2

It has 6 : 3 coordination. The radius ratio is 0.732 to 0.414. The radius ratio of two kinds of atoms, which crystallize in the rutile structure, permits the inclusion of the smaller ions in the octahedral holes of a close packed structure of the larger ions. In rutile, titanium dioxide, TiO_2, (r of Ti^{4+} is 0.64 and of O^{2-} is 1.32) and O^{2-} ions are arranged in a close-paced hexagonal structure and the Ti^{4+} ions are in one – half of the octahedral holes. In another way of regarding the rutile structure the Ti^{4+} ions are placed at the relative positions of a body – centered cubic structure. The O^{2-} ions are arranged so that each is equidistant from its three nearest titanium neighbors. The rutile structure is adopted by many metallic oxides of the type MO_2 including PbO_2, MoO_2 and MnO_2 and the difluorides of many traditional metals.

All T sites are filled by F^- in a cubic close packing (CCP) array of Ca^{2+} ions (in P sites) in the mineral fluorite CaF_2. Many MX_2 compounds of large cations have the fluorite structure and the M_2X compounds have the antifluorite structure with reversed roles of cations and anions.

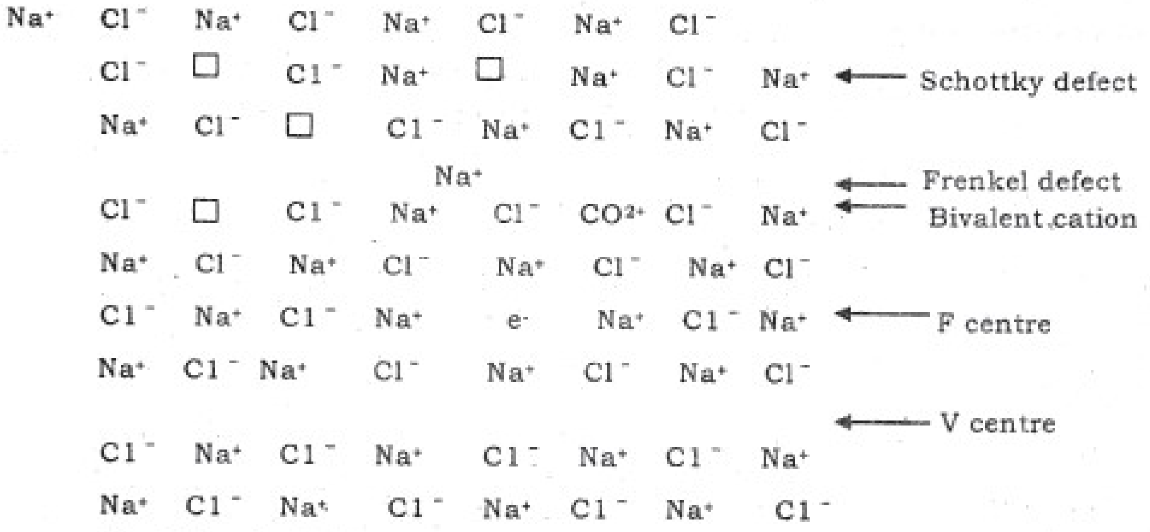


Cinographi projection of the unit cell of the tetragonal structure of rutile, T_iO_2

VIII. Crystal Defects in Solids

1.Point Defects

In 1896, Roberts – Austen showed that gold diffuses faster in lead at 300° C than sodium chloride in water at 15°C. This is one example of the surprising case with which atoms can sometimes move about in the solid state. It was difficult to believe that atoms or ions could move easily in solids by changing places with one another. The activation energy for such a process would be too high. I. Frenkel suggested more reasonable mechanisms in 1926 and by W.Schottky in 1930. They proposed models for what are now called point defects in crystals. Various point defects are illustrated below;



The Schottky defect consists of a pair of vacancies of opposite signs. The Frenkel defect consists of an ion that has moved to an interstitial site in the crystal structure plus the vacancy left behind. Frenkel and Schottky defects are called intrinsic defects. They do not alter the exact stoichimetry of a crystal. They provide mechanisms through which atoms and ions can move within a crystal, either by jumping from an occupied site into a vacancy or by jumping from one interstitial site to the next.

We can calculate the concentrations of point defects from simple statistical consideration It costs energy to make a defect, but entropy S is gained owing to the disorder associated with the entropy of mixing of the defects with the occupied lattice sites. If N defects are distributed among the total of No crystal sites, the entropy of mixing is $S = k \ln W = k \ln No!/(No-N)!$.

If ε is the increase in energy per defect the change in Helmholtz free energy is ? A = ?U - T?S = N ε -kT $\ln No!/(No-N)!\,N!$ and at equilibrium, ($\delta A = \delta N$).
Applying the Stirling formula ($\ln X! = X \ln X - X$), we find that

$$\ln \frac{N}{No - N} = \frac{\varepsilon}{kT} \quad \text{and thus if } N < No \text{ we get } N = No\,e^{-\varepsilon/kT}$$

As an example, if ε is about 1 eV and T is 1000 k, then N/No ? 10^{-5}. For a pair of vacancies, the expression for the number of ways of forming the defect is squared and for Schottky defects

$$N = No\,e^{-\varepsilon/2kT}$$

For Frenkel defects, if No is the number of interstitial sites,

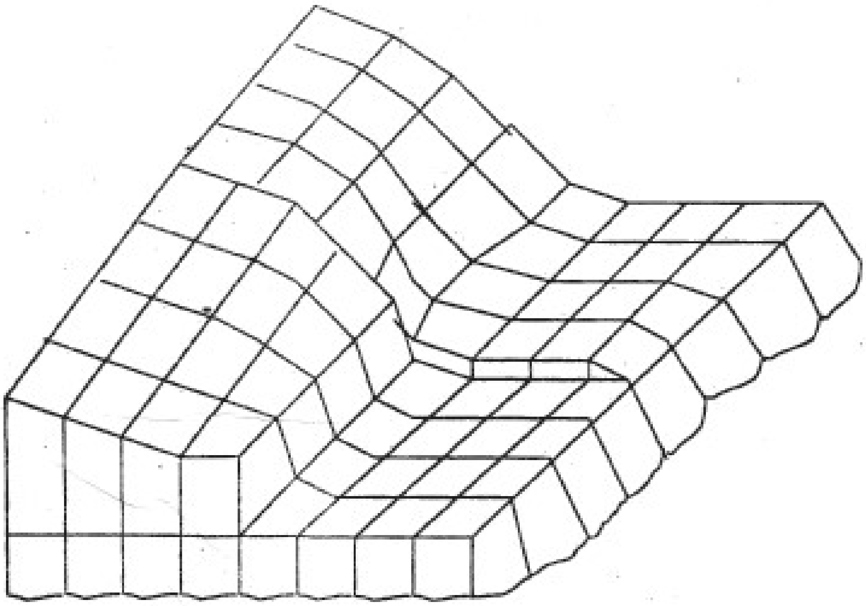
$$N = (No/No')^{1/2}\,e^{-\varepsilon/2kT}$$

If a NaCl crystal is heated in Na vapour, it acquires a deep yellow colour; KCl crystals heated in K vapour acquire a magenta colour. The colour centers are called F centers. When NaCl takes up extra Na, there is an excess of occupied sodium sites in the crystal so that some Cl^- sites are vacant. There are six Na^+ sites adjacent to a vacant Cl^- site. The extra electron on the excess Na atom can be shared between all six Na^+ ions to give a delocalized electron in a box. Light is absorbed as the electron makes a transition from its ground state to an excited state.

2.Linear Defects – Dislocations

The problem for metals under stress is not why they are so strong, but why they are so weak. The calculated elastic limit of a perfect crystal is 10^2 to 10^4 times that actually observed. There must be some imperfections or defects in actual metal crystals that cause them to deform plastically under quite small loads.

Taylor, Orowan and Polanyi worked out a solution to this problem independently in 1934. Crystals contain linear defects called dislocations. These defects can be compared to rucks in carpets. We all have pulled carpets over floors and know that there are two ways of doing it. One can take hold of one end and tug or one can make a ruck in one end of the carpet and gently edge it to the other end. For a big heavy carpet, the second way involves less effort. The dislocation most like a ruck is the edge dislocation shown in which represents a model a crystal structure viewed along a dislocation line.



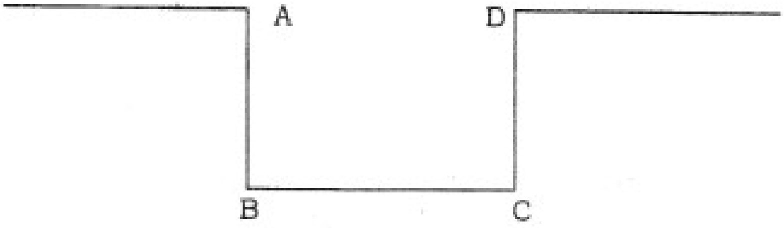
The dislocation line is perpendicular to the plane represented by the plane of the paper. The presence of the dislocation allows the crystal to deform readily under the influence of a shear stress. The atoms are displaced in the slip plane that includes the dislocation line. Thus the dislocation can move across the crystal from one side to the other, the result being a displacement of the top half of the crystal relative to the bottom half.

The other basic kind of dislocation is the screw dislocation. We can visualize this defect by cutting a rubber stopper parallel to its axis, and then pushing on one end so as to create jog at the other end. If we suppose that initially the stopper contained atoms at regular lattice points, the results of the deformation would be to convert the parallel planes of atoms normal to the axis into a kind of spiral ramp. Such a displacement of the atoms constitutes a screw dislocation; the dislocation line is along the axis of the stopper. A model of the emergence of a screw dislocation is at the surface of a crystal.

IX. Free Electron Theory

The first theory of the metallic state is from the work of Drude and Lorentz. We have to visualize metals as metallic ions immersed in a sea of mobile electrons (metals have low ionization energy). A metal is regarded as an assembly of positive ions immersed in a gas of free electrons. A potential gradient exists at the surface of the metal to imprison electrons but within the metal, the potential is uniform.

This can be represented as follows. Within the metal from B to C the potential is uniform.



Free Electron Model

But at the surface a potential difference (V) prevents electrons from escaping. Thus we visualize attraction between the positive metal ion and electron gas, which is responsible for the cohesive force and we can explain the free mobility of the electron gas under the influence of electrical or thermal stress as responsible for the high conductivity.

Here if the electrons are assumed to obey the laws of classical mechanics, their energies will correspond to Boltzmann distribution appropriate to the temperature of the specimen. That is, at room temperature, a quite negligible fraction of electrons will have energies sufficient to surmount the potential barrier (V). But as the temperature is raised the fraction will increase and a number of electrons escape in the form of thermionic current. One objection for this is that if electrons have Boltzmann distribution of energies like gases, they should contribute to the specific heat (i.e) the specific heat of metal should be substantially larger than the specific heat of an insulator. However no such difference was found in the experimental observation.

X. Band Theory

The combination of atomic orbitals to form molecular orbitals results in the splitting of energy levels of the original atomic orbitals and further the magnitude of splitting depends upon the extent of overlapping which in turn is dependent upon internuclear separation involved and directions of the atomic orbitals. In the structure of the metals with an assembly of 'N' atoms, there are N energy states formed for each energy state.

Here the combination of 'N' orbitals of a given type will give rise to N molecular orbitals of closely spaced energies called an energy band. Due to a low degree of orbital overlap the bandwidth for inner electron shells is small.

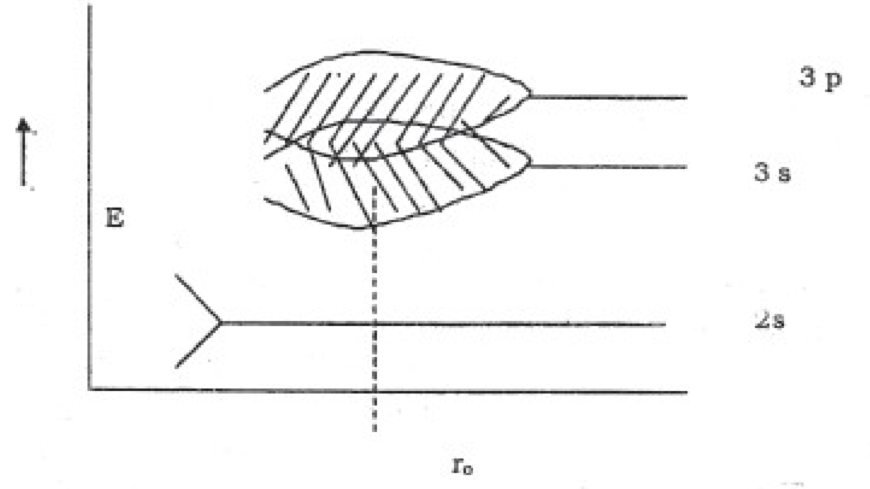
Na – Atomic No. 11

Electronic configuration is $1S^2 2S^2 2P^6 3S^1 3P^0$

The 3S orbital (partially filled) overlap with empty 3P orbital.

Here the energies of the band are virtually the same as in the isolated atoms. For outer orbital valence electrons, the energy range may be given in a band, which may be relatively larger. The width of different bands may cause different bands to overlap in an atom as the electrons occupy definite energy levels. A solid consists of a three dimensional arrangement of atoms which interact with one another. Definite energy levels are replaced by bands of energy levels.

We have broad quasi-continuous range of energy levels available to valency electrons. How far this range is filled is dependent upon the number of electrons.We can explain this by taking sodium as an example.



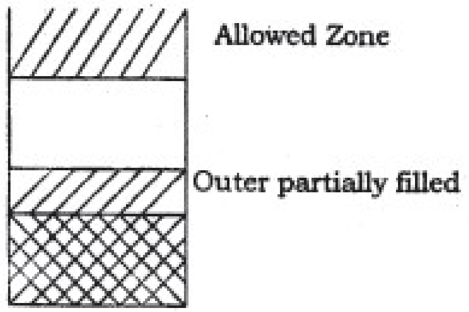
Internuclear distance

We see 3S electrons spread over a finite range and closer approach of atoms makes this range broad. If we consider 3P orbitals, which are slightly higher than 3S orbitals of isolated atoms they will spread and at r_o overlap with 3P will take place.

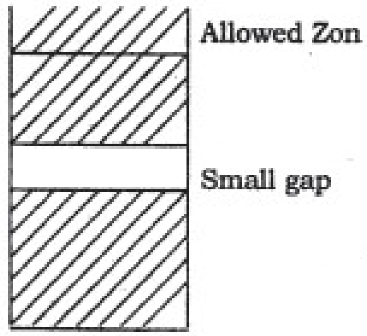
XI. Semi Conductivity

In conductors, the outermost occupied Brillouin zones is not completely filled, so that when an electric field is applied to the crystal, the electrons in some of the lower energy states of the crystal, the electrons in some of the lower energy states of the unfilled zone are transferred to higher energy states. So, there is a resultant unidirectional movement of charge throughout the crystal. This is shown by the passage of an electric current (e.g sodium one electron metal i.e. one electron in the outermost shell). In some metallic conductors all the bands are full. But an empty band overlaps with an inner full band. Free electron movement can occur to similar bands in other atoms like Mg, Zn.

Metallic conductors



Semi conductors



The conductivity of metals generally decreases with increase in temperature. Absorption of thermal energy causes vibration of atoms within the crystal lattice, which hinders the free movement of electrons through bands.

Insulator

When an electric field is applied to an insulator, there is no unidirectional movement of electrons since there are no unfilled energy states in the zones, which they occupy and there is a large energy gap between the zones. If the applied field is very large the electrons may be given sufficient energy to bridge the gap and to transfer them to energy states in a higher zone, which has hitherto been entirely unoccupied.

Semiconductors

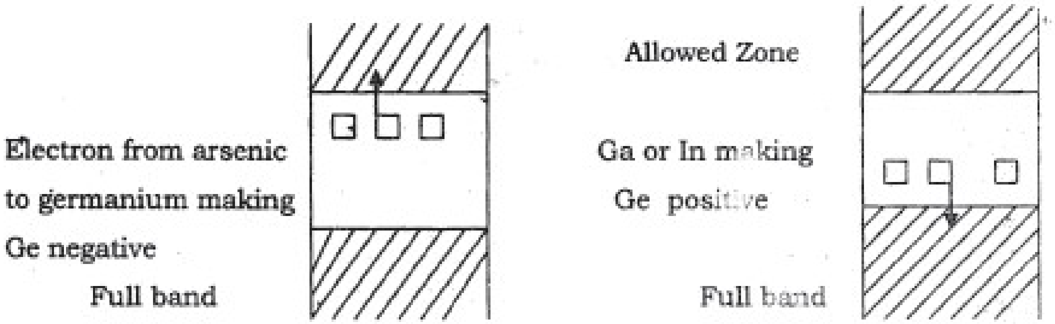
These are substances with crystalline structures, which are insulators under normal conditions,, but which may be made conducting by rise of temperature or by the presence of impurities. They are divided into two classes (a) Intrinsic semi conductors and (b) Extrinsic semiconductors.

(a)Intrinsic semi conductors

In these semi conductors the Brillouin zones do not overlap but are contiguous and there are no partially filled zones. A small amount of energy such as that acquired by thermal excitation is sufficient to raise some of the electrons from the higher energy states of the filled zone to the lower energy states of the next zone, which has hitherto been empty. There are then two partially filled zones and when an external electric field is applied some of the electrons can move into the unoccupied energy states. The heated substances therefore behave as a conductor. Graphite is a well known example of an intrinsic semi conductor, but there are not many such substances which have their Brillouin zone exactly or very nearly contiguous without overlapping. Ultraviolet light may provide sufficient energy for such promotion and these semi conductors are called photo conductors.

(b)Extrinsic semi conductors

These are substances which are not conductors in the pure state but which may be made conducting by the introduction of impurities. Their energy levels have small energy gaps, which contain energy levels due to impurity. They are classified as n-type and p-type semiconductors, which are shown in the figure.



n – type Semi conductor p - type

i) n-type semi conductors

When germanium is crystallized from a melt containing small quantity of arsenic, some arsenic atoms are incorporated into germanium. Germanium has four valence electrons whereas arsenic has five valence electrons. So only four electrons of arsenic are utilized to bond with germanium. The fifth electron enters into an upper energy band and can readily pass into the outer band of germanium acquiring a negative charge. This type is referred to as the n-type semi conductor because germanium acquires a negative charge.

If there are only small traces of the impurity present continued application of heat uses up all the electrons available from the impurity energy levels between the Brillouin zones and at higher temperatures conductivity may diminish owing to the increased vibration of the lattice.

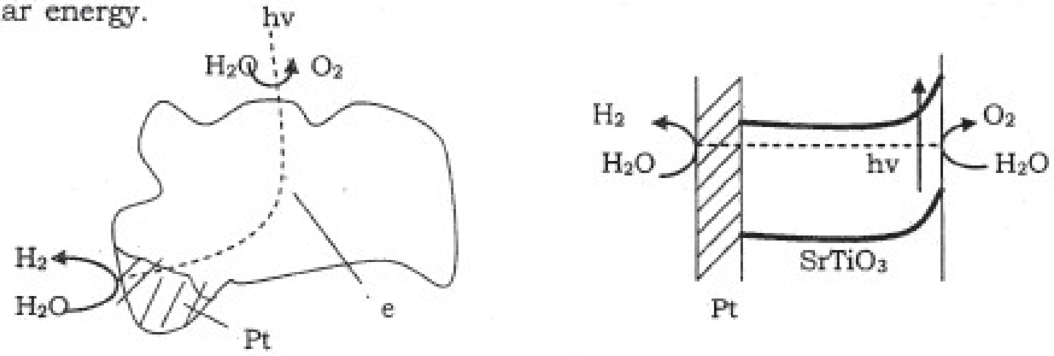
ii) p-type semiconductors

When gallium is incorporated into germanium, the absorption of heat energy causes the extra germanium electron to enter an upper energy band, which can readily pass into the energy band of gallium (gallium has 3 valence electrons whereas germanium has 4 valence electrons). Germanium atoms thus acquire a positive charge and they are called p – type semiconductors.

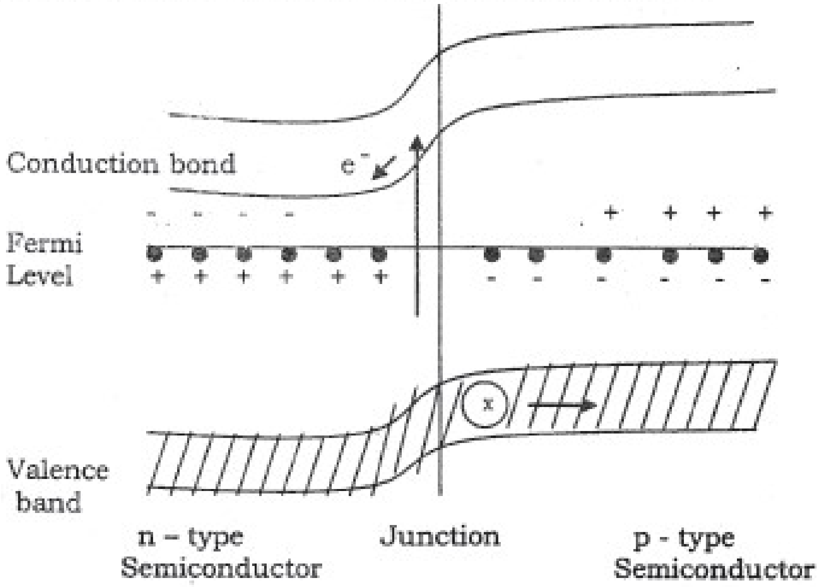
In substances of this type the application of heat causes some of the electrons from the first zone to be transferred to some of the energy levels of the impurity. The first zone remains only partially filled, and so the crystal shows conducting properties. A greater increase of temperature may result in a diminution of conductivity as with n – type.

XII. Photovoltaic – Solar Energy Conversion

Let us suppose that a p-n junction is irradiated with light. If the photon energy equals or exceeds the band gap, electron – hole pairs will be formed in the irradiated region, as indicated. Because of the band bending, the electrons will migrate toward the bulk of the n-type semiconductor and the holes will migrate toward the bulk of the p – type semiconductor. Thus the n-type region will achieve a negative potential relative to the p – type region are electrically connected to an external circuit, a current will flow as long as the junction is irradiated. Obviously such a crystal can be used as a kind of band whose energy is derived from light. One of the aims of solid–state chemists is to prepare efficient cells of this type economically enough to permit their use in harnessing solar energy.



Representation of $SrTiO_3$ – Pt particle and the corresponding energy level diagram. When an aqueous suspension of such particles is irradiated with ultra violet light, water is electrolyzed into hydrogen and oxygen.



Solar Energy Conversion and Storage

The photosynthetic membrane in green plant resembles a semiconductor electrode since it can separate the positive and negative charge carriers. This concept is supported by direct measurement on intact chloroplasts, which demonstrate the Hall effect on illumination in presence of a magnetic field. Two different charge carriers are produced, one positive and the other negative, with different lifetimes and different mobilities. The capacity of such membranes to convert solar energy into chemical energy in an endoenergetic reaction ($\Delta G>0$) in photosynthetic cycle has stimulated interest in development of such model systems for storage and utilization of solar energy by direct conversion of light quanta. In photosynthesis solar energy is stored in two products, carbohydrate and oxygen. The energy is released when carbohydrates burn in air.

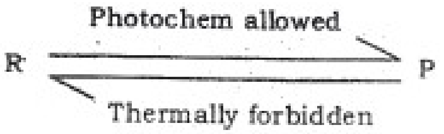
Solar energy quantum conversion devices are based on two objectives.

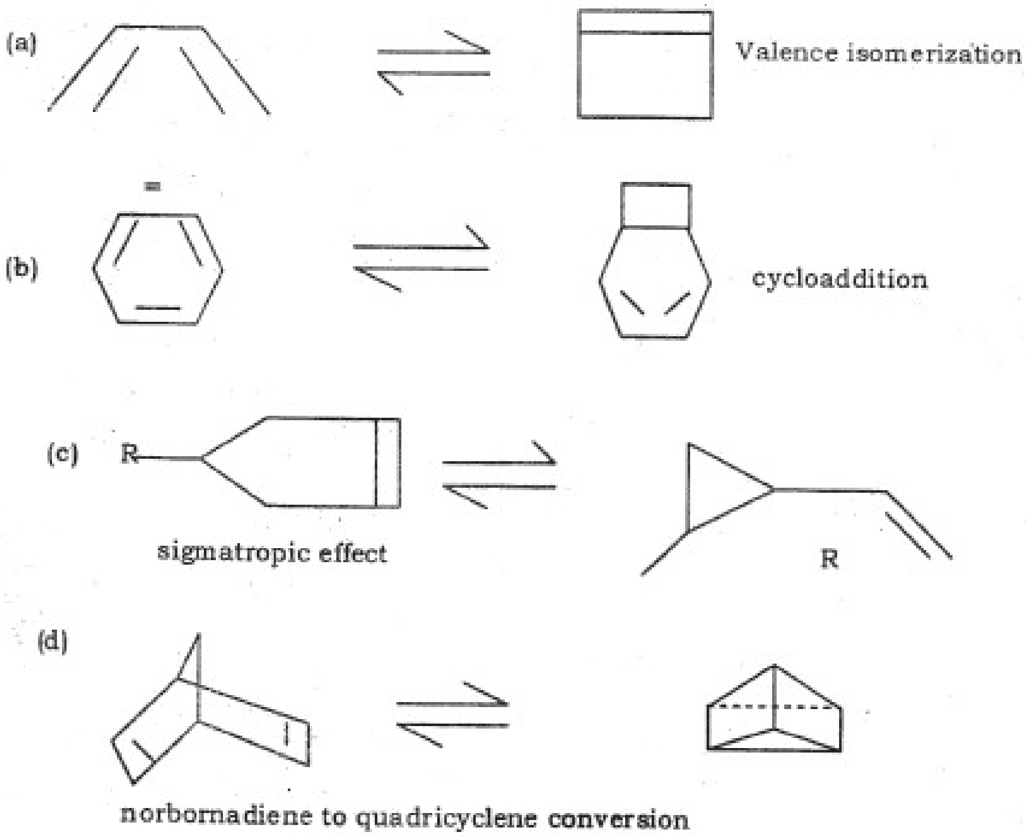
1. Conversion of light energy into thermal energy by suitable energy storing i.e endergonic photochemical reactions.
2. Conversion of light energy into electrical energy by suitable photo electrochemical devices.

The energy storing photoreactions occur with positive free energy change ($+\Delta G$) and are hence, thermodynamically unstable.

If the reverse back reaction is prevented or is forbidden by other considerations, the energy remains stored in the photoproducts. Some simple photo rearrangement reactions, which are governed by Woodward-Hoffman rules, have been found useful. These rules provide the stereo chemical course of photochemical rearrangement based on symmetry properties of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecule. A reaction, which is photo chemically allowed may be thermally forbidden. From the principle of microscopic reversibility, the same will be true for the reverse reaction also. Thermally forbidden back reaction will produce stable photoproducts. Such electro cyclic rearrangements are given.

A reaction, which can store about 1092 J per gram of material and has shown some promise in valence isomerization of norbornadiene (NBD) to quadricyclene. The disadvantage is that it does not absorb in the visible region and therefore the sunlight efficiency is poor. By attachment of chromophoric groups or by use of suitable sensitizers it might be possible to shift the absorption region towards the visible for better utilization of solar energy.





Endergonic and reversible electro cyclic reactions obeying Woodward Hoffman rule

XIII. Super Conductivity

Ordinary metals at ordinary temperature such as copper at room temperature have a small but nevertheless significant resistance to the flow of the electricity. Such resistance means that a percentage of the electrical energy is converted into heat as the electricity flows in wires. In long distance power transmissions this leads to waste of energy. Electrical resistance is also a factor that has limited the capacity of computer chips.

When a material is in the state in which it offers no resistance to electricity, it is called super conductor, and the phenomenon is super conductivity. Prior to 1987, only few metals and metal alloys could be put into such a state and only when their temperatures are lowered to just a few degrees above absolute zero. This meant immersion of the material in a bath of liquid helium, which boils at 4.2K. In order to keep the material in a super conducting state refrigeration technology must be used, which is too expensive and too cumber some to permit any practical applications at normal temperatures.

C = 1/R (or) R = 1/C where R = Resistance C = Conductance

As resistance increases conductance decreases.

Property of some pure metals and metallic alloys at very low temperatures of having negligible resistance in the flow of electric current is called super conductivity. Each material has its own critical temperature (Tc) above which it is a normal conductor. When a current is established, it persists almost indefinitely. Magnetic fields can destroy the super conductivity, their strength depending on how far below the critical temperature the material is maintained. Generally Tc has been < 20 K, but in 1986 – 87 a class of materials with pervoskite structures has been discovered which have Tc _ 90 K.

XIV. Cooper Electrons

A superconductor is a substance that conducts electricity without resistance. Until 1987, the only known superconductors (which included metals, some oxides, and some halides) needed to be cooled to below about 20 K before they became super conducting. However, in 1987 the first 'high temperature' superconductors were discovered; then super conduction is well established at 120 K and spasmodic reports of even higher temperatures have appeared. We will not consider these high-temperature materials at this stage but sketch ideas behind the mechanism of low-temperature super conduction.

The central concept of low-temperature super conduction is the existence of Cooper pair, a pair of electrons that exists on account of their interaction indirectly through vibrational displacements of the atoms in the lattice. Thus, if one electron is in a particular region of a solid, the nuclei there move toward it to give a distorted local structure. Since that local distortion is rich in positive charge, it is favourable for a second electron to join the first. Hence, there is a virtual attraction between the two electrons, and they move together as a pair. The local distortion can be easily disrupted by thermal motion of the ions, so the virtual attraction occurs only at very low temperature.

A cooper pair undergoes less scattering than an individual electron as it travels through the solid, since the distortion caused by one electron can attract back the other electron should it be scattered out of its path in a collision. This has been likened to the difference between the motion of a herd of cattle, with members of the herd that are deflected from their path.

XV. Meissenner Effect and Levitation

A super conducting material cooled below its critical temperature in the presence of an applied magnetic field expels all magnetic flux from its interior. If the field is applied after the substance has been cooled below its critical temperature the magnetic flux is excluded from the super conductor. These are the Meissenner effects and show that the super conductor is perfectly diamagnetic.

If a small permanent magnet is placed on a surface, which is then made superconducting by lowering its temperature below its critical temperature then the magnet will rise and float above the surface. This is called levitation. The super conductor as a perfect diamagnetic excludes the flux associated with the magnet and so provides a large enough repulsive force to balance the weight of the magnet.

Questions

1. Discuss Bragg method for the study of structure of crystals.
2. Comment briefly on the defect structures in crystals?
3. What are Miller indices?
4. Discuss insulators, conductors and semi- conductors on the basis of the band theory.
5. Describe the features observable in the powder pattern of X – rays for the crystals of NaCl and CsCl.
6. Write notes on the structures of zinc blende, rutile and fluorite.
7. What are the symmetry elements present in a cube?
8. Define symmetry elements and their operations.
9. What is the difference between free electron theory and band theory?
10. What are Super conductors?
11. Explain how solar energy can be converted into electrical energy? Mention some of its applications.
12. Write notes on Meisenner effect and Levitation.

UNIT – III

NUCLEAR CHMISTRY

SYLLABUS

Radioactivity and modes of decay – a, β and γ – Different types of reactions with natural and artificial particles – Q value, cross section, spallation, fission and fusion – characteristics of fission reaction product distribution and for fission liquid drop model, fissile and fertile isotopes nuclear fusion and stellar energy – Transmutation of elements and chemical effects of transmutation – Isotopes and their applications – Radioactive analysis and counting techniques Geiger – Muller, Jonisation, proportional, scintillation, counters.

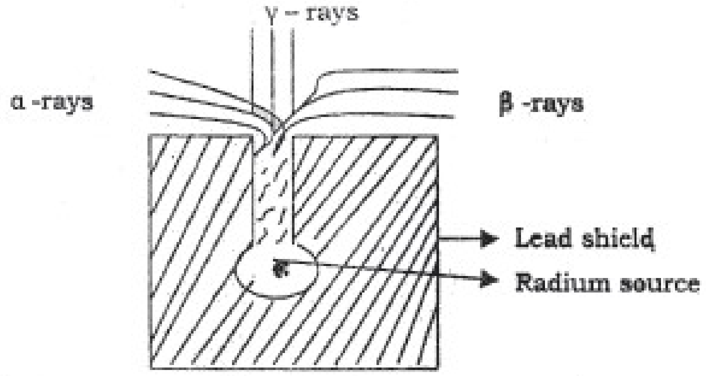
I. Introduction

Henry Becquerel accidentally discovered the phenomenon of radioactivity when he was trying to find a relationship between X – ray and fluorescence. A fluorescent substance potassium uranyl sulphate wrapped in a photographic plate was exposed to sunlight and then the photographic plate was developed. The portion under the salt was found to be blackened. When thin sheets of metals such as aluminum and copper were introduced between the salt and the plate the rays were not cut down. This established a similarity of the ray to X – ray. But it was later found that the material emanated ray even in cloudy days and affected the photographic plate. Since fluorescence will not occur without sunlight, but these radiations. Later 'Radioactivity' was coined by m.m.e. Curie, who showed that it is not uranium atom that exhibits radiations. It was found out by here that this property was independent of temperature and they could penetrate opaque mateials in ordinary light. They discharged gold leaf electroscope.

Curie noted that two of these minerals, namely, pitch blende (uranium oxide) and chalconite (copper uranyl phosphate) are much more active than uranium itself and on analysis it was found that more active species besides uranium were present in the minerals. The one with 400 times activity that U was called polonium (in honour of her mother land, Poland). The other element in pitchblende was chemically different from Po and 900 times more active than U and it was named 'Radium' (RA) Another radioactive element Actinium (Ac) was discovered in pitchblende. At present 42 radioactive species of high atomic weights are known to exist in nature. A few of the lighter elements like K, Rb, Sm, Lu, Re possess feeble radioactive property in their normal state.

1. Radioactive Rays

The radioactive substance usually gives rise to 3 types of radiations known as alpha (a), beta (β) and gamma (y) rays. Becquerel, Rutherford and Willard studied their characteristic properties.



A radium source was kept inside a small hole in a lead block and subjected to the action of magnetic field directed to the place of the paper. The alpha particles were slightly deflected to the left, the beta particles were sharply deviated to the right and gamma rays went straight through.

The a – Particles are + vely charged particles having charge + 2 units and mass 4 units and so they are identical to He nuclei. This was proved by the fact that a strong a – source in a sealed glass tube produced helium gas, which was identified by the characteristic atomic spectrum. They were ejected with velocity ranging 1.5 – 2.00 x 10^9 cm/ sec. They have great momentum due to their large mass, but they can be stopped by aluminum foil less than o.1mm thickness. The absorption values of a metal foil depends no only on its thickness but also upon the atomic weight of the foil. The higher the atomic weight of the foil . The higher the atomic weight, greater is the absorption.

The a – rays ionize molecules present in air. The range of particles through a gas depends upon the nature of the gas and inversely proportional to its pressure and directly proportional to absolute temperature and pass through a few cm of air, whereas a – particles can penetrate 4 times further in H_2 than in O_2. The elements with rapid decay periods emit a – particles with greater ranges. For eg. At 15°C and 1 atmospheric pressure.

Th232 ($t_{1/2}$ = 1.39 x 10^{10} yrs) = 2.8 cm

And P_o 2/12 ($T_{1/2}$ = 3 x 10^{-7} sec) = 8.6 cm

The β - rays are – vely charged and their composition is that of electrons. The mass is 0.00055 amu and they travel at the velocity of light. They produce less number of ions on passing through the molecules of air. Neutrons decompose to produce a proton and electron (β- particle) and neutrino.

$${}^{1}_{0}n \rightarrow {}^{1}_{1}H + \beta + \gamma^{-}$$

The mechanism of beta decay is based on neutron – proton transformation with simultaneous emission of neutrino. These β - ray are also having ionizing power.

The y – rays are short wave radiation undeflected by magnetic field. They are identical to X – ray except that their wavelength is much shorter. These rays have no mass and they are not considered as particles. Instead they may be described as form of electromagnetic radiations. They have greater penetrating power due to their short wave length and greater energy. It may penetrate 25cm iron, and up to 8cm lead. Thus lead is about 8 times effective than A1 and 4 times better than Cu.

Theory of Radioactive Decay

Rutherford and Soddy advanced a theory known as radioactive disintegration theory. According to the theory, atoms of radio elements undergo spontaneous disintegration with the emission of a – and β-particles and to formation of atoms of new elements. Physical and Chemical properties of the new element are different from those of the original parent element. The disintegration is not simultaneous but is a series of successive ejections with measurable velocities in each case. The type of elements formed depends upon the nature of radioactive disintegration.

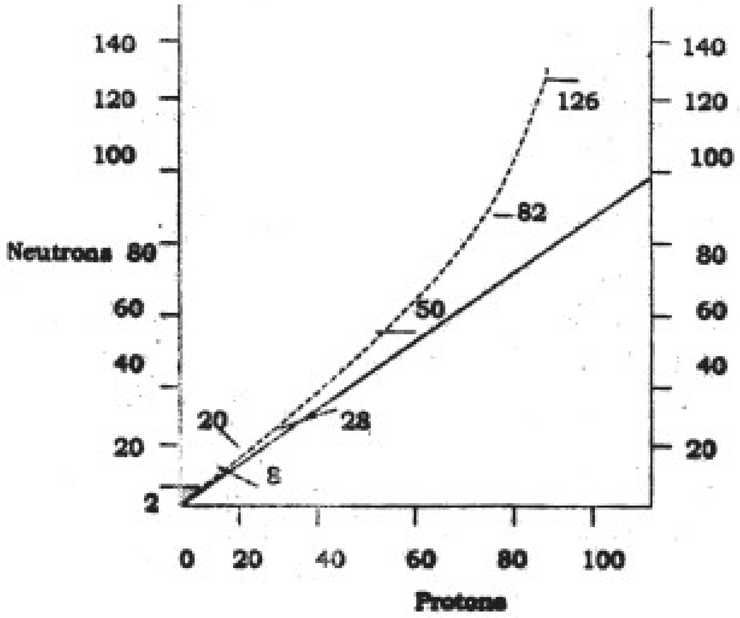
The nuclear stability and N/P ratio

Except in the case of ordinary hydrogen ${}^{1}_{1}H$ all other elements (nuclides) contain both neutrons and protons. A look at the stable nuclides shows that the ratio N/P in them is ≥1. The radio is ~ 1 in all the light stable nuclides up to

20^{Ca40} and thereafter the ratio is > for heavy nuclei.

	${}^{2}H$	${}^{20}Ne$	${}^{40}Ca$	Zn	${}^{90}Zr$	${}^{120}Sn$	${}^{150}Nd$	${}^{202}Hg$
P	1	10	20	30	40	50	60	80
N	1	10	20	35	50	70	90	122
N/P	1.00	1.00	1.00	1.13	1.25	1.40	1.50	1.53

Stable heavy nuclei are ${}^{208}_{82}Pb$ and ${}^{209}_{83}Bi$ and others with higher P or N decay by a or $\beta^{\pm}$ or by fission process. The nuclei with N/P ratio > 1.6 are unstable and undergo spontaneous decay at a finite rate until a stable isotope (stable N/P ratio) is got.



Magic numbers

With the success of Bohr's concept of compound nucleus and of the liquid drop model to which it was related the reality of nuclear stability was shown by Mrs. Meyer that nucleus with 2, 8, 20, 50, 82 and 126 which apparently represents closed shell of the nucleus are stable. These numbers are called magic numbers. Larges stable isotopes are containing 20 and 50 protons or 20,50 and 82 neutrons. For eg. Sn with an atomic number 50 has 10 isotopes. This element is unique in the aspect that it has three stable isotopes of odd mass numbers 115, 117 and 119. The more abundant nuclides in the universe viz, ${}^{16}_{8}O$, ${}^{40}_{20}Ca$,

${}^{88}_{38}Sr$, ${}^{89}_{30}Y$, ${}^{90}_{40}Zr$, ${}^{118}_{50}Sn$, ${}^{138}_{56}Ba$, ${}^{139}_{57}La$, ${}^{140}_{58}Ce$ and ${}^{208}_{82}Pb$

These nuclei Contain magic numbers of neutrons or protons.

Radioactive changes could not be affected by high or low temperature. They are spontaneous. Catalysts do not affect them. These changes involve the nucleus of the atom. The energies are in the range of MEV whereas in ordinary chemical changes, they are markedly influenced by changes in temperature and pressure. Catalysts enhance valence electrons in their reactions. The energies are only few electron volts (eV)

2. Modes of Decay

There is a direct relationship between loss of particles and the type of element being formed.

$$ {}_{92}U^{234} \xrightarrow{\alpha-\text{emission}} {}_{90}Th^{230} \xrightarrow{\alpha-\text{emission}} {}_{88}Ra^{226} $$

By α - emission 4 units of mass and 2 units of charge are taken away from the original parent. The nucleus when emits β- particle, the mass of nucleus is not affected, but the +ve unit in nucleus is increased by 1 unit.

$$ {}_{84}Po^{215} \xrightarrow[\text{emission}]{\alpha} {}_{82}Pb^{211} \xrightarrow[\text{emission}]{\beta} {}_{83}Bi^{211} \xrightarrow[\text{emission}]{\beta} {}_{84}Po^{217} $$

During β – particle emission ${}^{1}_{0}n \rightarrow {}_{1}H^{1} + {}_{-1}e^{0}$ (i.e.) a proton is produced from a neutron along with a neutrino as already seen. Since the proton is left in the nucleus, mass number remains the same, where as atomic number increases by one unit during β – particel emission.

When an element emits y – rays there is no change in mass number and the atomic number. But there is change only in the energy of the parent element and thus the daughter element will be different in nuclear energy.

$$ {}_{12}Mg^{27} \xrightarrow{\beta} {}_{13}Al^{27} \xrightarrow{\gamma} {}_{13}Al^{27} $$

The above said facts are illustrated by Pajan – Soddy's Group displacement law "When an α - particle is emitted in a radioactive change, the daughter element occupies a position two places left to its parent element in the Periodic Table, whereas the emission of β - particle result in a shift of one place to the right of the Periodic Table".

Rate of Decay (Disintegration)

The law of radioactive decay is stated that the quantity of radioelement, which disappears in unit time, is directly proportional to the amount present. If the number of atoms that are present at a given time is denoted as N, then the change in number of atoms with time $-\frac{dN}{dt} = \lambda N$ where λ is a proportionality constant which Rutherford and Soddy called radioactive constant, although decay constant is a better term.

$$-\frac{dN}{dt} = \lambda N \quad \ldots .(1)$$

The equation (1) may be changed as

$$\frac{dN}{N} = -\lambda dt \quad \ldots .(2)$$

This may be integrated to give

$$\ln N + C = -\lambda t \quad \ldots .\ (3)$$

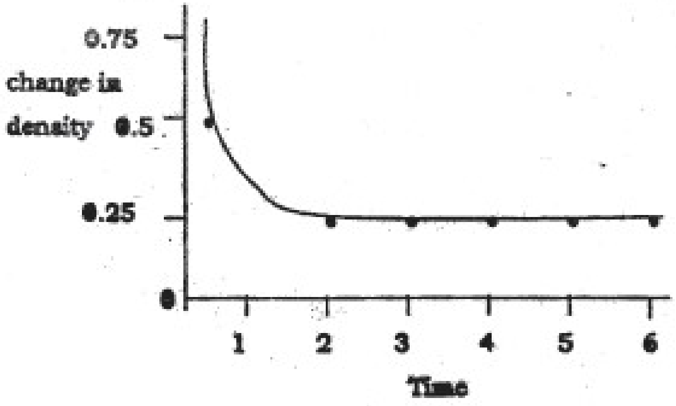
The integration constant C may be evaluated because when t = 0, N has an initial value of No. Therefore upon substituting for t and N in equation (3) the result is $\ln No + C = 0 \quad \ldots . \quad (4)$

$$\therefore \ln N - \ln No = \lambda t \quad \ldots .\ (5)$$

When equation (5) is put into equivalent exponential form

$$\frac{N}{N_0} = {}_e^{-\lambda t} \text{ (or) } N = {}_{Noe}^{-\lambda t} \qquad (6)$$

Radioactive decay is a first order reaction, which diminishes in an exponential manner.



$$Nt = Noe^{-\lambda t} \text{ (or) } \frac{N_t}{N_o} = e^{-\lambda t}$$

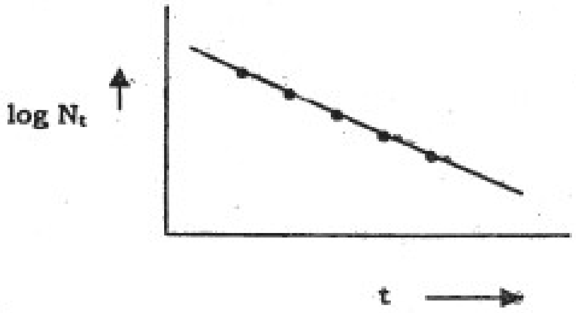
$$\ln \frac{N_t}{N_o} = -\lambda t \text{ (or) } \ln \frac{N_o}{N_t} = \lambda t$$

To get log to the base 10, multiply with 2.303

$$\therefore\ 2.303 \log \frac{N_o}{N_t} = \lambda t$$

$$\therefore\ \frac{2.303}{t} \log \frac{N_o}{N_t} = \lambda$$

If log N_t is plotted against t then the points should lie on a straight line $-\frac{\lambda}{2.303}$ is the slope and hence it can be used to obtain the value of λ.



Mean Life of a radioelement is determined, because it is not possible to predict which atom of a radioactive substance will disintegrate at any instant. The length of time it can exist may vary from 0 to ∞.

$$\text{Mean life of a radio element} = \frac{\text{Sum of lives of all atoms}}{\text{Total Number of atoms}}$$

Value of mean life

At any instant t, the atoms present may be given as $N_t = Noe^{-\lambda t}$

Let dN be the number of atoms disintegrating between time t and (t + εt) These dN atoms have life between t and (t + εt) is very small, each of these atoms have a life of t.

Total life of dN atoms = t dN

The possible life of any of the total No radioactive atoms varies from 0 to ∞.

∴ Total life for all No atoms $= \int_0^\infty tdN$

$$\text{Now mean life} \quad \tau = \frac{\text{Total lifetime}}{\text{Total Number of atoms}}$$

$$= \int_0^\infty \frac{tdN}{N_o}$$

Differentiating with respect to t

$$\therefore \frac{dN}{dt} = -\lambda N_{O\,e}{}^{-\lambda t}dt$$

(or) $dN = \lambda_{Noe}{}^{-\lambda t}dt$ **leaving the –ve sign, which merely indicates the decrease in number atoms with time.**

$$\text{Hence} \quad \tau = \int_0^\infty \frac{t\,\lambda\,N_o e^{-\lambda t}dt}{N_o}$$

$$= \lambda \int_0^\infty te^{-\lambda t}dt$$

Integrating by parts leads to $T = 1/\lambda$. Thus the mean life is equal to the reciprocal the decay constant of the radioelement. The average lives of natural radio elements vary from 10^{-16} sec to 10^{10} yrs.

Half-life period

Rutherford introduced the concept of half-life period and it is the time required for the radioactivity of a given amount of the element to decay to decay to half its initial value and it is denoted by T or $t_{1/2}$. After the lapse of time t, the number of radioactive atoms N_t will be half the initial number of atoms N_o.

$$\text{So,} \quad \frac{Nt}{No} = \frac{1}{2}$$

$\frac{Nt}{No} = \lambda t$, Multiply **both sides with –ve sign, then**

$ln\frac{No}{Nt} = -\lambda t$, **convert it to log to the base 10,**

$$\text{then } 2.303 \log(\frac{N_o}{N_t}) = \lambda t$$

$$\lambda = \frac{2.303 \log 2}{T} = \frac{0.693}{T} \quad \text{(or)} \quad T = \frac{0.693}{\lambda}$$

Units of Radioactivity

The activity of one gram of ^{226} Ra is considered the unit of radioactivity and is called a curie (C_i).

Since 1 g of Ra ^{226} has $6.023 \times 10^{23}/226 = 2.27 \times 10^{23}$ atoms and

$\lambda = 1.38 \times 10^{-11}$ disintegrations/sec, the disintegration rate of 1g of Ra^{226} (i.e.) 1 curie of activity is given by

$1\ Ci = 1.38 \times 10^{-11} \times 2.7 \times 10^{21} = 3.7 \times 10^{10}$ dps (disintegration/sec)

A radioactive preparation of any element, which decays at this rate is said to have an activity one curie. Fractions of the unit as the mCi, μCi and multiples of KCi and MCi are also used when necessary (G = Giga, M = Mega, μ = micro, m = milli).

The SI unit of radioactivity recently proposed is the becquerel (BΣ), which is defined as the activity due to one disintegration per second (1dps).

Hence $1C_i = 3.7 \times 10^{10}\ B_{\Sigma} = 37\ G\ B_{\Sigma}$

A Rutherford $1\ Rd = 10^{6}$ dps $= 10^{6} = B_{\Sigma}$ had also been suggested as a unit of radioactivity but the same has not been in use. The strength in curies is the absolute number of atoms of the element decaying per second (dps).

II. Reactions with Natural and Artificial Particles

The overall energy liberated are taken up in a nuclear process is called nuclear reaction energy represented by Q. the value of Q may be + ve or – ve depending on the nature of the process. According to Einstein's theory of equivalence of mass and energy, the nuclear reaction energy must be exactly balanced by the changes in mass associated with the reaction.

If Q is + ve, then the process is accompanied by liberation of energy and it is known as Exoergic reaction. There must be a decrease of mass; the total mass of products will be lesser than that of interacting nuclei by amount equivalence to this energy.

On the other hand, a – ve value of Q means that energy is taken up and the reaction is known as Endoergic reaction. There is a gain of mass in the nuclear reaction; such a result implies that the total mass of the products exceeds that of the original reactants.

Calculate the mas of ^{17}O in the reaction $^{14}N + ^{4}He \rightarrow ^{1}H + ^{17}O + Q$ given that

^{14}N = 14.00307, ^{4}He=4.00260, ^{1}H=1.00782 and Q = 1.16 MeV we get Mx 931 = -1.16.

∴ m = 0.00124 amu.

Since O is – ve, the mass of products is grater than the interacting particles.

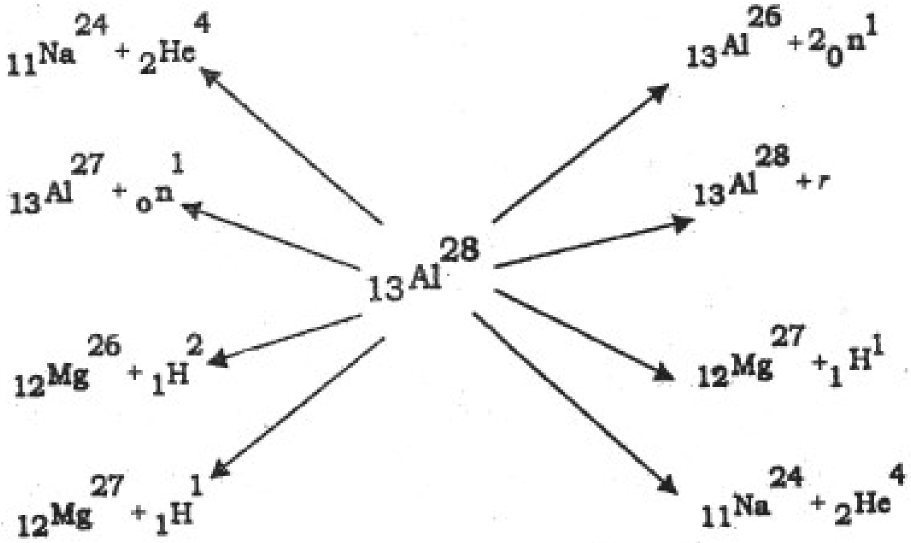
$\therefore 14_N = 14.00307\ ^{1}H = 1.00782$

$^{4}He = \frac{4.00260}{18.00567}\ \underset{(amu)}{Q} = \frac{-0.00124}{1.00658}$

∴ Atomic Weight of ^{17}O = 18.00567 - 1.00658 = 16.9991 amu

Compound Nucleus

In 1936 Bohr developed a theory that projectiles with kinetic energy 40 MeV enters the nucleus to form metastable structure termed compound nucleus which has a half-life 10^{-14} to 10^{-12} sec. during this interval the additional energy is distributed throughout the nucleus causing an excited state so that one particular nuclear or combination of nucleons of nucleons acquiring sufficient energy escape out.



Here the compound nucleus is $_{13}Al^{28}$

III. Types of Nuclear reactions

Nuclear reactions are of the following types, viz. 1. Stripping reaction and pickup reaction, 2. Fission reaction, 3. Spallation and Fragmentation, 4. Scattering, 5. Fusion and 6. Transmutation.

1. Stripping reaction

It is one in which the target nucleus captures one or two (or three) nucleons from the incident particles without the formation of a compound as an intermediate. The remaining portion, here sometimes energy may be released, as gamma rays, otherwise neutrons, protons or – particles may be emitted.

$$_{37}Rb^{85} + _{0}n^{1} \rightarrow _{37}Rb^{86} + r\ (n,r)$$

$$_{6}C^{12} + _{1}H^{1} \rightarrow _{7}N^{13} + r\ (p,r)$$

$$_{7}N^{14} + _{0}n^{1} \rightarrow _{6}C^{14} + _{1}H^{1}\ (n,p)$$

Projectile picks up a nucleon from the target as in $^{9}Be(d,{}^{3}He)^{8}$ Li is called pick up reaction.

A special reaction **$^{14}N(^{14}N,{}^{13}N)^{15}$ N the projectile**, ejectile, target and the residue are all **isotopes of nitrogen.**

$$_{5}B^{11} + _{1}H^{1} \rightarrow _{6}C^{11} + _{0}n^{1}\ (p,n)$$

$$_{13}Al^{27} + _{1}H^{1} \rightarrow _{12}Mg^{24} + _{2}He^{4}\ (p,\alpha)$$

$$_{15}P^{31} + _{1}H^{2} \rightarrow _{15}P^{32} + _{1}H^{1}\ (d,p)$$

2. Fission reaction

A fission reaction **is one in which a heavy nucleus is broken into two or** more medium heavy fragments accompanied by neutron emission. Fission occurs in nuclei with masses over 200 when bombarded with a sufficient energy projectile, viz. neutron.

$$_{92}u^{235} + _{0}n^{1} \rightarrow _{56}Ba^{141} + _{36}Kr^{92} + 2\text{-}3\ {}^{1}n_{0} + \underset{meV}{200}$$

3. Spallation reaction

High – speed projectiles with energies approximating 400 MeV may chip fragments from a heavy nucleus, many neutrons and protons are ejected leaving a smaller nucleus, which can be identified. Usually the nucleus so produced has an atomic number less by 10 and 20 units of the original nuclear reactions to the extent that in the ordinary type of reactions the nucleus is rarely reduced in atomic number by more than 2. Spallation differs from fission in that the reaction is not self – sustaining. Moreover the change in mass for a spallation reaction is not so great as that in fission. A hypothetical spallation reaction is

$${}_{29}Cu^{63} + {}_{2}He^{4}(400MeV) \rightarrow {}_{17}Cl^{37} + {}_{14}{}^{1}H + 16\ {}_{0}n^{1}$$

4. Scattering

Here the projectile and the target nucleus remain unaltered in nature at the end of interaction. There are elastic and inelastic scatterings. Where there is exchange of kinetic energy between the projectile and target nucleus elastic scattering occurs. Both kinetic energy and momentum are conserved. In inelastic scattering the resultant nucleus is unchanged in composition (i.e) it has the same number of n, p as before the interaction, but it is in an exited state of higher internal energy where part of K.E. is converted into potential Energy.

5. Fusion

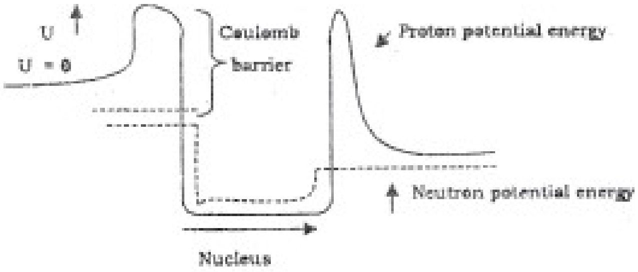
Isotopes of very light elements may react with one another to form heavier and more stable nuclei. The potential barriers for reactions of this type are extremely high. Only at very high temperature of the order of million degrees, these barriers may be overcome. It is believed that energies of stars may be derived form the reactions of this type. A typical fusion reaction takes place between heavy isotopes of hydrogen, deuterium and tritium in which helium nucleus is produced.

$${}_{1}H^{2} + {}_{1}H^{3} \rightarrow {}_{2}He^{4} + {}_{0}n^{1} + {}_{17.6}MeV$$

- A nuclear fusion reaction is the source of the tremendous energy developed in the detonation of the so – called hydrogen bomb.

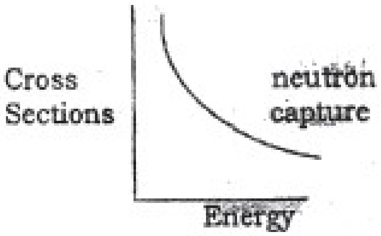
Coulomb Barrier

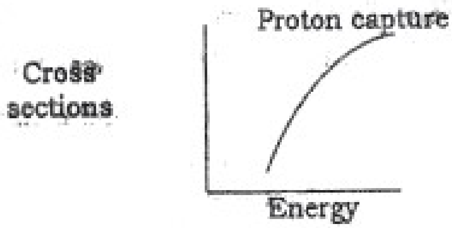
Neutrons which have no charge are not facing any electrostatic potential barrier or Coulomb barrier and are more readily absorbed and emitted by than are protons, deutrons and α – particles.



The figure is a plot of potential energies of proton and neutron near nucleus. The Coulomb barrier is about 3 MeV in height for C nucleus and 13 MeV for Ag nuclei and 20 MeV for pb nuclei.

Evidently a neutron of any energy can enter a nucleus by "falling into" its potential well just as a rolling ball falls into a hole in a ground while an approaching proton is faced with a potential hill. Classically, the proton would have to possess at least as much energy as the height of the barrier in order to enter the nucleus. Quantum mechanically, of course, the proton can get in with less than this amount of energy, but the probability of its doing so is small. Hence the height of Coulomb barrier represents effective threshold energy for nuclear reactions initiated by such particles as protons, deuterons and á – particles, while no such threshold is present for incoming neutrons.





The above figure shows how the cross sections for comparable neutron and proton – induced nuclear reactions vary with energy. The neutron cross section decreases with increasing energy because the likelihood that that a neutron be captured depends upon how much time it spends near a particular nucleus, which is inversely proportional to its speed. The proton cross-section increases with increasing energy because of the presence of the Coulomb barrier.

The Coulomb barrier also acts to impede the emission of charged particle from a nucleus. A suitably excited nucleus is therefore usually more likely to eject a neutron than proton and reaction of the type (d,n) for example, are more common than those of the type (d,p)

6. Transmutations

Transmutations by Protons

Projectiles with energy not less than 50 MeV can cause transmutations through the formation of compound nucleus.

$${}_{13}Al^{27} + {}_{1}H^{1} \rightarrow {}_{14}Si^{28} + \gamma$$

It is written as ${}^{27}Al(p,\gamma){}^{28}Si$

Similarly ${}^{19}F(p,\gamma){}^{20}Ne, {}^{7}Li(P,\gamma){}^{8}Be, {}^{14}N(p,\gamma)O^{15}, {}^{50}Cr(p,\gamma){}^{51}Mn$

reactions occur. If proton has sufficient energy to penetrate the energy barrier and form a compound nucleus and transmutation occur.

$${}_{11}Na^{23} + {}_{1}H^{1} \rightarrow {}_{12}Mg^{23} + {}_{0}n^{1}$$

Similarly ${}^{63}Cu(p,pn){}^{62}Cu$, ${}^{63}Cu(p,2n){}^{62}zn$, and ${}^{88}Sr(p,2n){}^{86}Y$

Transmutation by deuterons

The deuteron is an effective projectile causing nuclear transmutations because a small energy of 2 MeV is sufficient to cause its rupture into neutrons and protons. In these reactions (d,p) type reactions take place. Oppenheimer and Phillips proposed a mechanism for this transmutation. The deuteron behaves as a loose combination of neutron and proton. When the deuteron approaches a nucleus, the electrostatic repulsions of positive charges tend to repel the proton away, but the neutron is not affected. If the energy of entering deuteron exceeds 2 MeV, the proton portion will break off and be repelled but the neutron will enter the target nucleus and captured by it. The increased energy in the nucleus is emitted as γ ray and neutron is retained. Sometimes it leads to (d, pn) reaction by emission of neutrons along with the protons

$${}_{3}^{7}Li + {}_{1}^{2}D \rightarrow {}_{3}^{8}Li + {}_{1}^{1}H$$

$${}_{48}^{114}Cd + {}_{1}^{2}D \rightarrow {}_{48}^{115}Cd + {}_{1}^{1}H$$

A special reaction is

$${}_{1}^{2}D + {}_{1}^{2}D \rightarrow {}_{1}^{3}T + {}_{1}^{1}H$$
$${}_{1}^{2}D + {}_{1}^{2}D \rightarrow {}_{2}^{3}He + {}_{0}^{1}n$$

Other examples are, ${}^{3}T(d,n){}^{4}He$, and ${}^{6}Li(d,n){}^{7}Be$.

Fragmentation reactions

When a nucleus on heavy excitation around 0.5 GeV splits into a light and a heavy fragment having about the same N/P ratio as in the parent, the prooess is referred to as fragmentation or star process. The excitation energy not being equally distributed between the light and the heavy fragments, the former decays by β^{-} and later by evaporation.

Transmutation by particles of Mass 3

The particles with mass 3 are ${}_{1}^{3}T$ and ${}_{2}^{3}He$. When ${}_{1}T^{3}$ is used as a projectile with energy 10 MeV (t,p) type reactions occur.

$${}_{27}^{59}Co + {}_{1}^{3}T \rightarrow {}_{27}^{61}Co + {}_{1}^{1}H$$

Oppenherimer – Phillips mechanism is operative in the (t,d) reactions such as ${}^{6}Li(t,d)\,{}^{7}Li$ and ${}^{63}Cu(t,d)\,{}^{64}Cu$ at moderate triton energy.

There is evidence for ${}^{28}si^{(3He,p)}\ 30_{p}$ reaction.

A process of the same type is ${}^{2}D({}^{3}He,p)^{4}$

Using ${}^{3}He$ as projectile

${}^{14}N({}^{3}He,n){}^{16}F$,

${}^{12}C({}^{3}He,d){}^{13}N$, ${}^{13}C({}^{3}He,t){}^{13}N$,

${}^{14}N({}^{3}He,\alpha){}^{13}N$, and

${}^{3}He({}^{3}He,2p)^{4}\ He$, had been studied.

$${}_{7}^{14}N\ {}_{2}^{3}He \rightarrow {}_{9}^{16}F + {}_{0}^{1}n$$

Transmutation by neutrons

The neutron being electrically neutral is not subjected to electrostatic repulsion as are charged particle, when it approaches and atomic nucleus. The first transmutations with neutron were reported in 1932. the ${}^{1}_{0}n$ is captured by the nucleus and gamma rays are emitted along with the product. This is called radioactive capture.

$${}_{1}^{1}H + {}_{0}^{1}H \rightarrow {}_{1}^{2}H + \gamma$$

The (n,γ) reaction product is found to be radioactive

$${}_{45}^{103}Rh + {}_{0}^{1}n \rightarrow {}_{45}^{104}Rh + \gamma$$

Processes of (n,p), (n,d), (n,t) and (n,α) are also taking place.

$${}_{7}^{14}N + {}_{0}n^{1} \rightarrow {}_{6}C^{14} + {}_{1}^{1}H + Q(n,p)$$

The radioactive C^{14} decays by the process

$${}_{6}^{14}C \rightarrow {}_{7}^{14}N + {}_{-1}e^{0} + E_{max}$$

$${}_{3}Li^{6} + {}_{0}n^{1} \rightarrow {}_{1}T^{3} + {}_{2}He^{4}(n,\alpha)$$

$${}_{9}F^{19} + {}_{0}n^{1} \rightarrow {}_{7}N^{16} + {}_{2}He^{4}(n,\alpha) \text{ followed by}$$

$${}_{7}^{16}N \rightarrow {}_{-1}e^{0} + {}_{8}O^{16}$$

with neutrons of 10 MeV energy or more processes of (n,2n) process decay by positron emission.

$${}_{6}C^{12} + {}_{0}n^{1} \rightarrow {}_{6}C^{11} + 2{}_{0}n^{1}$$

$${}_{6}C^{11} \rightarrow {}_{1}e^{0} + {}_{5}^{11}B$$

By alpha particles

The experiments of Rutherford produced the (α, p) transmutation with nitrogen nucleus. In 1932 the (α,n) reaction led to the discovery of neutron.

Important example is

$${}_{4}^{9}Be + {}_{2}^{4}He \rightarrow {}_{6}^{12}C + {}_{0}^{1}n$$

This is a very good laboratory source of neutrons. Using energetic alpha particles (á,n) reactions have been observed with the heaviest elements including uranium. Increasing the energy of the projectile leads $(\alpha,2n)$, (α,np), $(\alpha,3n)$, $(\alpha,4n)$ $(\alpha,3np)$etc. types of reactions.

Transmutation by Radiation

If r – ray are having sufficient energy (2.62 MeV) than $^{2}D(r,n)^{1}$ H takes place. Similarly $^{9}Be(r,n)^{8}$ Be occurs. These reactions are known as photonuclear reaction. In heavier nuclei if the energy is only 2.62 MeV, then transmutations failed to take place. At 17 MeV the transmutations occur. This leads to emission of energy, which, which is equal to or less than that in the incident γ – photons. Eg. $^{83}Kr(\gamma,\gamma')^{83}Kr$. At low energies (γ,n) reactions occur. At higher energy (γ,np), $(\gamma,2n)$, $(\gamma,n2p)$, (γ,α) reactions occur.

Nuclear Reaction Cross Sections

The probability or efficiency of a nuclear equation can be defined in terms of the number of particles emitted or of nuclei undergoing transmutation for specified number of incident particles. This is done with the help of 'nuclear cross section' σ ,

$$\text{which is measured as } \sigma = \frac{A}{NaI} \text{ sq.cm/nucleus.}$$

Where A is the number of nuclei undergoing interaction, I is the number of in incident particles striking in a given time, containing Na target nuclei per sq.cm.

A/Na is the number of nuclei and dividing by I, larger the fraction of the incident particles with a single nucleus the greater is the probability that the reaction will occur in the given condition. Depending on reaction type, the nuclear reaction cross section varies. $^{7}Li(p,n)^{7}$ Be, ^{7} Li(p,á)^{4} He may occur simultaneously. Usually the nuclear reaction cross section varies from 10^{-25} to 10^{-23} sx.q. cm per nucleus (or from 0.1 to 10 barns (i.e.) 1 barn = 10^{-24} sq.cm.).

Artificial Radioactivity

When α – particles attack lighter nuclei like B, Mg and A1, even after the emission of neutrons ceased, the positron emission was continued. This is due to formation of new radio emitting and finally stable nuclei are produced. Thus

$$_{13}Al^{27} + {}_{2}He^{4} \rightarrow {}_{15}P^{30} + {}_{0}n^{1}$$

$$_{15}P^{30} \rightarrow {}_{14}Si^{30} + {}_{1}e^{0} \text{ Positron}$$

15^{p30} is not existing in nature and then be a radioactive isotope decaying in an experimental manner. Similar transmutations with B and Mg and the radioactive isotopes produced are ^{13}N and 27Si, which decay at measurable rate. This phenomenon is known as 'Artificial Radioactivity' and the unstable isotopes are identified by prefix 'radio'.Eg. Radiophosphorus, radioitrogen, and radiocalcium.

Artificial radioisotopes with low as well as high atomic number decay by positron emission. If in a particular species N/P ratio is larger than stability range, the species will acquire stability by β - particle emission. Hence proton – deficient species are beta active.

C^{14}, N^{16}, O^{19}, Al^{28}, Cl^{38} and Br^{83}

Are obtained by (d,p), (t,α) (α,p) (n,α) and (γ, P) processes

When N/P ratio is less than stability range, this neutron deficient nucleus will tend to change in such a manner as to replace proton by a neutron. There are 3 ways in which this can occur.

i. Emission of β + (positron)

ii. Expulsion of α – particles

iii. Capture of electrons

Positron activity is observed with isotopes having mass number smaller than the stable values (eg). ^{11}C, ^{13}N, ^{15}O and ^{26}Al which are obtained a by (p,n), (p,d), p,2n) and (p,α) type of nuclear reactions.

In high – energy spallation reactions the radioactive nuclides are produced and decay by emission of positrons; the end product being the most abundant stable isotope. ^{64}Cu decays by emission of β - and β^{+}.

$$ {}^{64}_{29}Cu \rightarrow {}_{28}Ni^{64} + {}_{1}e^{0} $$

(stable)

$$ {}^{64}_{29}Cu \rightarrow {}_{-1}e^{0} + {}_{30}Zn^{64} $$

(stable)

The positron emission produces the daughter element, which moves 1 position left in the periodic table.

Orbital Electron Capture (OR) K – Electron Capture

In some instances where N/P ratio is low and hence positron activity would be expected, another type of decay occurs with artificial radionuclide. Instead of a proton being converted into a neutron with the emission of a positron, the nucleus captures on of the extra nuclear. (K – orbital electron, which immediately combines with a proton to form a neutron.

Thus ${}_{1}H^{1} + {}_{-1}e^{0} \rightarrow {}_{0}n^{1} + {}_{0}neutrino^{0}$ with a neutrion being formed at the same time. The decay of an unstable species like ${}^{55}Fe$ by orbital electron capture is represented as ${}^{55}_{26}Fe + {}_{-1}e^{0} \rightarrow {}^{55}_{26}Mn$. The electron, which is captured by the iron nucleus is indicated by ${}_{-1}e^{0}$. This phenomenon is known as K-electron capture because the e^{-} is absorbed from the K-shell nearest to the nucleus.

The detection of orbital e^{-} capture on the fact that removal of extra nuclear e – leaves a vacancy in the appropriate quantum level usually the K – level. An e – in the higher energy level moves in to fill the vacant position and the excess energy is emitted as the corresponding characteristic X – rays. Usually the intensity of X–ray decreases as the active material decays. ${}^{49}V$(330 days) decays with X-ray characteristic of element Ti, which precedes V in the periodic Table.

In many cases when K – electron is captured the product nucleus is formed in a high energy (excited state) and the energy is given off in the form of radiation. This radiation is internally converted and γ–rays are emitted along with a characteristic secondary electron line spectrum of definite energy associated with X – ray.

III. Fission Reaction

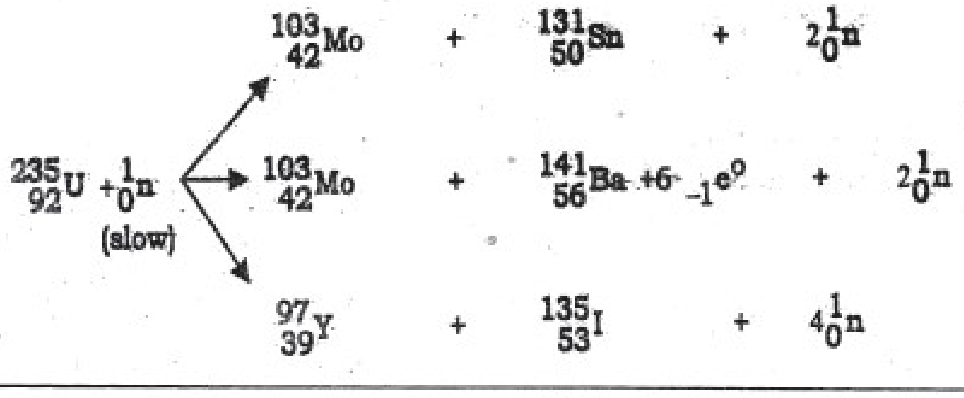
The fact that (n,y) reaction following by beta emission leads to an element of atomic number one unit greater than the parent element led Fermi and this associates to examine the action of neutrons on uranium in the expectation that an element of atomic number 93 could be synthesized in this way. Their first experiments revealed four different beta activities in a uranium sample bombarded with slow neutrons, which they attributed (in 1934) to the transuranium elements. Similar results were also obtained with thorium. Further work showed the number of activities was even greater.

Curie and Savitch (1938), however found that of the active products of the action of neutrons on uranium resembled lanthanum in its chemical properties. Re-examination of the problem by Hahn and Strassman (1939) showed conclusively they lanthanum and barium could be definitely identified among the radioactive products formed in the bombardment of uranium with neutrons. They also found that one of the supposedly trans-uranium element was actually a homologue of rhenium and it seemed possible that it was the missing element of atomic number 43.

Hahn and Strassman suggested that all their observations could be explained by assuming that the neutron causes a cleavage of the uranium nucleus into two more or less equal fragments, which was thus a new type of reaction not known so far. It may be pointed out in this connection that some five years earlier (in 1934) Noddack criticizes the earlier conclusion of Fermi and co-workers and suggested the possibility of nuclear fission in the bombardment of a heavy nucleus with neutrons.

Meitner (a former associate of Hahn) and Frisch offered in 1939 what appeared to be the correct interpretation of the results described above. According to them the uranium nucleus has just the stability of form so that by capturing a neutron it becomes so unstable that it divides itself into two nuclei of roughly equal size. The process was termed fission (nuclear fission). Similar results were also observed with thorium bombarded with fast neutrons. Meitner and Frisch further indicated that because of their high neutron; proton ratio the fission fragments should be radioactive and undergo a chain of beta disintegrations. These beta active products were previously erroneously attributed to trans uranium elements.

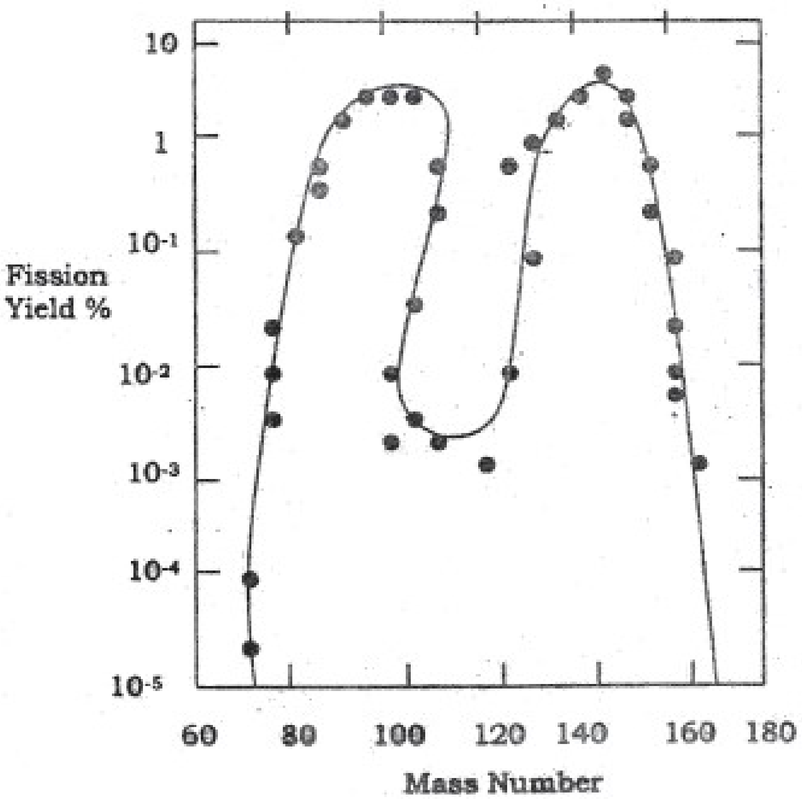
It has now been established that on bombardment with slow neutrons, the following types of changes occur in ordinary uranium, which has ^{238}U and ^{235}U isotopes. Fission of ^{235}U.;



$$^{235}_{92}U + ^{1}_{0}n \ (\text{slow}) \rightarrow ^{103}_{42}Mo + ^{131}_{50}Sn + 2\,^{1}_{0}n$$

$$^{235}_{92}U + ^{1}_{0}n \ (\text{slow}) \rightarrow ^{103}_{42}Mo + ^{141}_{56}Ba + 6\,^{0}_{-1}e + 2\,^{1}_{0}n$$

$$^{235}_{92}U + ^{1}_{0}n \ (\text{slow}) \rightarrow ^{97}_{39}Y + ^{135}_{53}I + 4\,^{1}_{0}n$$



Fission fragment yield as a function of mass number in the fission of ^{235}U by the thermal neutrons

(n,γ) Reaction with ^{238}U;

$$^{238}_{92}U + ^{1}_{0}n \longrightarrow ^{238}_{92}U \xrightarrow{\beta(23.5min.)} ^{239}_{93}Np \xrightarrow{\beta(2.33\ d)} ^{239}_{94}Pu .....$$

The ^{239}Pu is an alpha active with a half-life of 2.44 x 10^4 yr. and is a transuranium element.

The three changes shown in Equation are only few of the thirty or more ways in which uranium nucleus splits. Actually in the fission of ^{235}U about 160 isotopes of over 30 different elements are formed with atomic number ranging from 30 (Zn) to 60 (Eu) and atomic masses from 72 to 162. Most of the fission products are radioactive and they emit beta and gamma rays until stable isotopes are formed. They are;

$$ {}^{141}_{56}\mathrm{Ba} \xrightarrow{\beta} {}^{141}_{57}\mathrm{La} \xrightarrow{\beta} {}^{141}_{58}\mathrm{Ce} $$

$$ \xrightarrow{\beta} {}^{141}_{59}\mathrm{Pr} $$

$$ {}^{92}_{36}\mathrm{Kr} \xrightarrow{\beta} {}^{92}_{37}\mathrm{Rb} \xrightarrow{\beta} {}^{92}_{38}\mathrm{Sr} $$

$$ \longrightarrow {}^{92}_{39}\mathrm{Y} \xrightarrow{\beta} {}^{92}_{40}\mathrm{Zr} $$

$$ {}^{133}_{51}\mathrm{Sb} \xrightarrow{\beta(10\ \text{min.})} {}^{133}_{52}\mathrm{Te} \xrightarrow{\beta(60\ \text{m n})} {}^{133}_{53}\mathrm{I} $$

$$ \xrightarrow{\beta(22\ \text{hr.})} {}^{133}_{54}\mathrm{Xe} \xrightarrow{\beta(53\ \text{d})} {}^{133}_{55}\mathrm{Cs} $$

The $t_{1/2}$ values quoted in the last example show that the nucleus gets progressively stabilized (increase in $T_{1/2}$ value) by successive emission of beta particles as is expected. The energy released. The energy released in the fission of uranium nucleus is ca. 200MeV.

Several other nuclei can also undergo fission. Among these are ^{239}Pu and ^{233}U both of which are fissionable by slow neutrons; while ^{238}U and ^{232}Th are also fissionable but only under the action of fast neutrons. ^{239}Pu and ^{233}U are obtainable from ^{238}U and ^{232}Th respectively by irradiation with slow neutrons. The transformation of ^{238}U under the action of slow neutrons has already been mentioned and action slow neutrons on ^{232}Th is shown below.

$$ {}^{232}_{90}\mathrm{Th} + \underset{(\text{slow})}{{}^{1}_{0}\mathrm{n}} \longrightarrow {}^{233}_{90}\mathrm{Th} \xrightarrow[(23.5\ \text{min.})]{\beta} {}^{233}_{91}\mathrm{Pa} \xrightarrow[(27.4\ \text{d})]{\beta} {}^{233}_{92}\mathrm{U} $$

^{233}U is alpha active with a T ½ = 1.62 x 10^5 yr. since 1966 Choppin and other have reported on the fission of ^{238}U induced by low and medium energy protons.

IV. Product Distribution

The fission fragments F_1 and F_2 are not a unique pair but could be one of about 30 possible pairs such that the mass number of the lighter fragment (say F_1) ranges from about 85 to 105 and that of the heavier fragment (F_2) from about 150 to 130. these limits refer to fission yields of 1. percent and above. Following are some possibilities;

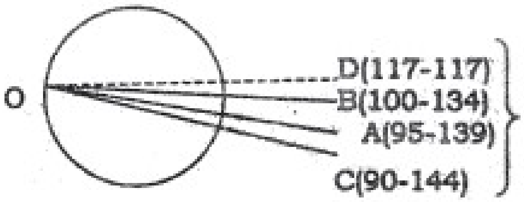
(a) $^{236}_{92}U$ $^{94}_{36}Kr + ^{140}_{56}Ba + 2n$

(b) $^{236}_{92}U$ $^{94}_{38}Sr + ^{139}_{54}Xe + 2n$

(c) $^{236}_{92}U$ $^{96}_{40}Zr + ^{137}_{52}Te + 3n$

(d) $^{236}_{92}U$ $^{99}_{41}Nb + ^{133}_{51}Sb + 4n$, and so on

It must be noted that all the primary fission fragments have invariably excess neutrons compared to their stable isotopes as per their position in the Periodic Table and the N/Z stability chart.



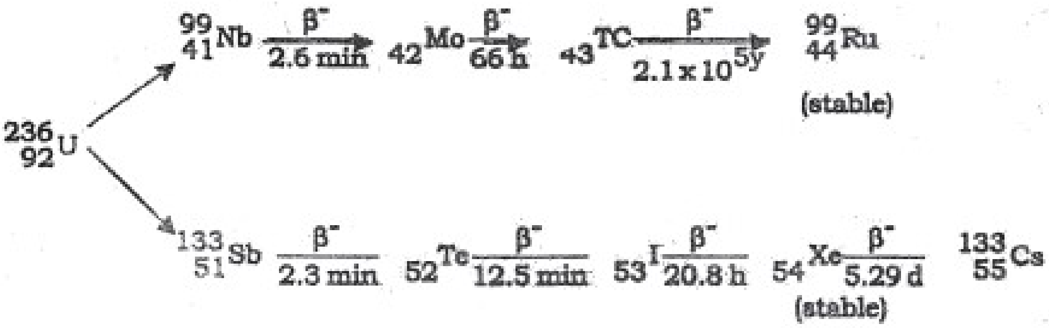
Probable fissioning sections;

OA : most probable fission,

OD : least probable fission,

+2n OB-OC : limits of fission with yields ≥ 1%.

Hence primary fission fragments display β^- activity and continue to decay by successive β^- emissions of increasing half-lives till a stable nuclide isobaric with the primary fragment is reached, as shown for a fission fragment pair.

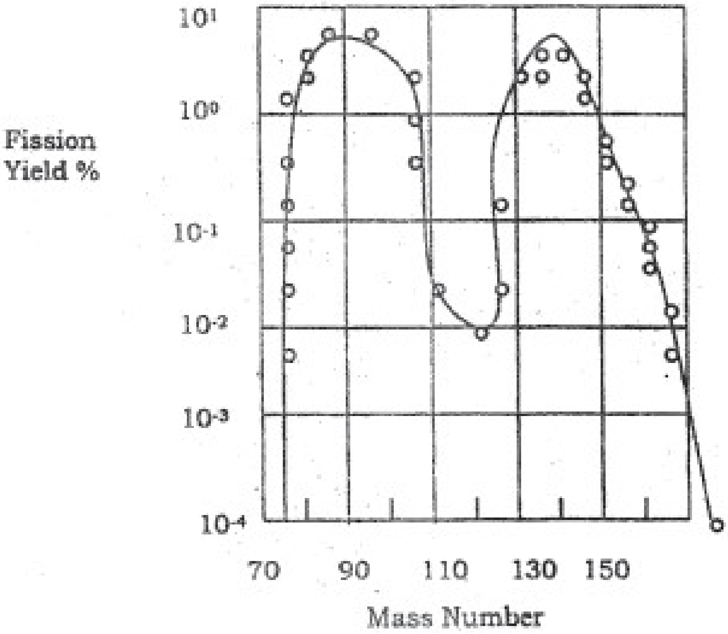


A term frequently employed in describing mass distribution between the fragments is the cumulative chain fission yield defined as

$$Y(A) = \frac{\text{Number of product nuclei of mass number A}}{\text{Total number of nuclei fissioned}} = X\ 100$$

A typical fi [illegible] mass yield curve as a fanatic of the mass number A is shown in below fig. experimentally, the mass number is given by the yield of the final stable isotope of that mass number. It may be noted that a majority of the fissions are asymmetric, i.e. $A_1 \neq A^*_2$. the mass distribution curve shows that yield $\geq$ 1% range from 85 – 105 for A_1 and 150 – 130 for A_2, as stated before. The maximum yields of close on seven per cent are 90 – 100 for A_1 and 134 – 144 for A_2 with an average loss of 2.5 neutrons per fission.

It is interesting to note the presence of two spikes at 100 and 134 for A_1 and A_2 respectively. It should further be noted that the yield of symmetrical fission, i.e $A_1 = A_2 = 117$ is the lowest being around 0.05 per cent. This is true for fission by thermal or low energy neutrons. However, as the energy of the particle effecting fission increases, the depth of the valley between the two peaks diminishes and the two peaks approach till there is a single peak of symmetric fission.



Fission fragment yield as a function of mass number in the fission of ^{235}U by neutrons

While fission into two fragments is more common, tripartite fission into three fragments has also been observed, E.g., Fission of ^{226} Ra by 11 MeV protons and 14.5 and 21.5 deuterons.