



Uttar Pradesh Rajarshi Tandon
Open University

UGCHE-101

Inorganic Chemistry-I

Inorganic Chemistry-I (Basic Inorganic Chemistry)

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Block

1

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Unit -1

Atomic Structure

7

Unit-2

Periodic Properties of Elements

34

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Chemical Bonding

52

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UGCHE-01 INORGANIC CHEMISTRY I

(BASIC INORGANIC CHEMISTRY)

Introduction

This is the first course of the undergraduate chemistry programme. This course is divided into two blocks in the first block we shall introduce atomic structure of the atoms and molecules with their historical and modern concepts. In the unit one and two, the periodic properties of the elements with their compounds are discussed. Types of bonds and bonding properties are elements with their compounds are discussed in unit three of the block one. In the block second, unit are discussed with properties and general study of s and p-block elements and compounds. Specific 3rd unit have introduction as well as role of oxidation reduction in the field of chemistry.

UNIT 1: ATOMIC STRUCTURE

Structure

- 1.1 Introduction
 - Objectives
- 1.2 Historical concepts of atomic structure
- 1.3 Idea of de-Broglie's matter waves
- 1.4 Heisenberg's uncertainly principle
- 1.5 Significant of ψ and ψ^2 , Schrodinger's wave equation (for HAtom)
- 1.6 Radial and angular wave functions (quantum numbers and shapes of s, p, d and f orbitals)
- 1.7 Aufbau and Pauli Exclusion Principle
- 1.8 Variation of orbital energies (atomic number and energy level diagram)
- 1.9 Long form of periodic table based on electronic configuration
- 1.10 Summary
- 1.11 Terminal Questions
- 1.12 Answers

1.1 INTRODUCTION

After studying this unit, you should be able to know about the classical concepts of atom models to explain the atomic structures. An atom consists of a minute positive charged centre called nucleus. The nucleus composed of protons and neutrons. The mass of an atom resided in the nucleus. The nucleus is surrounded by the definite number of electrons revolve around positive charge nucleus and balance the positive charge. Further they based their theories on the postulate that all interactions between matter and radiation occur in terms of definite packets of energy, known as quanta. Their ideas, when extended further, led to the evolution of wave mechanics, which shows the dual nature of

matter and energy. and explain it in the light of Einstein's theory, list Bohr's postulates and derive an expression useful in calculating the radius of the hydrogen atom, explain the atomic spectra of hydrogen in the light of Bohr's theory analyse critically the advantages and limitations of Bohr's theory and state the refinements in the atomic spectra theory.

Objective:

After studying this unit, you should be able to know

- Classical concepts of atom model
- Modern concepts of atomic model
- Schrodinger's wave equation for H
- Radial and angular wave functions
- Long form of periodic table

1.2 HISTORICAL CONCEPTS OF ATOMIC STRUCTURE

In early concept of the atom as a hard, dense and smallest individual particle according to John Dalton (1809) but different properties like radioactivity i.e. emission of positive and negative particles, and conductivity of gasses at low temperature, convinced scientists that atom consists of three major fundamental particle called electrons, protons and neutrons. The some important models as follows:

In 1904 Thomson, proposed a model for the atomic structure known as "plum pudding" model (Figure 1), he considered an atom to be a uniform sphere of positive electricity of about 10^{-8} cm radius, with the electron embedded in such a way as to give the most stable electrostatic agreement. But fail to explain scattering of the α -particles directed towards thin gold foil experiment of Geiger and Marsden.

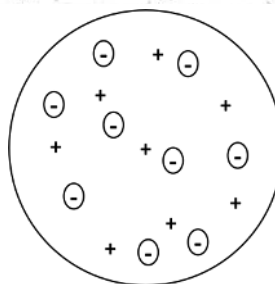


Figure 1: Thomson "plum pudding" model for the atom

Rutherford (1911) on the basis of the X-ray scattering experiment of Geiger and Marsden (1909) regarding the scattering of the α -particles directed towards thin gold foil, suggested that positive charge and mass of the atom are concentrated in a space which is very much smaller than that occupied by the atom as a whole.

According to Rutherford atomic model

- i. An atom consists of a minute positive charged centre called nucleus. The nucleus composed of protons and neutrons. The mass of an atom resided in the nucleus.
- ii. The nucleus is surrounded by the definite number of electrons revolve around positive charge nucleus and balance the positive charge.
- iii. Most of the space between nucleus and the revolving electrons is empty.
- iv. The centrifugal force due to the circular motion of electrons balanced the force of electrostatic attraction between the nucleus and electrons. Thus the electrons do not fall into nucleus.

Drawback of Rutherford atomic model

Niels Bohr pointed out that Rutherford's atom should be highly unstable. According to J. C. Maxwell that whenever an electric charge subjected to acceleration it emits radiation and loss energy thus Niels Bohr argued that in Rutherford atomic model the electron should therefore continuously emit radiation and loss energy as a result electron emit energy regularly and orbit become smaller and smaller and finally it should fall into the nucleus. However, this does not happen. Bohr supplied solution to this trouble by the concept of the quantum theory of radiation put forth by Max Plank.

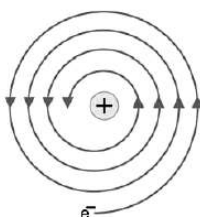


Figure 2: Drawback of Rutherford atomic model

Plank's quantum theory

According to Planck's quantum theory, energy is not continuous but is discrete. This means that energy occurs in 'packets' called **quanta**, of magnitude h/λ , where h = Planck's Constant = 6.6262×10^{-34} Js. These quanta of energy are emitted when an oscillator changes from one quantized energy state to another. Thus, if the oscillator goes from the level $n+1$ to n , the amount of energy radiated as

$$\Delta E = E_2 - E_1 = (n+1)h\nu - nh\nu = h\nu$$

Planck's theory was extended by Einstein to explain heat capacity variation with temperature. Energy was considered to be taken up by the vibrations of particles. Einstein assumed that each atom could vibrate about its equilibrium position with a single frequency ν . He derived an expression to calculate the heat capacity and used it successfully to explain the decrease of heat capacity at low temperatures.

Einstein's theory of photoelectric effect

Applying the photon concept to the photoelectric effect, Einstein proposed that an electron at the surface of the metal gains an energy $h\nu$, by the absorption of a photon from the electromagnetic radiation. If the frequency ν of the photon is greater than the minimum value ν_0 , called threshold frequency which is characteristic of a particular metal, then the emission of photoelectron occurs. The difference, $h\nu - h\nu_0$, is transformed as the kinetic energy of the photoelectron which is equal to $m\nu^2/2$. Thus, **photoelectron emission** does not take place when ν is less than ν_0 .

BOHR ATOM MODEL

Niels Bohr recommended an atomic model which is advance over Rutherford model. With the quantum theory of radiation put forth by Max Plank in 1901, Danish physicist, Niels Bohr on 1913 was proposed to explain the spectrum of hydrogen atom. The energy of an electron in an orbit is equal to that is its angular momentum mvr , must be equal to a whole number n (number of orbit), of quanta. Where m and v stand for the mass and velocity of the electron, r is the orbit radius n is an integer called principal quantum number. The orbits are called K, L, M, N, .. depending on the values of n , viz., 1, 2, 3, 4,

$$mvr = \frac{nh}{2\pi}$$

Bohr based his theory on the following postulates:

- i) An electron can exist only in orbits of definite energy and angular momentum. Each orbit is known as a stationary state.
- ii) The electron does not radiate energy when it is in permitted orbit.
- iii) For an electron remain in its orbit the electrostatic attraction between electron and nucleus must be equal to the centrifugal force which tends to throw out the electron out of its orbit.

$$\text{Centrifugal force} = \frac{mv^2}{r} = \text{Coulombic attractive force} = \frac{Ze^2}{r^2}$$

Where m = mass of electron, v = velocity of electron, r = radius of orbit, e = charge on the electron, Z = number of charges on nucleus and ϵ_0 = permittivity of a vacuum.

Hence

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

$$v^2 = \frac{Ze^2}{mr} \quad \text{----- (i)}$$

- iv) While in an orbit the angular momentum of the electron, mvr , is an integral multiple of $h/2\pi$ units.

$$mvr = \frac{nh}{2\pi}$$

or

$$v = \frac{nh}{2\pi mr}$$

$$v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2} \quad \text{----- (ii)}$$

Combining the equation (i) and (ii)

$$\frac{Ze^2}{mr} = \frac{n^2 h^2}{4\pi^2 m^2 r^2}$$

hence

$$Ze^2 = \frac{n^2 h^2}{4\pi^2 mr}$$

Thus

$$r = \frac{n^2 h^2}{4\pi^2 Zme^2} \quad \text{----- (iii)}$$

For hydrogen atom $Z=1$, hence

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

$$r = \frac{(4\pi\epsilon_0) 4\pi^2 h^2}{4\pi^2 m e^2}$$

For SI system

Where factor $4\pi\epsilon_0$ is permittivity factor, its numeric value is $1.1126 \times 10^{-10} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$

Bohr's radius: On substituting the values in the above equation as for hydrogen atom the radius is obtained called **Bohr's radius**.

$$r = \frac{(4\pi\epsilon_0) 4\pi^2 h^2}{4\pi^2 m e^2} \dots \dots \dots \text{(iv)}$$

$$4\pi\epsilon_0 = 1.1126 \times 10^{-10} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$$

$$n = 1$$

$$m = 9.109 \times 10^{-31} \text{ kg}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$r = 0.529 \times 10^{-10} \text{ m} = 0.529 \text{ \AA}$$

For hydrogen atom in ground state $n=1$, the radius r_1 is designated as **Bohr radius**.

$$r_1 = \frac{h^2}{4\pi^2 m e^2}$$

Energy of electron: The total energy of electron revolving in the orbit is the sum of the kinetic and the potential energy.

Thus
$$E = \frac{1}{2} m v^2 + \left(-\frac{Z e^2}{r} \right)$$

From equation $m v^2 = \frac{Z e^2}{r}$, substituting the value of the value of $m v^2$ in above equation.

$$E = \frac{1}{2} \times \frac{Z e^2}{r} - \frac{Z e^2}{r}$$

$$E = -\frac{Z e^2}{2r} \dots \dots \dots \text{(v)}$$

Substituting the value of r from the equation (iii)

$$E = -\frac{Z e^2}{2r} \times \frac{4\pi^2 Z m e^2}{n^2 h^2}$$

$$E = -\frac{2\pi^2 Z^2 m e^4}{n^2 h^2} \dots \dots \dots \text{(vi)}$$

This equation is called Bohr equation for the calculation for total energy of the electron.

For SI system

$$E = - \frac{2\pi^2 Z^2 m e^4}{(4\pi\epsilon_0)^2 n^2 h^2}$$

Where factor, $4\pi\epsilon_0$ = permittivity factor = $1.1126 \times 10^{-10} C^2 N^{-2} m^{-2}$

For hydrogen atom electron in ground state, $n = 1$

$$m = 9.109 \times 10^{-31} \text{ kg}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$Z = 1$$

On substituting the values

per atom

$$\text{Since } E = -2.179 \times 10^{-18} \text{ J}$$

$$\text{Hence } 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$E = \frac{-2.179 \times 10^{-18} \text{ J}}{1.602 \times 10^{-19} \text{ J/eV}} = 13.6 \text{ eV (per atom)}$$

The kinetic energy of an electron is . Rearranging equation (v)

$$-\frac{1}{2}mv^2$$

$$E = -\frac{1}{2}mv^2 = -\frac{Ze^2}{8\pi\epsilon_0 r}$$

Substituting the value of r from the equation (iv)

$$E = -\frac{Z^2 e^4 m}{8\epsilon_0^2 n^2 h^2}$$

If an electron jump from an initial orbit i to final orbit f , thus

Change in energy

$$\begin{aligned} \Delta E &= \left(-\frac{Z^2 e^4 m}{8\epsilon_0^2 n_i^2 h^2} \right) - \left(-\frac{Z^2 e^4 m}{8\epsilon_0^2 n_f^2 h^2} \right) \\ &= \frac{Z^2 e^4 m}{8\epsilon_0^2 h^2} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \end{aligned}$$

Energy is related to wavelength $E = h\nu$, and then this equation is

$$\nu = \frac{Z^2 e^4 m}{8\epsilon_0^2 h^3 C} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

as Rydberg equation

$$\bar{\nu} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \dots\dots\dots (vii)$$

where Rydberg constant

$$R = \frac{Z^2 e^4 m}{8 \epsilon_0^2 h^3 c} = 109677.58 \text{ cm}^{-1}$$

iv) Each spectral line is produced by a single electron. When an electron jumps from one orbit to another, radiation of a definite frequency is emitted or absorbed giving rise to a definite spectral line. The frequency of the spectral line is related to the difference in energy, E , between initial and final levels, as per the equation:

$$E = h\nu = \frac{hc}{\lambda} = hc \bar{\nu} \dots\dots\dots (viii)$$

Using the above postulates, he was able to calculate the radius of different orbits in hydrogen atom, the energy of the electron in its orbits and the frequency of the spectral Lines.

ATOMIC SPECTRA OF HYDROGEN

Atomic spectra showed that each element emit light of specific energies when excited by an electric discharge or heat. In 1885 Balmer showed that wave number ($\bar{\nu}$) of any line in visible light emitted by the hydrogen atom are given by equation:

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

Where R = Rydberg constant = $2.179 \times 10^{-34} \text{ J} = 1.097373 \times 10^7 \text{ m}^{-1}$ (Experimentally) and $1.096776 \times 10^7 \text{ m}^{-1}$ (Theoretically) and n has the values 3, 4, 5..., thus giving a series of lines. The lines observed in the visible region are called the Balmer series.

Similar equations were found to hold for the lines in the other series in the hydrogen spectrum.

$$\text{Lyman} \quad \bar{\nu} = E = R \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \quad n = 2, 3, 4, 5 \dots$$

$$\text{Balmer} \quad \bar{\nu} = E = R \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \quad n = 3, 4, 5, 6 \dots$$

$$\text{Paschen} \quad \bar{\nu} = E = R \left(\frac{1}{3^2} - \frac{1}{n^2} \right) \quad n = 4, 5, 6, 7 \dots$$

Brackett

$$\bar{\nu} = E = R \left(\frac{1}{4^2} - \frac{1}{n^2} \right) \quad n = 5, 6, 7, \dots$$

Atomic Structure

Pfund

$$\bar{\nu} = E = R \left(\frac{1}{5^2} - \frac{1}{n^2} \right) \quad n = 6, 7, 8, 9, \dots$$

Table 1: Spectral series found in atomic hydrogen

Spectral series	Region of spectrum
Lyman	Ultraviolet
Balmer	visible
Paschen	infrared
Brackett	infrared
Pfund	infrared

Question 1: Calculate the energy of electron, radius of second orbit, frequency and wavelength of spectral line when the electron revolves in second orbit of hydrogen atom?

Answer:

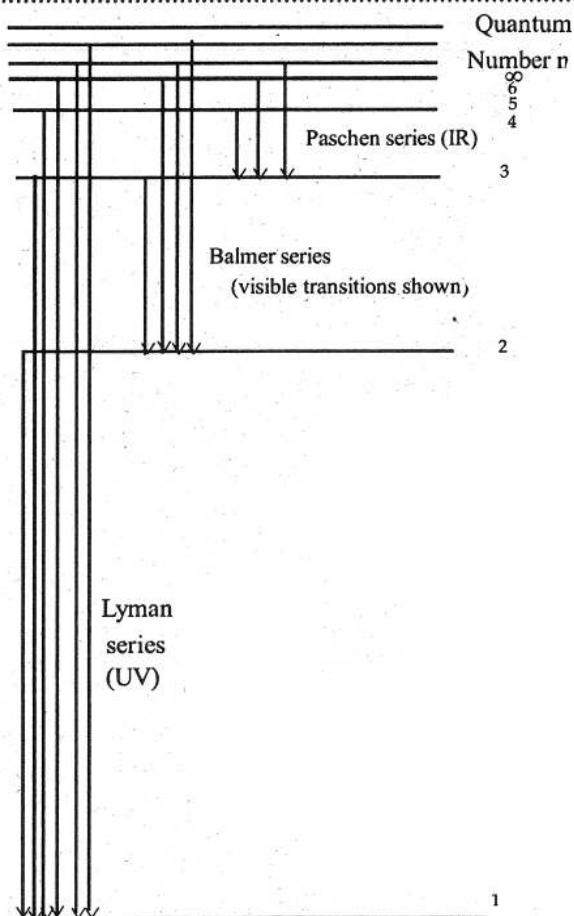


Figure 3: Spectral series found in atomic hydrogen

Limitations of Bohr's Theory

The hyperfine structure in the atomic spectra of hydrogen is not well explained by Bohr's theory. Bohr's theory is not able to explain the spectra of multi-electron atoms.

Bohr's theory does not explain how molecules are formed from atoms.

According to Bohr's theory, electron moves in orbits known as stationary states. The path of this orbit can be known only if we know simultaneously both the position and the velocity of electron. It therefore, assumes the accurate and simultaneous determination of both position and velocity of the electron. It therefore, assumes the accurate and simultaneous determination of both position and velocity of the electron. Theories of Sommerfeld, Heisenberg and Schrodinger explain these shortcomings by their theories.

SOMMERFELD THEORY

When electron moves from one orbit to another it should give a single line in the spectrum but when the hydrogen spectrum observed with a high resolution spectrometer it found that some of the line reveal 'fine structure'. In 1916, Sommerfeld modified Bohr's theory and tried to interpret the fine structure in the atomic spectra of hydrogen as due to elliptical path of the electron.

For the orbit closest to the nucleus, the principle quantum number $n=1$, and there is a circular orbit. For the next orbit, the principle quantum number $n=2$, both circular and elliptical orbit are possible. To define an elliptical orbit defined by the ratio of the length of the major and minor axes.

$$\frac{\text{major axis}}{\text{minor axis}} = \frac{n}{k}$$

He introduced another quantum number, known as azimuthal or subsidiary quantum number k , and may have values form 1, 2, ... n . Thus for $n=2$, n/k may have value 2/2 (circular orbit) and 2/1 (elliptical orbit). For the principal quantum number $n=3$, may have value 3/3 (circular orbit), 3/2 (elliptical orbit) and 3/1 (narrow ellipse) shown in figure 4. Which was by later modifications represented as ' l ' and shown to have values 0, 1....($n-1$), where n is the principal quantum number. Thus if $n=2$, then 1 can have values 0 and 1.

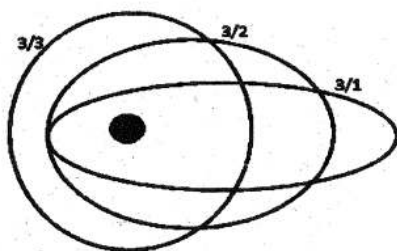


Figure 4: Bohr-Sommerfeld orbits when $n=3$.

The splitting of spectral lines when atoms are placed in a strong magnetic field, known as Zeeman effect, could also be partially explained by introducing magnetic quantum number (m_l) describing the allowed orientations of electron orbits in space. It was shown that for each value of l , m_l can have $(2l + 1)$ values namely from $+l$ to $-l$. Hence if $l = 1$, m_l can have three values, $+1$, 0 and -1 . You will see in the next unit, an alternate way of arriving at the quantum numbers n , l and m_l .

1.3 DE BROGLIE MATTER WAVES

WAVE MECHANICS

According to Wave Mechanical Theory light exhibits both a wave and a particle nature. This theory was further extended to matter *i.e.* electrons, protons and atoms. The new quantum mechanics which takes into account the particulate and wave nature of matter is termed as wave mechanics.

DE BROGLIE EQUATION

In 1924 de Broglie proposed that matter as atoms, neutrons, protons, electrons, etc. has dual character *i.e.* it is associated with the properties of waves and their wavelengths λ is given by the relation

$$\lambda = \frac{h\nu}{mv} = \frac{h}{\text{momentum}}$$

where m is the mass, v , the velocity of the particle and h the Planck's constant. de Broglie equation has no significance for large objects.

1.4 HEISENBERG'S UNCERTAINTY PRINCIPLE

It is impossible to measure simultaneously both the position and velocity (or momentum) of a microscopic particle with absolute accuracy or certainty. Mathematically,

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

or

$$\Delta x \times m \Delta v \geq \frac{h}{4\pi}$$

where Δx is the uncertainty in position, Δp the uncertainty in momentum and Δv is the uncertainty in velocity and m is the mass of the particle. It also has no significance for large objects. Therefore the concept replaced by the probability of finding an electron in a particular position or in a particular volume of space. Solution of Schrödinger wave equation provides wave function represented as symbol ψ . The probability of finding an electron at a point in space whose coordinates are x , y , and z is $\psi^2(x, y, z)$.

Question 2: A plastic ball weighing 150 g is to be located within $0.1\text{\AA}$. what is the uncertainty in its velocity?

Answer:

.....

Question 3: The velocity of electron in first orbit is and located within $0.1\text{\AA}$. What will be the uncertainty in its velocity?

Answer:

.....

1.5 SIGNIFICANCE OF ψ AND ψ^2

According to Heisenberg's uncertainty principle, we can never know the exact position of the electron moving around the nucleus with a particular velocity. Thus we only have probability of finding electron in any given region or defined in probability function. If $\psi(x, y, z)$ is a probability function in three dimensional space around the point, the function ρ is known as **probability density**. The total probability of finding the electron in the whole space will be given by the summation of all types of terms $\rho dx dy dz$ or $\rho d\psi$. Thus total probability must be equal to unity in space.

$$\int_{-\infty}^{+\infty} \rho d\psi = \int_{-\infty}^{+\infty} \rho dx dy dz = 1$$

For the wave equation for a single particle is a function $\psi(x, y, z)$, called wave function, represent amplitude of the wave. It has no physical significance as such. In the case of wave the square of the amplitude 2 has significance than the amplitude itself. According to wave theory the intensity of radiation is measured by the square of the amplitude of the wave.

The probability density in three dimensional volumes around the point, get related to the square of the amplitude of the associated wave. By analogy ψ^2 , will be measure of finding electron in the given volume.

Thus

$$\int_{-\infty}^{+\infty} \rho \, d\tau = \int_{-\infty}^{+\infty} \psi^2 \, d\tau = 1$$

The factor $\psi^2 d\tau$ represents the probability of locating the electrons I the small volume element $d\tau$.

SCHRÖDINGER'S WAVE EQUATION

Schrödinger derived an equation based upon the idea of the electron as standing wave around the nucleus. For a standing wave such as vibrating, of wavelength λ with amplitude w at any point along x , at time t may be described by equation such as wave motion as

$$\frac{\partial^2 w}{\partial x^2} = \frac{1}{u^2} \times \frac{\partial^2 w}{\partial t^2} \dots\dots\dots(ix)$$

where u velocity of wave propagates.

w , can be written as two mathematical functions, x and t .

thus
$$w = f(x) g(t)$$

for stationary waves, the function $g(t)$ represented as

$$g(t) = A \sin (2\pi vt)$$

where v = frequency of vibration and A = maximum amplitude of wave

After double differentiation of above equation with respect to time gives

$$\frac{\partial^2 g(t)}{\partial t^2} = -4\pi^2 v^2 A \sin (2\pi vt) = -4\pi^2 v^2 g(t)$$

In the same way double differentiation of above equation with respect to time and respect to coordinate x , yields

$$\frac{\partial^2 w}{\partial t^2} = f(x) \frac{\partial^2 g(t)}{\partial t^2} = -f(x) 4\pi^2 v^2 g(t)$$

And

$$\frac{\partial^2 w}{\partial x^2} = \frac{\partial^2 f(x)}{\partial x^2} g(t)$$

Substituting the values of $\frac{\partial^2 w}{\partial t^2}$ and $\frac{\partial^2 w}{\partial x^2}$ in equation (ix)

$$\frac{\partial^2 f(x)}{\partial x^2} g(t) = -\frac{1}{u^2} 4\pi^2 v^2 g(t) f(x)$$

$$\frac{\partial^2 f(x)}{\partial x^2} = -\frac{4\pi^2 v^2}{u^2} f(x)$$

As we know that $u = v\lambda$, where λ is the wave length,

Hence $\frac{v}{u} = \frac{1}{\lambda}$ substituted in above equation

$$\frac{\partial^2 f(x)}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} f(x)$$

If an electron is considered as a wave which moves in one dimension

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \psi$$

When an electron may move in three dimensions x , y , and z so this becomes

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2} \psi \quad \dots\dots\dots(x)$$

Instead of the three partial differentials, the symbol **∇^2 = Laplacian mathematical operator** is used then equation become short as

$$\nabla^2 \psi = -\frac{4\pi^2}{\lambda^2} \psi$$

The total energy E of a particle is the sum of its kinetic and potential energy, thus

$$E = \frac{1}{2} mv^2 + V$$

or

$$mv^2 = 2(E - V)$$

$$v^2 = \frac{2}{m} (E - V)$$

Substituting the value of v^2 in the equation

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2 m}{h^2} \times \frac{2}{m} (E - V)\psi$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0 \quad \dots\dots\dots(xi)$$

The equation (xi) is known as Schrödinger's wave equation

where

ψ is a mathematical function representing the amplitude of the wave,
 m , the mass of the particle,

v , the velocity,
 E the total energy of the particle,
 V , the potential energy and x, y, z are three space coordinates.

It may be noted that square of the wave function, ψ^2 , represents the probability of finding the electron in different regions.

1.6 Radial and angular wave functions: quantum numbers and shapes of s, p, d and f orbitals

SCHRÖDINGER'S WAVE EQUATION FOR HYDROGEN

In the hydrogen atom, the nuclear charge is $+e$ and charge on electron is $-e$. Then

$$\text{Potential energy of electron, } V = -\frac{e^2}{r}$$

Therefore Schrödinger's wave equation,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} \left(E - \frac{-e^2}{r} \right) \psi = 0$$

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi + \frac{8\pi^2 m}{h^2} \left(E + \frac{e^2}{r} \right) \psi = 0$$

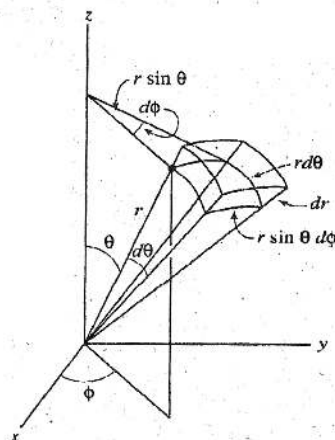
In the three dimensions, ψ may be expressed in terms of Cartesian coordinates (x, y, z) or in terms of polar or spherical coordinates (r, θ, ϕ) . Spherical coordinates are shown in figure given below where r represents the distance from the nucleus, the spherical coordinate θ is the angle from the z axis, varying from 0 to π and ϕ is the angle from the x axis, varying from 0 to 2π .

If we replace the Cartesian coordinates (x, y, z) to polar coordinates (r, θ, ϕ) using following expressions:

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

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

$$z = r \cos \theta$$



Therefore, polar coordinates transforms as

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi(r, \theta, \phi)}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi(r, \theta, \phi)}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi(r, \theta, \phi)}{\partial \phi^2} + \frac{8\pi^2 m}{h^2} \left(E + \frac{e^2}{r} \right) \psi(r, \theta, \phi) = 0$$

Evaluation of $\psi(r, \theta, \phi)$, is possible only if function ψ can be written as

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

$R(r)$ is a function depending on distance (r) from nucleus which depends on the quantum number n and l .

$\Theta(\theta)$ is a function of θ , depends on the quantum number l and m .

$\Phi(\phi)$ is a function of ϕ , depends only on quantum number m .

The equation may be written as

$$\psi = R(r)_{nl} \cdot A_{ml}$$

This splits the wave function into two parts

1. $R(r)_{nl}$ the radial function, which depends on the quantum number n and l .
2. A_{ml} the total angular wave function which depends on the quantum number m and l .

$R(r)$ called *radial wave function* is independent of other polar coordinates gives the energy and size of the orbitals.

$\Theta(\theta)$ is a function depends on θ but independent of other polar coordinates and

$\Phi(\phi)$ is a function depends on ϕ but independent of other polar coordinates are called *angular wave function* gives the shape of the orbitals.

The Radial wave function, R has no physical meaning, but R^2 gives the probability of finding the electron in a small volume dv near the point at which R is measured. For a value of r the number of small volumes is $4\pi r^2$, thus probability of finding electron at the distance r from the nucleus is $4\pi r^2 R^2$, is called radial distribution function. For hydrogen radial distribution function plotted against r shown in figure 5. The radial probability distribution curves can be drawn suitably by remembering the **radial nodes** i.e. the radial spaces at which radial probability is almost zero, is equal to $(n - l - 1)$ and the curves starts from origin and the areas of envelopes increasing from left to right so that

the last envelop covers maximum area. In case of hydrogen atom the radius of maximum probability is $0.529 \text{ \AA}$.

Figure 5: Radial distribution function for various orbitals of hydrogen

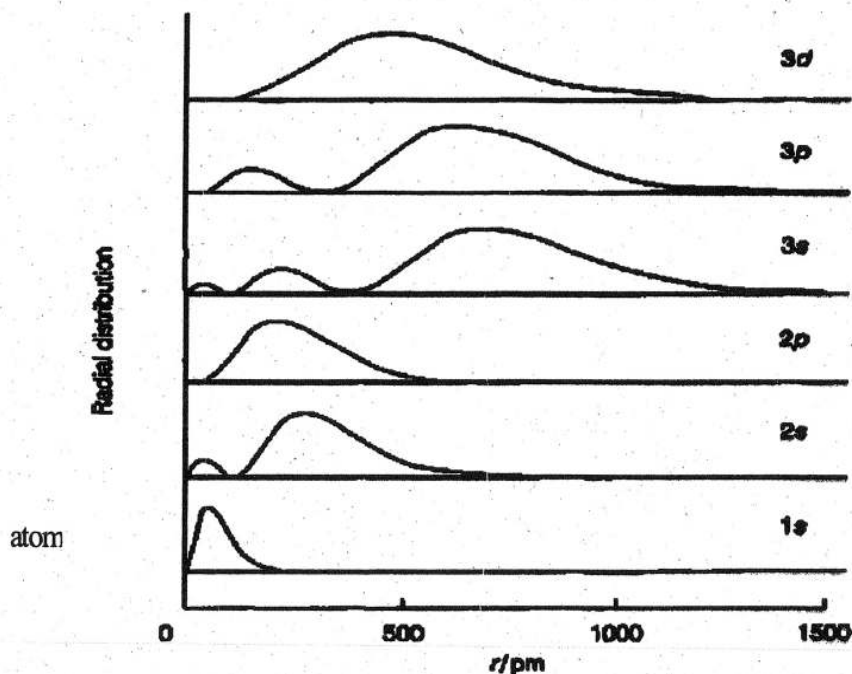


Figure 5: Radial distribution function for various orbitals of hydrogen atom

The angular wave function and shape of orbitals

The angular wave function (A), depends only on the direction and is independent of the distance from the nucleus (r). Thus A^2 is the probability of finding an electron at given direction θ, ϕ at any distance from the nucleus to infinity. The angular wave function A are plotted as polar diagrams only represent angular part of the wave function in Figure 6. From the transformed equation of polar coordinates an additional quantum numbers m originates. The maximum value of m can be $\pm l$, so that can have values $0, \pm 1, \pm 2, \pm 3 \dots \dots \pm l$.

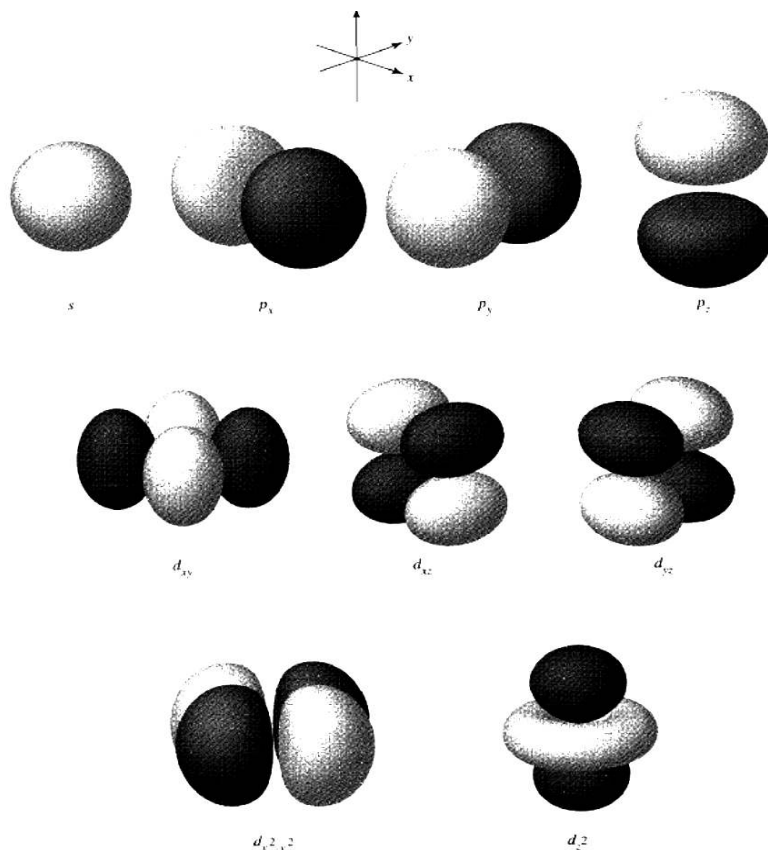


Figure 6: Polar diagrams only represent angular part of the wave function

Spherical nodes [$R(r) = 0$]

Examples (number of spherical nodes)					
1s	0	2p	0	3d	0
2s	1	3p	1	4d	1
3s	2	4p	2	5d	2

Angular nodes [$Y(\theta, \phi) = 0$]

Examples (number of angular nodes)	
s orbitals	0
p orbitals	1 plane for each orbital
d orbitals	2 planes for each orbital except dz^2

For hydrogen like systems yields two quantum numbers, n and l , the principal and angular momentum quantum numbers. **The radial probability function** is $4\pi r^2 R^2$. This function describes the probability of finding the electron at a given distance from the nucleus, summed

over all angles, with the $4\pi r^2$ factor the result of integrating over all angles. The radial wave functions and radial probability functions are plotted for the $n=1, 2$, and 3 orbitals. Both $R(r)$ and $4\pi r^2 R^2$ are scaled with a_0 , the **Bohr radius** to give reasonable units on the axes.

The Bohr radius, $a_0 = 52.9$ pm, is a common unit in quantum mechanics. It is the value of r at the maximum of ψ^2 for a hydrogen $1s$ orbital and is also the radius of a $1s$ orbital according to the Bohr model.

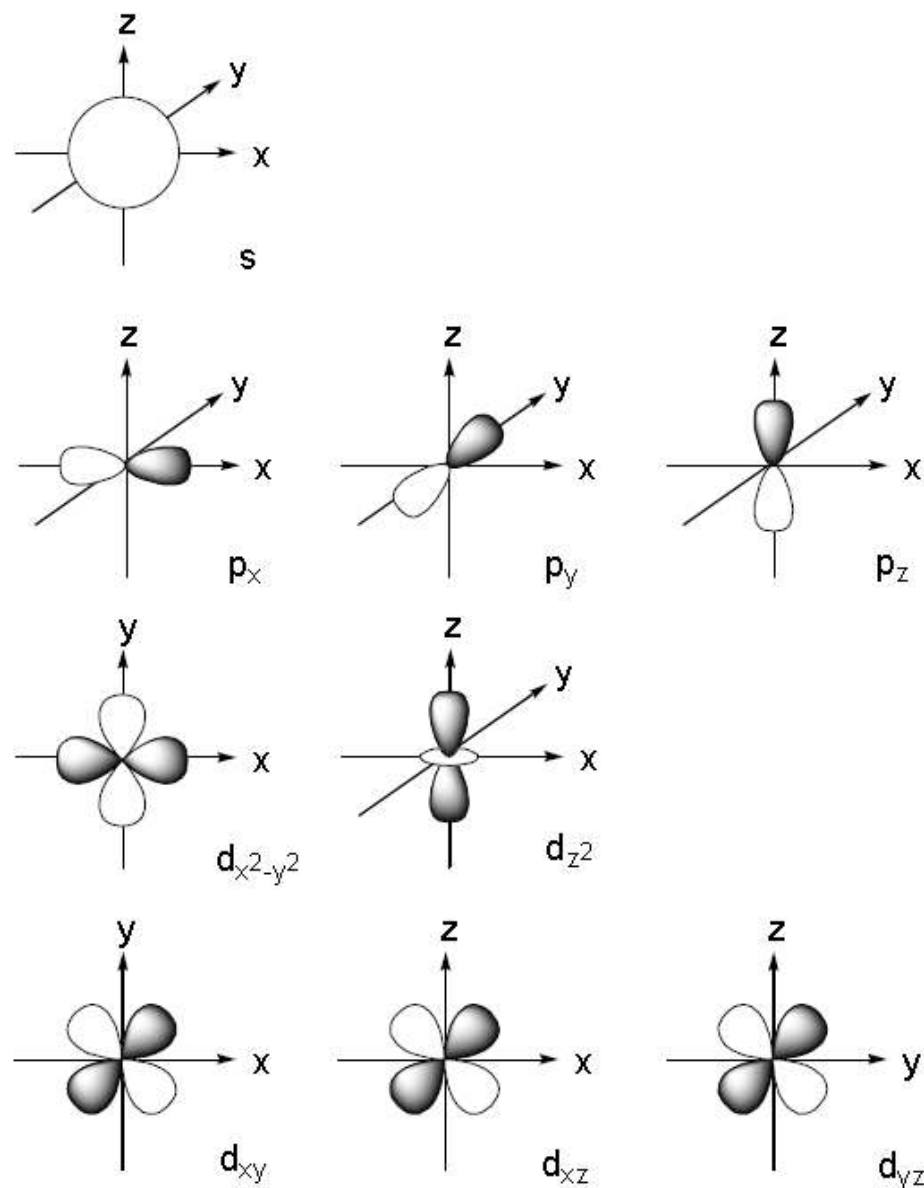


Figure showing shape of the s, p and d-orbitals

Quantum numbers

The solutions of Schrodinger wave equation for atom yield three quantum numbers n , l and m . These quantum numbers are designated as principal quantum number (n), angular momentum quantum number or azimuthal quantum number or orbital quantum number (l) and magnetic quantum number (m). These are the same quantum numbers- principal, subsidiary and magnetic as were used in Bohr Theory.

Principal quantum number (n)

This quantum number represents the main energy level or energy shell in which the electron is present. It is represented by n and can have values 1, 2, 3, ...etc. It also determines the average distance of an electron from the nucleus. As the value of n increases, the electron gets far away from the nucleus and energy increases.

Azimuthal quantum number or orbital quantum number (l)

The azimuthal quantum number or orbital quantum number (l) describes the shape of the orbital occupied by the electron. l may have values 0, 1, 2 or 3 from relation $l = 0$ to $(n - 1)$. When $l = 0$, the orbital is spherical and is called an s orbital, when $l = 1$, the orbital is dumb-bell shaped and is called an p orbital, when $l = 2$, the orbital is double dumb-bell shaped and is called an d orbital and when $l = 3$, the orbital is more complicated and is called an f orbital. The letters s , p , d and f come from the spectroscopic terms sharp, principle, diffuse and fundamental which are used to describe the lines in the atomic spectra.

Magnetic quantum number (m)

The magnetic quantum number m describes the orientation of orbital around the nucleus, which can have values depending on the azimuthal quantum number (l) $m = +l, (l - 1) \dots 0 \dots \dots \text{to} (l + 1) \dots \dots -l$. Thus a single line in the normal spectrum will appear as $(2l+1)$ lines if a magnetic field is applied.

Spin quantum number (s)

The spin quantum number (s) has values $\pm \frac{1}{2}$. This is explained by assuming that an electron spins on its axis in either a clockwise or an anticlockwise direction. This explains why some of the spectral lines are split into 2, 3, 4 or more and in addition some spectral lines are split still further into two lines or doublets.

n	l	m	<i>symbol</i>
1	0	0	1s (one orbital)
2	0	0	2s (one orbital)
2	1	+1,0,-1	2p (three orbitals)
3	0	0	3s (one orbital)
3	1	+1,0,-1	3p (three orbitals)
3	2	+2,+1,0,-1,-2	3d (five orbitals)
4	0	0	4s (one orbital)
4	1	+1,0,-1	4p (three orbitals)
4	2	+2,+1,0,-1,-2	4d (five orbitals)
4	3	+3,+2,+1,0,-1,-2,-3	4f (seven orbitals)

1.7 AUFBAU AND PAULI EXCLUSION PRINCIPLE

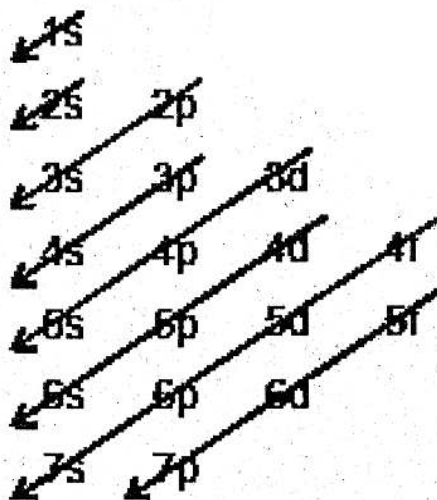
Aufbau a German term, **building up**, a principle, where the buildup or filling of electrons in atoms results from continually increasing the quantum numbers of increasing energies.

1. Electrons are placed in orbitals to give the lowest total energy to the atom. This means that the lowest values of n and l are filled first.
2. The *Pauli exclusion principle* requires that each electron in an atom have a unique set of quantum numbers. At least one quantum number must be different from those of every other electron. This principle does not come from the Schrodinger equation but from experimental determination of electronic structures.
3. *Hund's rule of maximum multiplicity* requires that electrons be placed in orbitals to give the maximum total spin possible or the maximum number of parallel spins.

1.7 VARIATION OF ENERGY LEVELS

To know the sequence in which the electrons are filled in increasing energy levels are an be represented as in figure given below. It can be seen that the order of filling of energy as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, etc.

After the 1s, 2s, 2p, 3s and 3p levels have been filled at argon, the next two electrons go into the 4s level and once the 4s level is full the 3d level is the next lowest in energy not the 3p level, thus 3d starts filling first than 4s. Similarly once 5s level is filled then lowest next energy level is 4d not 5p, thus electrons filling in 4d takes place. A further complication arises after 6s electrons are start filling in lower orbital 5d but after one electron 4f lower energy orbital starts filling and after completely filling 5d level start filling further.



Sequence of filling energy levels

1.8 LONG FORM OF PERIODIC TABLE BASED ON ELECTRONIC CONFIGURATION

The Russian chemist Mendeleeff in 1969, firstly attempted to divide elements on the basis of their chemical and physical properties in the order of increasing atomic weights, elements with similar properties appear at regular intervals called **periodic law**. He state that "*The physical and chemical properties of elements are periodic functions of their atomic weights.*"

In 1912, British physicist, H. Moseley, discovered new properties of elements called atomic number. As well known atomic number of an atom is equal to the number of protons present in the nucleus, which is equal to the number of electrons present outside the nucleus of the atom.

Thus the **modern periodic law** as "*The properties of elements are periodic functions of their atomic numbers.*"

According to increasing atomic number of elements are arranged in a table with similar properties fall in same column is known as periodic table. The elements fall in a same column and resemble similar properties are belong to same group or family of elements. The filling of the energy levels for the first ten elements, hydrogen to neon, atomic numbers 1-10 is shown in table below.

Elements	Configuration	1s	2s	2p
H	$1s^1$	↑		
He	$1s^2$	↑↓		
Li	$1s^2, 2s^1$	↑↓	↑	
Be	$1s^2, 2s^2$	↑↓	↑↓	
B	$1s^2, 2s^2 2p^1$	↑↓	↑↓	↑
C	$1s^2, 2s^2 2p^2$	↑↓	↑↓	↑ ↑
N	$1s^2, 2s^2 2p^3$	↑↓	↑↓	↑ ↑ ↑
O	$1s^2, 2s^2 2p^4$	↑↓	↑↓	↑↓ ↑ ↑
F	$1s^2, 2s^2 2p^5$	↑↓	↑↓	↑↓ ↑↓ ↑
Ne	$1s^2, 2s^2 2p^6$	↑↓	↑↓	↑↓ ↑↓ ↑↓

Long form of periodic table

The objective of the periodic table is to organize and systematize the chemistry elements. The arrangements of elements in this table is also in keeping with their electronic structures and help us to understand the reason why certain elements resemble one another and why they differ from the other elements in their properties. Another significance of this that reason why similar properties of elements come again at certain regular interval when they are arranged in the increasing atomic numbers, called *periodicity*, i.e. after 2, 8, 8, 18, 18 and 32 elements. The number 2, 8, 18 and 32 are referred to as *magic numbers* (due to extra stability). This can be understood by the electronic configuration of these elements as we can see in the table given below, where Z is atomic number. In so far as the chemical (and physical) properties of an element derive from its electronic configuration, and especially the configuration of its least tightly bound electrons, it follows that chemical periodicity and the form of the periodic table can be elegantly interpreted in terms of electronic structure.

Electron Configurations of the Elements

Element	Z	Configuration	Element	Z	Configuration
H	1	1s ¹	Ce	58	*[Xe]6s ² 4f ¹ 5d ¹
He	2	1s ²	Pr	59	[Xe]6s ² 4f ³
Li	3	[He]2s ¹	Nd	60	[Xe]6s ² 4f ⁴
Be	4	[He]2s ²	Pm	61	[Xe]6s ² 4f ⁵
B	5	[He]2s ² 2p ¹	Sm	62	[Xe]6s ² 4f ⁶
C	6	[He]2s ² 2p ²	Eu	63	[Xe]6s ² 4f ⁷
N	7	[He]2s ² 2p ³	Gd	64	*[Xe]6s ² 4f ⁷ 5d ¹
O	8	[He]2s ² 2p ⁴	Tb	65	[Xe]6s ² 4f ⁹
F	9	[He]2s ² 2p ⁵	Dy	66	[Xe]6s ² 4f ¹⁰
Ne	10	[He]2s ² 2p ⁶	Ho	67	[Xe]6s ² 4f ¹¹
Na	11	[Ne]3s ¹	Er	68	[Xe]6s ² 4f ¹²
Mg	12	[Ne]3s ²	Tm	69	[Xe]6s ² 4f ¹³
Al	13	[Ne]3s ² 3p ¹	Yb	70	[Xe]6s ² 4f ¹⁴
Si	14	[Ne]3s ² 3p ²	Lu	71	[Xe]6s ² 4f ¹⁴ 5d ¹
P	15	[Ne]3s ² 3p ³	Hf	72	[Xe]6s ² 4f ¹⁴ 5d ²
S	16	[Ne]3s ² 3p ⁴	Ta	73	[Xe]6s ² 4f ¹⁴ 5d ³
Cl	17	[Ne]3s ² 3p ⁵	W	74	[Xe]6s ² 4f ¹⁴ 5d ⁴
Ar	18	[Ne]3s ² 3p ⁶	Re	75	[Xe]6s ² 4f ¹⁴ 5d ⁵
K	19	[Ar]4s ¹	Os	76	[Xe]6s ² 4f ¹⁴ 5d ⁶
Ca	20	[Ar]4s ²	Ir	77	[Xe]6s ² 4f ¹⁴ 5d ⁷
Sc	21	[Ar]4s ¹ 3d ¹	Pt	78	*[Xe]6s ¹ 4f ¹⁴ 5d ⁹
Ti	22	[Ar]4s ² 3d ²	Au	79	*[Xe]6s ¹ 4f ¹⁴ 5d ¹⁰
V	23	[Ar]4s ² 3d ³	Hg	80	[Xe]6s ² 4f ¹⁴ 5d ¹⁰
Cr	24	*[Ar]4s ¹ 3d ⁵	Tl	81	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ¹
Mn	25	[Ar]4s ² 3d ⁵	Pb	82	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ²
Fe	26	[Ar]4s ² 3d ⁶	Bi	83	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ³
Co	27	[Ar]4s ² 3d ⁷	Po	84	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁴
Ni	28	[Ar]4s ² 3d ⁸	At	85	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁵
Cu	29	*[Ar]4s ¹ 3d ¹⁰	Rn	86	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁶
Zn	30	[Ar]4s ² 3d ¹⁰			
Ga	31	[Ar]4s ² 3d ¹⁰ 4p ¹	Fr	87	[Rn]7s ¹
Ge	32	[Ar]4s ² 3d ¹⁰ 4p ²	Ra	88	[Rn]7s ²
As	33	[Ar]4s ² 3d ¹⁰ 4p ³	Ac	89	*[Rn]7s ² 6d ¹
Se	34	[Ar]4s ² 3d ¹⁰ 4p ⁴	Th	90	*[Rn]7s ² 6d ²
Br	35	[Ar]4s ² 3d ¹⁰ 4p ⁵	Pa	91	*[Rn]7s ² 5f ² 6d ¹
Kr	36	[Ar]4s ² 3d ¹⁰ 4p ⁶	U	92	*[Rn]7s ² 5f ³ 6d ¹
			Np	93	*[Rn]7s ² 5f ⁴ 6d ¹
Rb	37	[Kr]5s ¹	Pu	94	[Rn]7s ² 5f ⁶
Sr	38	[Kr]5s ²	Am	95	[Rn]7s ² 5f ⁷
Y	39	[Kr]5s ² 4d ¹	Cm	96	*[Rn]7s ² 5f ⁷ 6d ¹
Zr	40	[Kr]5s ² 4d ²	Bk	97	[Rn]7s ² 5f ⁹
Nb	41	*[Kr]5s ¹ 4d ⁴	Cf	98	*[Rn]7s ² 5f ⁹ 6d ¹
Mo	42	*[Kr]5s ¹ 4d ⁵	Es	99	[Rn]7s ² 5f ¹¹
Tc	43	[Kr]5s ² 4d ⁵	Fm	100	[Rn]7s ² 5f ¹²
Ru	44	*[Kr]5s ¹ 4d ⁷	Md	101	[Rn]7s ² 5f ¹³
Rh	45	*[Kr]5s ¹ 4d ⁸	No	102	[Rn]7s ² 5f ¹⁴
Pd	46	*[Kr]4d ¹⁰	Lr	103	[Rn]7s ² 5f ¹⁴ 6d ¹
Ag	47	*[Kr]5s ¹ 4d ¹⁰			[Rn]7s ² 5f ¹⁴ 7p ¹
Cd	48	[Kr]5s ² 4d ¹⁰			[Rn]7s ² 5f ¹⁴ 6d ²
In	49	[Kr]5s ² 4d ¹⁰ 5p ¹			[Rn]7s ² 5f ¹⁴ 6d ³
Sn	50	[Kr]5s ² 4d ¹⁰ 5p ²			[Rn]7s ² 5f ¹⁴ 6d ⁴
Sb	51	[Kr]5s ² 4d ¹⁰ 5p ³			[Rn]7s ² 5f ¹⁴ 6d ⁵
Te	52	[Kr]5s ² 4d ¹⁰ 5p ⁴			[Rn]7s ² 5f ¹⁴ 6d ⁶
I	53	[Kr]5s ² 4d ¹⁰ 5p ⁵			[Rn]7s ² 5f ¹⁴ 6d ⁷
Xe	54	[Kr]5s ² 4d ¹⁰ 5p ⁶			
			Uuu	110	*[Rn]7s ¹ 5f ¹⁴ 6d ⁹
Cs	55	[Xe]6s ¹	Uuu	111	[Rn]7s ¹ 5f ¹⁴ 6d ¹⁰
Ba	56	[Xe]6s ²	Uub	112	[Rn]7s ² 5f ¹⁴ 6d ¹⁰
La	57	*[Xe]6s ² 5d ¹			

* Elements with configurations that do not follow the simple order of orbital filling.

NOTE: Actinide configurations are from J. I. Katz, G. T. Seaborg, and L. R. Morss, *The Chemistry of the Actinide Elements*, 2nd ed., Chapman and Hall, New York and London, 1986. Configurations for elements 100 to 112 are predicted, not experimental.

The long form periodic table is constructed by arranging elements in the order of increasing atomic number. The horizontal rows constitute periods while vertical rows constitute group. The elements of each group are now analogous to one another. This can be seen below in the Long form of periodic table based on atomic number.

Figure: Long form of periodic table based on atomic number

In this unit we have focused attention on the developments leading to Bohr atom model. The instances and reasons for the failure of classical physics are given. Using quantum theory, Planck, Einstein and Bohr explained black body radiation, heat capacity variation, photoelectric effect and atomic spectra of hydrogen. But each of the above theories had limited success. No doubt these theories rejected the classical concept of the arbitrary energy values for an atomic system. Since wave mechanics is based on new quantum postulates, the theories proposed by Planck, Einstein and Bohr are collectively called **Old Quantum Theory**. This loophole was overcome by de Broglie, Heisenberg and Schrodinger collectively known as **Wave Mechanics**. Atomic number of an atom is equal to the number of protons present in the nucleus, which is equal to the number of electrons present outside the nucleus of the atom. The properties of elements are periodic functions of their atomic

numbers. With increasing atomic number of elements are arranged in a table with similar properties fall in same column is known as **Periodic table**.

1.11 TERMINAL QUESTIONS

- 1: Explain the two main reasons for the failure of classical mechanics?
- 2: Derive an expression useful in calculating the energy of an electron in n th orbit of hydrogen atom?
- 3: What is the value of Redberg's constant (R_H) in cm^{-1} ?
- 4: Calculate the radius of the second orbit in hydrogen atom using Bohr's theory?
- 5: Calculate the four quantum numbers for the last electron of Nitrogen?
- 6: Explain the position of element from the electronic configuration of Chlorine?
- 7: Explain why Chromium and Copper both electronic configurations do not follow general trends?
- 8: Explain the limitations of Bohr's theory?
- 9: How electronic configuration help to predict the periodicity?
- 10: Derive the Schrödinger wave equation and discuss the significance of the wave function ψ in this equation?
- 11: What are radial and angular wave functions? What information we get from these functions.
- 12: Write the possible values of n , l and m for the electron in $3p$ orbital?
- 13: Define the limitations of the Bohr's theory of atomic structure?

1.12 ANSWERS

1. See the section 1.2
2. See the section 1.2 of subtitle Bohr atomic model
3. Redberg's constant = **$1.096776 \times 10^9 \text{ cm}^{-1}$**
4. Radius of second orbit of hydrogen atom according to Bohr's theory is

5. The configuration of ${}_7\text{N}^{14} - 1s^2, 2s^2, 2p^3$. The principal quantum number $n=1$, Azimuthal quantum number (l) = 1, magnetic quantum number (m) = -1 and spin quantum number (s) = $+\frac{1}{2}$.
6. See section 1.9
7. Due to maximum multiplicity as well as exchange energy the configuration of Chromium and Copper actual electronic configuration is differ from the normal configuration.
8. See section 1.2 of the limitation of Bohr's theory.
9. See section 1.8
10. See section 1.5
11. See section 1.6
12. For 3p orbital the quantum numbers are as follows, principle quantum number (n) = 3, azimuthal quantum number (l) = ($n-1$) = 1, and for magnetic quantum number (m) = ($+l$ to $-l$) = +1, 0, -1.
13. See the section 1.2 of subtitle limitations of Bohr atomic model.

SUGGESTED READING

1. **Concise Inorganic Chemistry**, J D Lee, Oxford University Press
2. **Introduction to Inorganic Chemistry**, B.R. Puri, Sharma and Kalia, Milestone Publishers & Distributors
3. **Advance Inorganic Chemistry**, F. A. Cotton and G. Wilkinson, Interscience Publishers, J. Wiley and Sons.
4. **Inorganic Chemistry**, B. Sivasankar, Pearson Education

UNIT 2: PERIODIC PROPERTIES OF ELEMENTS

Structure

- 2.1 Introduction
 - Objectives
- 2.2 Types of radii
- 2.3 Ionisation potential
 - Factors affecting the magnitude of I. P.
- 2.4 Electron affinity and its variation
- 2.5 Electronegativity (Pauling, Mulliken and Allred Rochow scale) and its Variation
- 2.6 Concept of effective nuclear charge and shielding effect
(Calculation of Screening constant with Slater's rules.)
- 2.7 Summary
- 2.8 Terminal Questions
- 2.9 Answers

2.1 INTRODUCTION

To understand chemical bonding between atoms and geometry and shapes of the molecules, it is necessary have knowledge about the atomic sizes, their interactions and their impact to decide the atomic properties such as electron affinity, ionization potential and electronegativity. How and which factors are responsible to alter the properties of element with another elements explained by different laws.

Objective

- Periodic properties of elements
- Size of atoms and ions
- Types of ions
- Electron affinity of elements
- Ionisation potential of elements
- Electronegativity of elements
- Effective nuclear charge

2.2 TYPES OF RADII

The size of atoms and ions are generally reflected in the magnitude of their respective radii. If the atom or an ion is assumed to be spherical, the radius corresponds to the atomic and ionic sphere or may be taken as the distance between the centre of the nucleus and the outermost shell of electrons. However, the absolute size of an atom or ion is difficult to define because of following reasons:

1. According to quantum mechanics, there is no certainty with the exact position occupied by electrons at any time. It observed theoretically, an electron may be very close to the nucleus at times and it may be far from the nucleus at other times. Thus the probability of electron never zero even at very large distance from the nucleus.
2. The size of atom would change with change in the environment because it is not possible to have isolated atoms and probability distribution of electrons in an atom influenced by atoms present in its environment.

The **metallic radius** is half of the experimentally determined distance between the nuclei of nearest neighbors in the solid.

The **covalent radius** of a non-metallic element is half of the experimentally determined distance between the nuclei of nearest neighbors in the solid.

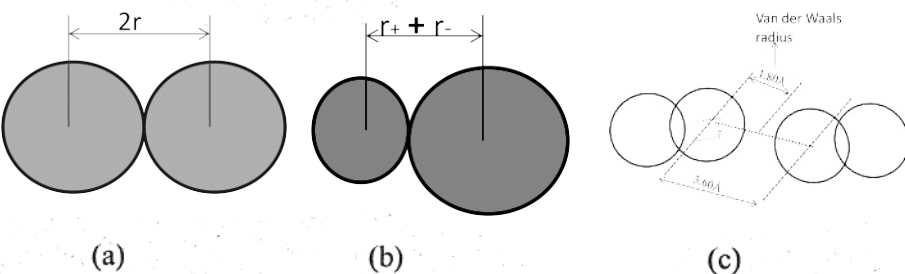


Figure 1: (a) covalent radius (b) ionic radius and (c) Van der Waals' Radius

Van der Waals' Radius

The Van der Waals' radius is defined as one half of the distance between the nuclei of two adjacent identical atoms of two neighboring molecules of an element in the solid state. The name van der Waals' radius is used because the forces existing between the molecules are van der

Waals' force of attraction. X-ray studies of solid state is used for determine the van der Waals' radii.

Variation of covalent radii in a periodic table

The covalent radii in a period can be easily explained on the basis of electronic configurations and effective nuclear charges i.e. shielding effect. Generally in a period from left to right the radii of atom decrease gradually because electrons increase within an orbit with increases of the nuclear charge. Where as in a group from top to bottom in periodic table atomic radii increases because there is increase of electrons with increases of number of orbit. The Variation of covalent radii in a periodic table may be observed in table 1.

Table 1: Non polar covalent radii (pm)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 32																	He 31
Li 123	Be 89											B 82	C 77	N 75	O 73	F 71	Ne 69
Na 154	Mg 136											Al 118	Si 111	P 106	S 102	Cl 99	Ar 98
K 203	Ca 174	Sc 144	Ti 132	V 122	Cr 118	Mn 117	Fe 117	Co 116	Ni 115	Cu 117	Zn 125	Ga 126	Ge 122	As 120	Se 117	Br 114	Kr 111
Rb 216	Sr 191	Y 162	Zr 145	Nb 134	Mo 130	Tc 127	Ru 125	Rh 125	Pd 128	Ag 134	Cd 148	In 144	Sn 140	Sb 140	Te 136	I 133	Xe 126
Cs 235	Ba 198	La 169	Hf 144	Ta 134	W 130	Re 128	Os 126	Ir 127	Pt 130	Au 134	Hg 149	Tl 148	Pb 147	Bi 146	Po (146)	At (145)	Ra

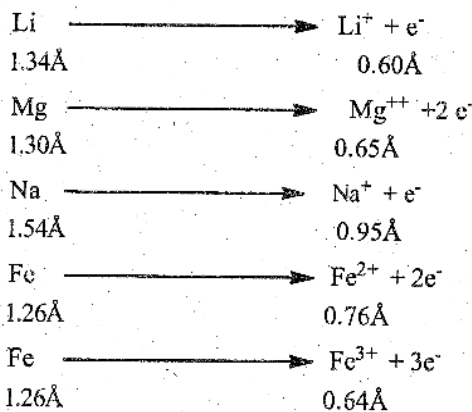
Source: R. T. Sanderson, *Inorganic Chemistry*, Reinhold, New York, 1967, p. 74; and E. C. M. Chen, J. G. Dojahn, and W. E. Wentworth, *J. Phys. Chem. A*, 1997, 101, 3088.

Ionic radius

The ionic radius of an element is related to the distance between the nuclei of neighboring cations and anions. It corresponds to the radius of an ion in an ionic crystal or the distance of electron charge cloud from the nucleus. For this purpose X-ray measurements is used to determine any ionic compound.

Radii of cations and anions

A positive charge ion i.e. a **cation** results from the loss of one or more electron from the valence shell of an atom. Now the effective nuclear charge acts on a lesser number of electron therefore cation is much smaller than the corresponding atom. For example atom changes into cation is shown below



A negative ion i.e. an **anion** results from one or more electrons are added to the valence shell of the atom. At this condition the same nuclear charge acts on a large number of electrons, in other words effective nuclear charge per electron decreases therefore electrons cloud expands due to less attraction by the nucleus. Consequently, the radius of a negative ion is larger than that of its corresponding atom.

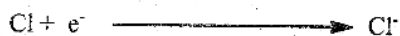


Table 2: Crystal radius and nuclear charges

Ion	Protons	Electrons	Radius (pm)
O^{2-}	8	10	126
F^-	9	10	119
Na^+	11	10	116
Mg^{2+}	12	10	86

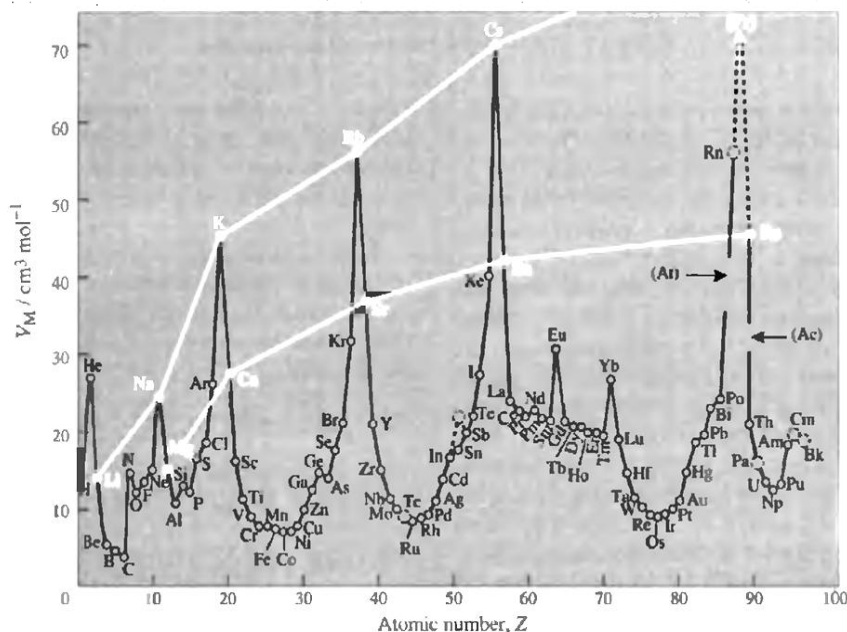


Figure 2: Atomic volumes (molar volumes) of the elements in the solid state.

Above figure given by Lothar Meyer's given atomic volume curve: the alkali metals appear at the peaks and elements near the centre of each period (B, C; Al, Si; Mn, Fe, Co; Ru; and Os) appear in the troughs. This finds a ready interpretation on the electronic theory since the alkali metals have only 1 electron per atom to contribute to the binding of the 8 nearest- neighbor atoms, whereas elements near the centre of each period have the maximum number of electrons available for bonding. Elements in other groups fall on corresponding sections of the curve in each period, and in several groups there is a steady trend to higher volumes with the increasing atomic number. As would be expected from the effects of shielding, the ionization energy varies with different nuclei and different numbers of electrons.

2.3 IONIZATION POTENTIAL

Ionization Energy (IE)

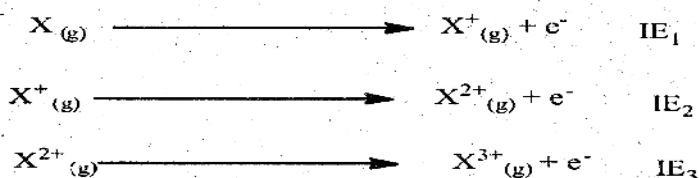
The ionization energy, also known as the **ionization potential**, is the energy required to remove an electron from a gaseous atom or ion. Ionisation energy is defined as the minimum energy required to remove an from an atom, ion or molecule leaving each without any kinetic energy. The unit for ionisation energy is kJ mol^{-1} and we use the symbol I for representing ionisation energy of an element.

Can be represented by the following equation



Trends for the first ionization energies of the early elements in the periodic table.

In the case of multielectron atoms, more than one electron can be removed; that is, second, third and higher ionisation energies are also possible. It is also observed that the second ionisation energy (IE_2) is larger than the first ionization energy, like wise third ionization energy (IE_3) is grater than second ionization potential. Since during the second or third ionization the electron is to be removed from a positively charged ion against forces of attraction.



Ionization energy is measure in electron volts (eV) as well as in joules or kilojoules.

Where,

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ joule} = 1.6 \times 10^{-22} \text{ kilojoule}$$

Factors affecting the Ionization Energy

1. **Atomic size:** The atomic size is larger, the smaller is the ionization energy because as size of the atom increases the outer electron lie far away the nucleus hence, attractive Coulomb's force decreases and it is much easier to knock out an electron from the outer shell of atom.
2. **Nuclear charge:** The force of attraction between the nucleus and outermost electron increases with increase in nuclear charge. Thus, the greater is the nuclear charge, the greater is the energy needed to pull out an electron from the atom. Hence, ionization energy increases with increases in nuclear charge.
3. **Screening effect:** The large number of electrons in inner shells, smaller is the ionization energy because inner shell electrons screen or shield between the nucleus and outer most shell's electron called shielding effect. As result the electron of valence shell experience less attraction consequently ionization energy would be low.
4. **Penetration effect:** The *s* orbital electrons have great probability of come close to nucleus or penetrate more towards the nucleus than *p*, *d* and *f* orbitals. Thus *s* orbital electrons experience more attraction other orbitals. We may thus say ionization energy of an electron from a given energy level decreases in the order $s > p > d > f$ electron.
5. **Electronic configuration:** Certain configurations are more stable than others such as fully filled or exactly half filled orbitals of atom; ionization energies are higher than expected normally from its position in the periodic table. For example He, Ne, Ar, Kr, Xe and Rn have highest ionization energies of their period because of fully filled orbitals and ionization energy of nitrogen is higher than the before element carbon and after element oxygen of its period due to exactly half filled orbital. Similarly, Beryllium (Be) ionization energy is greater than the before element lithium (Li) and after element Carbon (C) due to fully filled *s*-orbital.

Group trends

A general increase of radius and decrease in IE down most groups is dominated by the increasing principal quantum number of outer orbitals. Effective nuclear charge also increases, and can give rise to irregularities in the IE trends.

Periodic trends

Increasing nuclear charge causes a general increase of IE and a decrease of radius across any period. Breaks in the IE trend are found following the complete filling or half filling of any set of orbitals.

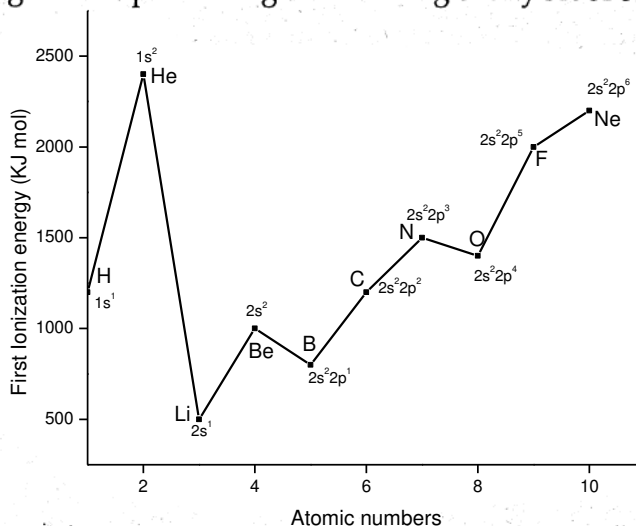


Figure 3: Variation of ionization energy with atomic number in the first and second period

The high ionisation energies of noble gases indicate the greatest stability of np^6 configuration (except in the case of helium having $1s^2$ configuration) known as **noble gas configuration**. You will soon see that attainment of noble gas configuration is one of the guiding factors in bond formation. When elements of group 1 (except hydrogen) lose their single ns^1 electron, their configuration becomes that of the preceding noble gas. Hence ionisation energy is low for alkali metals and they form cations easily.

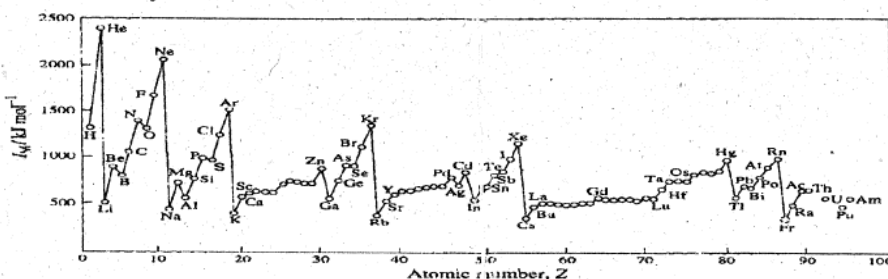


Figure 4: First ionization energies of various elements

2.4 ELECTRON AFFINITIES

Typical elements in Groups V, VI and VII would be expected to achieve a noble gas configuration more easily by gaining electrons rather than losing them. Electron affinity is a measure of the energy change when an atom accepts an extra electron represented by E_A



Group Trends: The electron affinity falls with the increasing size of the atom. The anomalous value for fluorine is explained on the grounds that since the fluorine atom is small, the incoming electron encounters strong repulsion by the nine electrons already closely shielding the nucleus. In each case, the ion produced by electron addition is *larger* than the atom from which it was formed.

Periodic Trends: The electron affinities, for the addition of *one* electron to elements in Periods 2 and 3. Energy is evolved by many atoms when they accept electrons. In the cases in which energy is absorbed it will be noted that the new electron enters either a previously unoccupied orbital or a half-filled orbital; thus in beryllium or magnesium the new electron enters the p orbital, and in nitrogen electron-pairing in the p orbitals is necessary.

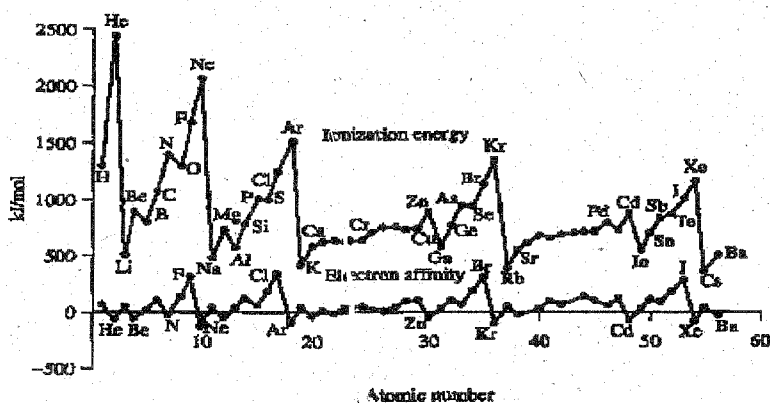


Figure 5: Showing energy / plot of the ionization energy (IE) and electron affinity in elements

2.5 ELECTRONEGATIVITY

The term electronegativity defined differently by different investigators. The approaches of some of the investigators are as follows

Pauling Approach

Pauling defined electronegativity as the power of an atom in a molecule to attract electrons to itself. He calculated electronegativity of different elements from the thermodynamic data. He considers the bond dissociation energy A-B is higher than the mean of the bond dissociation energies of A-A and B-B. The difference between energy of the bond dissociation energy A-B and the mean of the bond dissociation energies of A-A and B-B is related to the electronegativities of A and B by relation as

For reaction $\frac{1}{2} (A-A) + \frac{1}{2} (B-B) \longrightarrow A-B$

$$\Delta = E_{A-B} - \frac{1}{2} (E_{A-A} + E_{B-B}) = 23 (\chi_A - \chi_B)^2$$

or $\Delta = 23 (\chi_A - \chi_B)^2$

Later on he took the geometric mean instead of arithmetic mean as

$$\Delta' = E_{A-B} - (E_{A-A} + E_{B-B})^{1/2} = 30 (\chi_A - \chi_B)^2$$

The dissociation energies are taken in kcal par mole. Assuming arbitrarily the electronegativity of hydrogen to be 2.1, Pauling determined electronegativity of other elements. These values are given in table 3.

Table 3: Electronegativity (Pauling units)

1	2	12	13	14	15	16	17	18
H 2.300								He 4.160
Li 0.912	Be 1.576		B 2.051	C 2.544	N 3.066	O 3.610	F 4.193	Ne 4.787
Na 0.869	Mg 1.293		Al 1.613	Si 1.916	P 2.253	S 2.589	Cl 2.869	Ar 3.242
K 0.734	Ca 1.034	Zn 1.588	Ga 1.756	Ge 1.994	As 2.211	Se 2.424	Br 2.685	Kr 2.966
Rb 0.706	Sr 0.963	Cd 1.521	In 1.656	Sb 1.824	Te 1.984	I 2.158	Xe 2.339	
Cs 0.659	Ba 0.881	Hg 1.765	Tl 1.789	Pb 1.854	Bi (2.01)	Po (2.19)	At (2.39)	Rn (2.60)

SOURCE: J. B. Mann, T. L. Meek, and L. C. Allen, *J. Am. Chem. Soc.*, **2000**, *122*, 2780, Table 2.

Allred and Rochow’s Approach

They defined the electronegativity as the electrostatic force of attraction apply by the nucleus of an atom on the valency electrons. They use effective nuclear charge Z_{eff} for the calculating electronegativity by empirical relation

$$\text{Electronegativity } (\chi) = 0.359 \times \frac{Z_{eff}}{r^2} + 0.744$$

Where

 Z_{eff} = effective nuclear charge

r = covalent radius of the atom (Å)

The electronegativities are found remarkably close to those reported by Puling.

Mulliken's Approach

Mulliken suggested that the average of the ionization energy (EI) and electron affinity (EA) of an atom should be a measure of the electronegativity and proposes the empirical formula

$$\chi = 0.374 \left[\frac{IE + EA}{2} \right] + 0.17$$

Where, IE and EA are in electron-volts.

Factors determining Electronegativity

The ability of an atom in a molecule to attract electron itself depends upon many factors such as charge on the atom, hybridization, effect of substituents, effect of ionization energy (IE) and electron affinity (EA), effective nuclear charge, etc.

Electronegativities of elements in periodic table

The electronegativities of elements in **group** decreases as we move from up to down. Because effective nuclear charge (Z_{eff}) decreases with increase in size of atom in a group from up to down. Whereas the electronegativity goes on increasing with increases atomic number as we move left to right along a period because the effective nuclear charge (Z_{eff}) increases with decreases in size of atom in a period from left to right. The electronegativities of elements in periodic table a comparative graph is shown in figure 6.

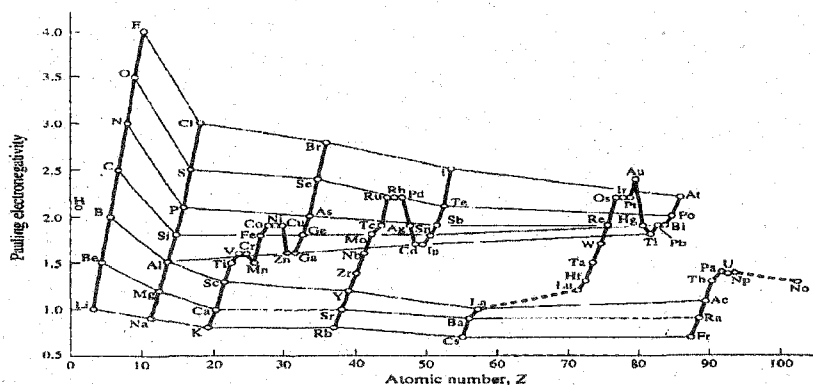


Figure 6: Graph of electronegativity of various elements

Applications of electronegativity

Electronegativity has very wide range of applications some are as calculation of percentage ionic character of covalent bond, calculation of enthalpies of formation of compounds, calculation of bond length, types of bonds, bond angles in molecules, reaction mechanisms, and explanation of diagonal relationship.

The development of **ionic character in a covalent bond** between two atoms due to difference in the electronegativities of them. The greater the difference in the electronegativities, greater would be development of ionic character and higher would be stability of resulting bond. Pauling suggested empirical equation for calculation the percent ionic character as

$$\text{Percent ionic character} = 18 (\chi_A - \chi_B)^{14}$$

Pauling also proposed the relation for calculating **enthalpy of formation** of a compound as

$$\Delta H_f = 23 \epsilon (\chi_A - \chi_B)^2 - 55.4 n_N - 26.0 n_O$$

Where

ΔH_f = enthalpy of formation

n_N and n_O are numbers of nitrogen and oxygen atoms in the molecule ϵ , would be 1, 2, 3, etc., depending upon the number of bonds in the molecule. For example, =1 for HCl, =2 for BeCl₂ and soon. The value from it is approximate for example BeCl₂ calculated value is 103.5 kcal mol⁻¹ where as experimental value is 122 kcal mol⁻¹.

Shoemaker and Stevenson proposed the relation for calculation **bond length** using electronegativity as

$$d_{A-B} = r_A + r_B - 0.09(\chi_A - \chi_B)$$

Where

d_{A-B} is the actual bond length between A and B

r_A and r_B are the covalent radii of A and B.

$\chi_A - \chi_B$ is the electronegative difference

From this relation the calculated value is very close or exacts the same with the experimental value.

Types of bond formed between two atoms would markedly depend upon the difference in their electronegativities. When this difference very small or zero the bond formed between two atoms would be

covalent and if the difference exceeds 2.5, the bond formed would be *electrovalent*. However, the electronegativity difference is appreciably less than 2.5 the bond formed would be *polar covalent*.

Explanation of **diagonal relationship**, the electronegativity increases as we go left to right in the period and decreases as we move from up to down in a group. As a result of these two opposite changes as we move diagonally, these two effects partly cancel and there is no remarkable change in electronegativity. This is the reason why Li (1.0) and Mg (1.2) have close values of electronegativity and hence Li and Mg have similar chemical properties.

2.6 CONCEPT OF EFFECTIVE NUCLEAR CHARGE AND SHIELDING EFFECT

Screening effect

In multi electron atoms there are the number of electrons, some of them occupies lower energy orbitals, because these orbitals occur between nuclear and higher energy orbitals they tend to decrease the effect of nuclear charge on the electrons present in higher energy orbitals, this effect is called **screening effect**. Since the electrons present in different types of orbitals such as s, p, d and f-orbitals are screened differently because they are attracted to different extents by the nucleus. The various orbitals are held at different distances from the nucleus and have different energies. The extent of screening of an electron by other electrons in the atom is calculated with the help of empirical rule known as **Slater's rules**.

Concept of effective nuclear charge (Slater's rules)

Consider an electron in one of the atomic orbital in multi electron atom, due to the electrostatic repulsion by other electrons in same and other orbitals, the nuclear charge felt by this electron will be less than the actual nuclear charge. This electron is said to be screened from the exact nuclear charge and the reduced charge felt by the electron is called **effective nuclear charge**. The intervening electrons screen the electrons present in peripheral orbitals. The effective nuclear charge of any electron in the configuration of an atom can be calculated by following relation:

$$Z_{\text{eff}} = Z_{\text{actual}} - S$$

Where

S = screening or screening constant

The screening constant can be evaluated by following empirical rules known as the Slater's rules:

1. The various orbitals are grouped in the order given below, starting from the nucleus:

(1s) (2s 2p) (3s 3p) (3d) (4s 4p) (4d) (4f) (5s 5p)....etc.

2. For an electron present in a group of s and p electrons, the value of the screening constant (S) is the sum of following contributions:

- (a) No contribution from any electron present in groups of orbitals lying right side of the group for which screening constant (S) is to be calculated.
 - (b) A contribution of 0.35 from every electron present in the group of orbitals as ns np under consideration. A contribution of 0.30 from the other electron in 1s, if screening constant (S) is to be calculated for 1s orbital.
 - (c) A contribution of 0.85 per electron from all electrons present in the $(n-1)^{\text{th}}$ shell.
 - (d) A contribution of 1.0 per electron from all electrons present in the $(n-2)^{\text{th}}$ shell.
3. For an electron present in a group of d and f electrons, rules for 2c and 2d replaced by for all electrons in the inner shell contribute per electron, 1.0 rule

Important applications of Slater's rules

The Slater's rules are also applied to explain the certain facts as follows:

Why a 4s orbital is filled earlier than a 3d orbital: Consider a potassium atom having atomic number 19. In this case out of 19, 18 electrons filled as in argon atom ($1s^2, 2s^2, 2p^6, 3s^2, 3p^6$). The 19th electron may enter a 4s or 3d orbital. Let us calculate the effective nuclear charge (Z_{eff}) for 19th electron when enters the 4s orbital.

$$Z_{\text{eff}} = 19 - 0 \times 0.35 - 8 \times 0.85 - 10 \times 1.0 = 19 - 16.80 = 2.20$$

If the effective nuclear charge (Z_{eff}) for 19th electron when enters the 3d orbital

$$Z_{eff} = 19 - 0 \times 0.35 - 18 \times 1.0 = 19 - 18.0 = 1.0$$

Therefore, we can say 4s electron feels much more electrostatic attraction than 3d electron due higher due to greater effective nuclear charge, consequently 4s associated with lower energy then 3d configuration. Thus, a 4s orbital is filled earlier than a 3d orbital.

Why transition metal ions lose ns -electron first during ionization:

For Manganese (Mn) atom of atomic number 25, has the configuration $1s^1 2s^2 p^6 3s^2 p^6 3d^5 4s^2$ according to Slater's rules. Let us calculate Z_{eff} for 3d and 4s electron.

$$Z_{eff} \text{ for 3d electron } Z_{eff} = 25 - (0.35 \times 4 + 1.0 \times 18) = 5.60$$

$$Z_{eff} \text{ for 4s electron}$$

$$Z_{eff} = 25 - (0.35 \times 1 + 13 \times 0.85 + 1.0 \times 10) = 3.60$$

Z_{eff} for the 4s is less than the 3d electron, suggest that 4s electron feels less attraction than 3d electron with nucleus. Hence, the removal of the 4s electron from an isolated Mn is much easier than the 4d electron.

Why an anion is always bigger and a cation is always smaller than the parent atom: For example a chlorine atom with electronic configuration $1s^2 2s^2 p^6 3s^2 p^5$. Z_{eff} for last electron of chloride atom

$$Z_{eff} = 17 - (0.35 \times 6 + 8 \times 0.85 + 1.0 \times 2) = 6.10$$

$$Z_{eff} \text{ for last electron of chloride ion}$$

$$Z_{eff} = 17 - (0.35 \times 7 + 8 \times 0.85 + 1.0 \times 2) = 5.75$$

Z_{eff} for Cl^- ion is less than in the case of Cl atom. Therefore, the electrostatic attraction in Cl atom is more than the Cl^- ion. Consequently, the size of the chloride ion will be larger than the chlorine atom.

Similarly in the Sodium (Na) atom and sodium ion (Na^+), the electronic configuration of sodium is $1s^2 2s^2 p^6 3s^1$.

$$Z_{eff} \text{ for last electron of sodium atom}$$

$$Z_{eff} = 11 - (0.35 \times 0 + 8 \times 0.85 + 1.0 \times 2) = 2.20$$

$$Z_{eff} \text{ for last electron of sodium ion}$$

$$Z_{eff} = 11 - (0.35 \times 7 + 1.0 \times 2) = 6.85$$

Z_{eff} for Na^+ ion is greater than in the case of Na atom. Therefore, the electrostatic attraction in Na atom is less than the Na^+ ion. Consequently, the size of the sodium ion will be lesser than the sodium atom.

Why atomic size decreases with increases atomic number in a period: If we consider the first transition series from Sc to Zn. The Z_{eff} goes on increases with increases atomic number. Therefore, the electrostatic attraction with nucleus also increases with atomic number. Thus the atomic size goes decreases with increases in atomic number in series.

Why ionization energy trends successively increases: the first ionization energy is always less than the second and second ionization energy is always less than the third ionization energy and so on. This is because effective nuclear charge (Z_{eff}) of the atom goes increases with removal of electron of atom. This may be verified by the students by calculation the Z_{eff} of free atom and unipositive, dipositive, tripositive ions.

Limitations of Slater's rules:

1. According to Slater's rules, the screening by s and p electrons of the same shell is equal. But we discussed that s shell electrons are more penetrating than the p electrons of the same shell therefore, screening by s electrons will be more than the p electrons.
2. According to Slater's rules, the outer shell electrons do not shield the inner electron. This might be not true for example; the outer s-shell electrons penetrate close to the nucleus and thus apply a shielding effect.
3. According to Slater's rules, s, p, d and f electrons of the same shell screen with same extent to the higher shell electron. But the electrons of s, p, d and f orbitals differ much in their penetrating power with order $ns > np > nd > nf$. Thus the electrons present in these orbital not have same screening power for the outer shell electrons.

2.7 SUMMARY

From the this unit you can understand which factors are responsible to alter the properties of element with another element. Comprehension about the atomic sizes, their interactions and their impact to decide the atomic properties such as electron affinity, ionization

potential and electronegativity. To understand the periodic properties and relation of elements, sizes of atoms and ions, stability of ions, stability of electronic configurations with the role of effective nuclear charges.

2.8 TERMINAL QUESTIONS

1. What is the effective nuclear charge felt by 1s electron of helium atom?
2. What is the effective nuclear charge felt by 2p electron for a oxygen atom?
3. Calculate the effective nuclear charge felt by a 3d electron of Chromium?
4. Arrange the following species in the order of increasing size
 - i) Ba^{2+} , Ca^{2+} , Sr^{2+} , Ra^{2+}
 - ii) Ca^{2+} , Cl^- , K^+ , S^{2-}
 - iii) P, S, Si, Cl,
5. What do you mean by isoelectronic ions? Arrange the following series by size? Mg^{2+} , Al^{3+} , O^{2-} , F^- , N^{3-}
6. Explain why a Van der Waals radius of Chlorine is greater than the covalent radii of chlorine.
7. Explain the term ionization energy of an element? What factors does it depend?
8. Why the second and third ionization energies is much higher than the first ionization energy.
9. Explain which of the pairs has higher ionization energy and why?
 - i) B, Be
 - ii) I, Br
 - iii) K, Na
 - iv) S, P
10. Which of the two has higher ionic radii and why? Al^+ and Al^{3+}
11. The second ionization energy of the sodium is greater than the first ionization energy?
12. Why the electron affinity of noble gases is zero?
13. Explain the term electronegativity, how it is related to the electron affinity and ionization energy?
14. How we can calculate the percentage ionic characters of the covalent bonds?

2.9 ANSWERS

1. The electronic configuration of helium atom is $1s^2$
There is one more electron thus the screening constant, $S = 1 \times 0.30$ Hence $Z_{\text{eff}} = 2 - 0.30 = 1.70$
2. Effective nuclear charge felt by 2p electron for a oxygen atom
The electronic configuration of Oxygen atom is $1s^2, 2s^2, 2p^4$
There are five outer electron in group ($2s^2, 2p^4$)
screening constant, S for 2p electrons = $5 \times 0.35 + 2 \times 0.85 = 3.18$
Hence Z_{eff} felt by 2p = $8 - S = 4.82$
 Z_{eff} felt by 1s = $8 - 0.30 = 7.70$
3. Effective nuclear charge felt by a 3d electron of Chromium as
Imagine an extra electron in last filled orbital 4s
Screening constant, S for 4s electrons = $1 \times 0.35 + (8+5) \times 0.85 + 1 \times 10 = 21.4$
 Z_{eff} at the periphery of Cr atom = $24 - 21.4 = 2.60$
4. Following species arrange in the order of increasing size
 - i) $\text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Ra}^{2+}$
 - ii) $\text{Ca}^{2+}, \text{K}^+, \text{Cl}^-, \text{S}^{2-}$
 - iii) $\text{Cl}, \text{S}, \text{P}, \text{Si}$,
5. isoelectronic means same electrons in ions. following series by size as $\text{N}^{3-} > \text{O}^{2-} > \text{F}^- > \text{Mg}^{2+} > \text{Al}^{3+}$
6. See section 2.2
7. See section 2.3
8. Answer as question 11.
9. i) B ii) Br iii) Na iv) P
10. Al^+ has higher ionic radii than Al^{3+} because effective nuclear charge in Al^+ is higher than Al^{3+} .
11. The second ionization energy of the sodium is greater than the first ionization energy because in sodium atom outer most orbital is only 1 electron after the removal of that electron in first ionization were as in second ionization the filled first orbital came

therefore removal of electron is not easy thus high ionization energy.

12. EA of Nobel Gas is zero because there is no vacancy to gain electron in its outer most orbital.
13. Pauling defines electronegativity as a power of an atom in a molecule to attract electrons to itself.

Mulliken's suggested

$$\text{Electronegativity } (\chi) = 0.187 (\text{IE} + \text{EA}) + 0.17$$

14. Percent ionic Character = $18(\chi_A - \chi_B)^{1.4}$

Or

$$\text{Percent ionic Character} = 16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2 \text{ By Symth.}$$

SUGGESTED READINGS

1. **Concise Inorganic Chemistry**, Lee, J. D., Blackwell science, Oxford University Press
2. **Principles of Inorganic Chemistry**, Puri, B.R., Sharma, L. R., Kalia, K. C., Vallabh Publication, Delhi, 2003
3. **Advance Inorganic Chemistry**, F. A. Cotton and G. Wilkinson, Interscience Publishers, J. Wiley and Sons.
4. **Inorganic Chemistry**, B. Sivasankar, Pearson Education

UNIT 3: CHEMICAL BONDING

Structure

- 3.1 Introduction
 - Objective
 - 3.2 Ionic Bonding
 - 3.3 Covalent bonding
 - 3.4 Valence bond theory (VBT)
 - 3.5 VSEPR theory/ concept
 - 3.6 Molecular Orbital Theory
 - 3.7 Weak Interactions (Hydrogen bonding)
 - 3.8 Metallic Bond
 - 3.9 Summary
 - 3.10 Terminal Questions
 - 3.11 Answers
-

3.1 INTRODUCTION

In this unit learner may learn how the atoms are combined with each other and how the atoms combination takes place to form molecules. Learner may also come to know what type of properties may help the atoms for combine the other or same atoms and what extent they may combine with other atoms. Learner also comes to know what types of bonding takes place between the atoms and how extent the theory applicable in the formation of molecules.

Objective

- Types of bonds
- Ionic bonds
- Covalent bonds
- VBT
- MOT
- Hydrogen Bonding
- Metallic bonds

TYPES OF BONDS:

CHEMICAL BOND AND VALENCE

The force which results from the interaction between various atoms that form a stable molecule is referred to as a chemical bond. It is defined as a force that holds two or more atoms together as a stable molecule. The valence electrons number can determine the number of bonds formed by an atom in a molecule.

OCTET RULE

Atoms interact by electron transfer or sharing so as to have the stable outer shell of eight electrons. This tendency for atoms to have eight electrons or near inert gas configuration in the outer shell is known as **Octet rule**.

IONIC BOND

The electrostatic attraction between the cations(+ve) and anions(-ve) produced by electron transfer constitutes an **Ionic** or **Electrostatic bond**. Following factors favour the formation of Ionic bond.

1. The ionisation energy of the metal atom which loses electrons should be low. That is why alkali metals and alkaline earth metals form Ionic bonds. The tendency to form ionic bond increases as we go down a group as there is a decrease in Ionisation Energy(IE).
2. The electron affinity(AE) of the electron accepting atom should be high. The elements of group VIA and VII B have high electron affinity. That is why they form ionic bonds with the metals. In moving down a group the electron affinity decreases and therefore, the tendency to form ionic bond decrease.
3. The Lattice Energy is the amount of energy released when one mole of an ionic compound is formed from its cations and anions. Greater the lattice energy, greater the strength of the ionic bond.

COVALENT BOND

The covalent bond is attractive force between atom created by sharing of an electron pair. It is indicated by a dash (–) between the two bonded atoms. After sharing both atoms have eight electrons in their outer most shell.

CONDITIONS FOR THE FORMATION OF COVALENT BOND

1. Each of the atoms should have 5, 6 or 7 valence electrons so as to have eight electrons by sharing 3, 2 or 1 electron respective form paired configuration. The non-metals of group VA, VIA and VIIA satisfy this condition and form covalent bonds.
2. Both the atom should have same for similar electronegativity.
3. Both the atoms should have equal or almost equal electron affinity.

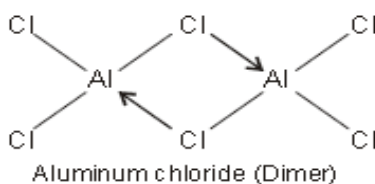
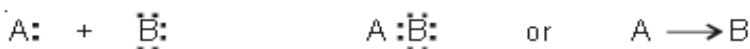
Examples given below:



COORDINATE BOND

In some cases a covalent bond is formed when both the electrons are supplied by one atom and sharing is done by both the atoms. Such a bond is called **Coordinate covalent bond** or **dative bond**. The atom which donates a pair of electrons is called **donor**, while the atoms which accepts the electron pair is called **acceptor**. This type of bond is represented by an arrow pointing towards the acceptor atom.

Example given below:



Ozone molecule

3.2 IONIC BONDING

Ionic bonding is characterized by a large difference in electronegativity. Because a large difference indicates that the electronegativity of one element is high and that of the other is low, the average electronegativity must be intermediate in value. Any description of bonding must be consistent with experimental data on bond lengths, bond angles, and bond strengths. Angles and distances are most frequently determined by diffraction (X-ray crystallography, electron diffraction, neutron diffraction) or spectroscopic (microwave, infrared) methods. For many molecules, there is general agreement on the

bonding, although there are alternative ways to describe it. For some others, there is considerable difference of opinion on the best way to describe the bonding. In Ionic Bonding, Conditions favoring the ionic bond, radius ratio and structure of ionic solids.

The radius ratio

The radius ratio indicates the likely coordination numbers of the ions in a binary compound. A parameter that figures widely in the literature of inorganic chemistry, particularly in the 'radius ratio', γ (gamma), of the ions. The **radius ratio** is the ratio of the radius of the smaller ion (γ -small) to that of the larger (γ -large):

$$\gamma = \frac{r_{\text{small}}}{r_{\text{large}}}$$

In most cases, γ -small is the cation radius and γ -large is the anion radius. The minimum radius ratio that can support a given coordination number is then calculated by considering the geometrical problem of packing together spheres of different sizes given in table given below. It is argued that, if the radius ratio falls below the minimum given, then ions of opposite charge will not be in contact and ions of like charge will touch. According to a simple electrostatic argument, a lower coordination number, in which the contact of oppositely charged ions is restored, then becomes favourable. Another way of looking at this argument is that as the radius of the M^+ ion increases, more anions can pack around it, so giving a larger number of favourable Coulombic interactions. In this respect, compare CsCl, and its (8, 8)-coordination, with NaCl, and its (6,6)-coordination.

We can use our calculations of hole size to put these ideas on a firmer footing. A cation of radius between 0.225γ and 0.414γ can occupy a tetrahedral hole in a close-packed or slightly expanded close-packed array of anions of radius γ . The correlation of structural type with radius ratio. However, once the radius of a cation reaches 0.414γ , the anions are forced so far apart that octahedral coordination becomes possible and most favorable. Note that 0.225γ represents the size of the smallest ion that will fit in a tetrahedral hole and that cations between 0.225γ and 0.414γ will push the anions apart. However, the coordination number cannot increase to 6 with good contacts between cation and anions until the radius goes above 0.414γ . Similar arguments apply for the tetrahedral holes that can be filled by ions with sizes up to 0.225γ .

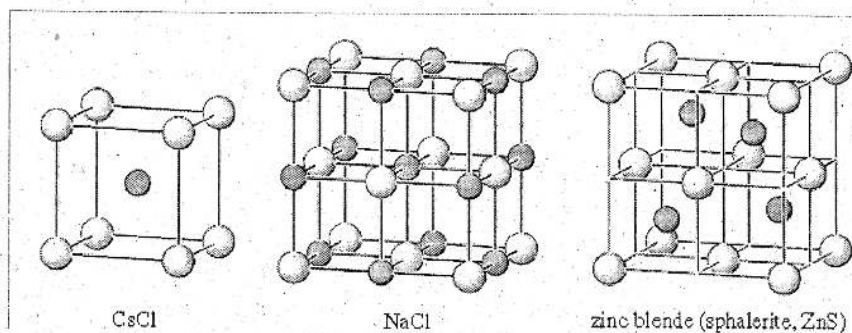
Radius ratio ($\tilde{a}$)	CN for 1:1 and 1:2 structure type	Binary AB Stoichiometries structure type	Binary AB ₂ Stoichiometries structure type
0.225-0.414	4:4	ZnS (ccp and hcp)	
0.414-0.732	6:6 and 6:3	NaCl (ccp), NiAs (hcp)	TiO ₂
0.732-1	8:8 and 8:4	CsCl CaF ₂	
1	12	None known	

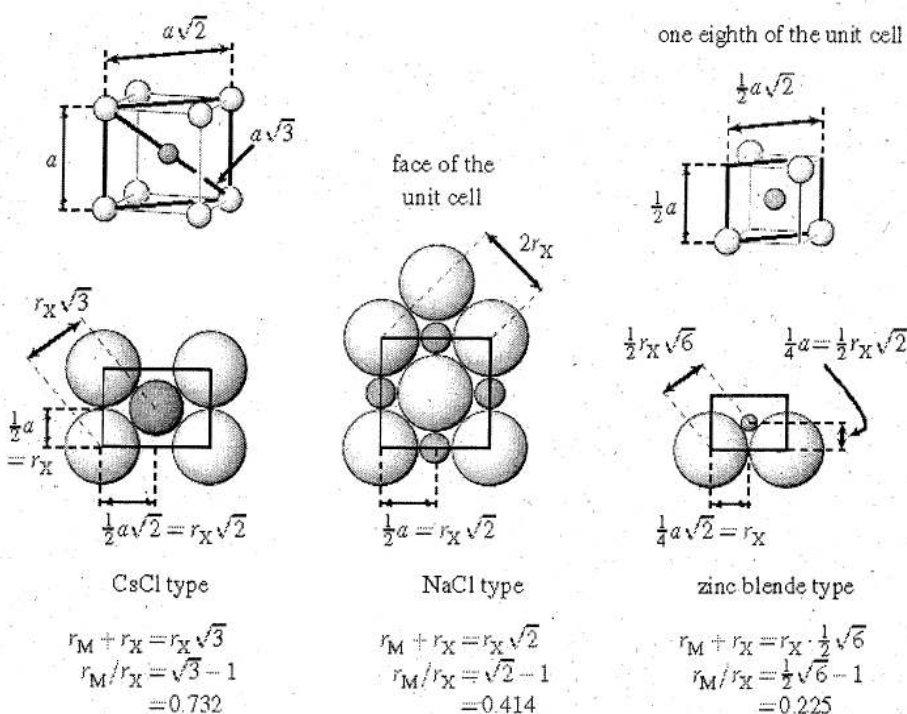
CN denotes coordination number.

These concepts of ion packing based on radius ratios can often be used to predict which structure is most likely for any particular choice of cation and anion. In practice, the radius ratio is most reliable when the cation coordination number is 8, and less reliable with six- and four-coordinate cations because directional covalent bonding becomes more important for these lower coordination numbers.

Some of the Radius ratios and observed structure types for the alkali metal halides

	Li	Na	K	Rb	Cs	
F	0.57	0.77	0.96*	0.88*	0.80*	
Cl	0.42	0.56	0.76	0.84	0.92	
Br	0.39	0.52	0.70	0.78	0.85	CsCl
I	0.35	0.46	0.63	0.69	0.76	type
	NaCl type					
	* r_X/r_M					





Above figure showing the calculation of the limiting radius ratios r_M/r_X

Ionic solids

Ionic solids, such as NaCl and KNO_3 , are often recognized by their brittleness because the electrons made available by cation formation are localized on a neighbouring anion instead of contributing to an adaptable, mobile electron sea. Ionic solids also commonly have high melting points and most are soluble in polar solvents, particularly water. However, there are exceptions: CaF_2 , for example, is a high-melting ionic solid but it is insoluble in water. Ammonium nitrate, NH_4NO_3 , is ionic in terms of its interactions between the ammonium and nitrate ions, but melts at 170°C .

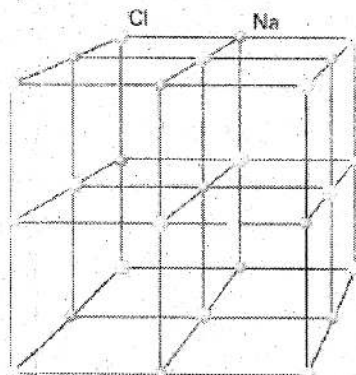
The classification of a solid as ionic is based on comparison of its properties with those of the **ionic model**, which treats the solid as an assembly of oppositely charged, hard spheres that interact primarily by nondirectional electrostatic forces (Coulombic forces) and repulsions between complete shells in contact. If the thermodynamic properties of the solid calculated on this model agree with experiment, then the solid may be ionic. However, it should be noted that many examples of coincidental agreement with the ionic model are known, so numerical agreement alone does not imply ionic bonding. The nondirectional nature of electrostatic interactions between ions in an ionic solid contrast with those present in a covalent solid, where the symmetries of the atomic

orbitals play a strong role in determining the geometry of the structure. However, the assumption that ions can be treated as perfectly hard spheres (of fixed radius for a particular ion type) that have no directionality in their bonding, is far from true for real ions. For example, with halide anions some directionality might be expected in their bonding that results from the orientations of their p orbitals, and large ions, such as Cs and I⁻, are easily polarizable so do not behave as hard spheres. Even so, the ionic model is a useful starting point for describing many simple structures.

We start by describing some common ionic structures in terms of the packing of hard spheres of different sizes and opposite charges. After that, we see how to rationalize the structures in terms of the energetics of crystal formation. The structures described have been obtained by using X-ray diffraction, and were among the first substances to be examined in this way.

Concept of lattice energy and Born-Haber cycle, Polarisation of ions and Fajan's rules were as Covalent and brief idea of other bonds, Concept of directed valence bond theory (VBT) and hybrid orbital description (sp , sp^2 , sp^3 , sp^3d and sp^3d^2) using simple illustrations, determination of the shapes of molecules and ions viz. NH_3 , H_2O , H_3O^+ , SF_4 , ClF_3 , ICl_2^- and I_3^- by VSEPR concept, Concept of maximum covalency. Odd electron bond, three centre bond. MO Theory, Homonuclear (H_2 , H_2^+ , B_2 , N_2 , O_2 , Cl_2) and Heteronuclear (CN, CO and NO) diatomic molecules, bond strength, and bond energy, percent ionic character from dipole moment and electronegativity. Multicenter bonding in the electron deficient molecules were as in weak interactions, Hydrogen bonding (Inter and Intra Molecular), Vander Waals forces were as in Metallic Bond, theories of bonding in metals; Free electron, VB and Band theories are very much promising to understand the approach of bonding are briefly describe.

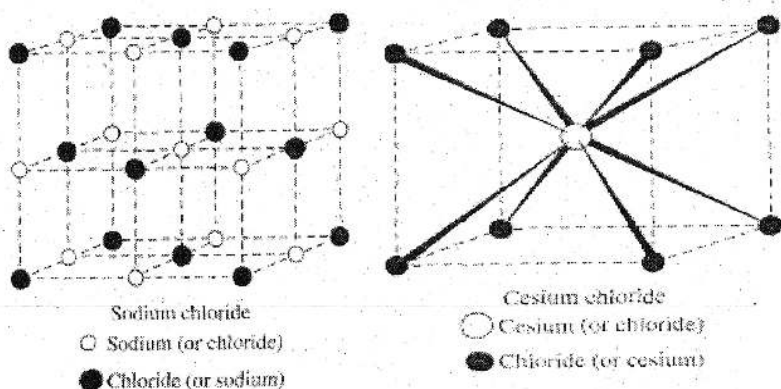
One common structure adopted is the (6,6)-coordinate rock-salt structure illustrate by NaCl. Here figure showing the rock-salt (NaCl) structure consists of two mutually interpenetrating slightly expanded face-centred cubic (fcc) arrays of ions. The entire assembly shown here is the unit cell.



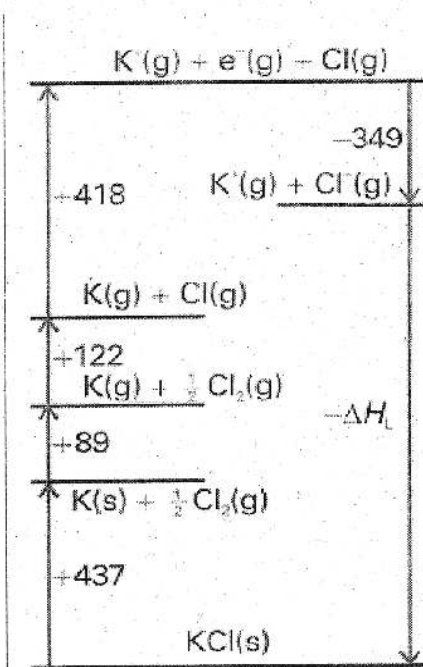
Lattice enthalpy and the Born-Haber cycle

Lattice enthalpies are determined from enthalpy data by using a Born-Haber cycle; the most stable crystal structure of the compound is commonly the structure with the greatest lattice enthalpy under the prevailing conditions.

The **lattice enthalpy**, ΔH_L , is the standard molar enthalpy change accompanying the formation of a gas of ions from the solid



Sodium Chloride and Cesium Chloride Unit Cells



The Born-Haber cycle for KCl at 298 K. Enthalpies changes are in kilojoules per mole.

Calculation of the lattice energy of a crystal may seem simple: Just take every pair of ions and calculate the sum of the electrostatic energy between each pair, using the equation below

$$\Delta U = \frac{Z_i Z_j}{r_o} \left(\frac{e^2}{4\pi\epsilon_0} \right)$$

Where Z_i, Z_j = ionic charges in electron units

r_o = distance between ion centers

e = electronic charge = 1.602×10^{-19} C

$4\pi\epsilon_0$ = permittivity of a vacuum = 1.11×10^{-10} C² J⁻¹m⁻¹

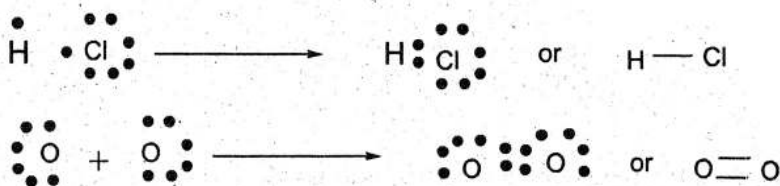
For a crystal as simple as NaCl, the closest neighbours to a sodium ion are six chloride ions at half the unit cell distance, but the set of next-nearest neighbours is a set of 12 sodium ions at 0.707 times the unit cell distance, and the numbers rise rapidly from there. The sum of all these geometric factors carried out until the interactions become infinitesimal is called the **Madelung constant**.

$$\Delta U = \frac{NMZ_i Z_j}{r_o} \left(\frac{e^2}{4\pi\epsilon_0} \right)$$

where N is Avogadro's number and M is the Madelung constant. Repulsion between close neighbors is a more complex function.

3.3 COVALENT BONDING

G. N. Lewis was the first to suggest in 1916, that atom combines with one other by sharing of electrons in their valance shells so that atom attains the nearest noble gas configuration. The shared electrons contribute towards stability of both atoms; this type of linkage is called covalent linkage or covalent bond. The compounds formed by this mechanism are called covalent compounds.



According to Lewis concept, number of electron which an atom contribute for sharing in a covalent bond is called covalency. Thus covalency of Hydrogen, chloride and oxygen is 1, 1 and 2 respectively.

3.4 VALENCE BOND THEORY

Valence-Shell Electron Pair Repulsion (VSEPR) model is the structure around a given atom is determined principally by minimizing electron pair repulsions. The valence-shell electron pair repulsion model predicts the shapes of molecules and ions by assuming that the valence shell electron pairs are arranged as far from one another as possible. To predict the relative positions of atoms around a given atom using the VSEPR model, you first note the **arrangement of the electron pairs around that central atom**.

The following rules and figures will help distinguish electron pair arrangements.

1. Draw the Lewis structure
2. Determine how many electron pairs are around the central atom. Count a multiple bond as one pair.
3. Arrange the electron pairs as shown in table given below. The direction in space of the bonding electron pairs gives the molecular geometry
4. Obtain the molecular geometry from the directions of bonding pairs.

<i>Electron pairs</i>	<i>Essential shape</i>
2	linear
3	trigonal planar
4	tetrahedral
5	trigonal bipyramidal
6	octahedral

3.5 V.S.E.P.R. THEORY/CONCEPT

Valence shell electron pair repulsion theory (VSEPR) provides a method for predicting the shape of molecules, based on the electron pair electrostatic repulsion. It was described by Sidgwick and

Powell in 1940 and further developed by Gillespie and Nyholm in 1957. In spite of this method's very simple approach, based on Lewis electron-dot structures, the VSEPR method predicts shapes that compare favorably with those determined experimentally. However, this approach at best provides approximate shapes for molecules, not a complete picture of bonding. The most common method of determining the actual structures is X-ray diffraction, although electron diffraction, neutron diffraction, and many types of spectroscopy are also used. Above we will discuss some of the molecular orbital arguments for the shapes of simple molecules. Electrons repel each other because they are negatively charged. The quantum mechanical rules force some of them to be fairly close to each other in bonding pairs or lone pairs, but each pair repels all other pairs. According to the VSEPR model, therefore, molecules adopt geometries in which their valence electron pairs position themselves as far from each other as possible. A molecule can be described by the generic formula AX_mE_n , where A is the central atom, X stands for any atom or group of atoms surrounding the central atom, and E represents a lone pair of electrons. The **steric number** ($SN = m + n$) is the number of positions occupied by atoms or lone pairs around a central atom; lone pairs and bonds are nearly equal in their influence on molecular shape.



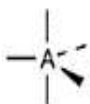
2: linear



3: trigonal planar



4: tetrahedral



5: trigonal bipyramidal



6: octahedral



7: pentagonal bipyramidal

Basic VSEPR geometries with 2–7 electron pairs.

The basic principles of the model are as follows:

1. Valence electron pairs round an atom (whether bonding or nonbonding) adopt a geometry that maximizes the distance between them. The basic geometries usually observed with 2–7 pairs are shown in figure given above.
2. Nonbonding electron pairs are closer to the central atom than

bonding pairs and have larger repulsions: in fact, the order of interactions is

nonbonding-nonbonding > nonbonding-bonding > bonding-bonding.

- 3 If double (or triple) bonds are present the four (or six) electrons involved behave as if they were a single pair, although they exert more repulsion than do the two electrons of a single bond.
4. As the terminal atoms become more electronegative relative to the central one, bonding electron pairs are drawn away from the central atom and so repel less.

Drawing a valence structure including nonbonding pairs on the central atom then gives the total number of 'pairs' (multiple bonds counted as a single 'pair'). This is sometimes called the **steric number** (SN) of the central atom. A equal to the number (n) of bonded atoms, plus the number of nonbonding electron pairs.

Steric numbers 2-4

The shapes shown in *Figure* are simple and the rules generally easy to apply. Examples without nonbonding electrons are:

1. **Linear species** (SN=2): BeH_2 (gas phase only), HgCl_2 , CO_2 and ions isoelectronic to it such as NO_2^+ , N_3^- and NCO^-
2. **Trigonal planar species** (SN=3): BF_3 , CO_3^{2-} and NO_3^- .
3. **Tetrahedral species** (SN=4): CH_4 , SiCl_4 , POCl_3 and SO_4^{2-}

In AX_2 species with SN=3 or 4 are **bent**, with the nonbonding pairs occupying positions of the trigonal plane or tetrahedron, respectively (e.g. water, H_2O). As predicted by rules 2 and 4 the XAX bond angles are less than the ideal values of 120° (SN =3) or 109.5° (SN=4), and tend to decrease as the electronegativity difference between A and X increases. Some examples with their bond angles are:

- SN=3: NO_2^- (115°), ClNO (113°);
- SN=4: H_2O (104.5°), H_2S (92°), F_2O (102°).

In AX_3 with SN=4 the nonbonding pair forces the bonds to be **pyramidal** (in ammonia, NH_3).

Steric number 5

The normal shape adopted by five groups is the **trigonal bipyramid**, as with PF_5 . There are now two inequivalent types of position, two **axial** and three **equatorial**. It appears that the equatorial positions allow more space than axial ones. Thus bulkier groups (e.g. Cl in PF_4Cl) tend to be found in these positions, as do nonbonding pairs when these are present. With successively one, two and three nonbonding pairs, the molecular shapes are as follows.

- AX_4 is often described as a '**see-saw**' with two axial and two equatorial X positions, the former being slightly bent out of the ideal linear configuration by the lone-pair repulsion. Examples are SF_4 , 3 and XeO_2F_2 (where O in preference to F occupies the equatorial position; see rule 3.)
- AX_3 gives a **T-shape**, as in ClF_3 , 4.
- AX_2 is **linear** as the bonded atoms are axial. Examples are XeF_2 , 5 and I_3^- .

Steric number 6

The basic shape is octahedral and is found with SF_6 and PF_6^- . All positions are equivalent and with one nonbonding pair AX_5 adopts a square pyramidal structure (e.g. BrF_5 , 6, and XeOF_4 , where repulsion between the double bond and the lone-pair is minimized by putting these trans to each other). When two non-bonding pairs are present they minimize their repulsion (rule 2) by adopting the *trans* configuration, giving a **square planar** molecule (e.g. XeF_4 , 7 and ICl_4^-).

Steric number 7

The only simple examples are the **pentagonal bipyramidal** IF_7 and the ion XeF_5^- which is pentagonal planar, having two lone-pairs occupying the axial positions (for XeF_6).

Steric Number	None	Number of Lone Pairs on Central Atom		
		1	2	3
2				
	$\text{:Cl}=\text{Be}=\text{Cl:}$			
3				
4				
5				
6				

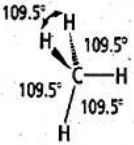
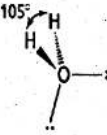
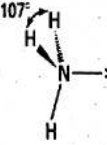
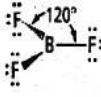
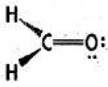
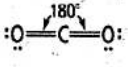
Extensions, difficulties and exceptions

One of the problems with VSEPR is that its rules appear somewhat arbitrary and hard to justify in a precise quantum-mechanical formulation. The interpretation of small variations in bond angle is often considered to be particularly uncertain. In spite of this the model is surprisingly useful. Although the discussion has concentrated on cases where single atoms are bound to a central one, VSEPR should be able to predict the geometry around any atom in a complex molecule, where main-group atoms are involved. For example, in hydroxylamine, H_2NOH , the bonds around the nitrogen are pyramidal, those around the oxygen bent as expected.

Multiple Bonds

The VSEPR model considers double and triple bonds to have slightly greater repulsive effects than single bonds because of the repulsive

effect of an electron. For example, the $\text{H}_3\text{C}-\text{C}-\text{CH}_3$ angle in $(\text{CH}_3)_2\text{C}=\text{CH}_2$ is smaller and the $\text{H}_3\text{C}-\text{C}=\text{CH}_2$ angle is larger than the trigonal 120° .

Compound	Structural Formula	Repulsive Electron Pairs	Arrangement of Electron Pairs	Molecular Shape	Molecular Model
Methane (CH_4)		Carbon has four bonded pairs	Tetrahedral	Tetrahedral	
Water (H_2O)		Oxygen has two bonded pairs + two unshared pairs	Tetrahedral	Bent	
Ammonia (NH_3)		Nitrogen has three bonded pairs + one unshared pair	Tetrahedral	Trigonal pyramidal	
Boron trifluoride (BF_3)		Boron has three bonded pairs	Trigonal planar	Trigonal planar	
Formaldehyde (H_2CO)		Carbon has two bonded pairs + one double bond, which is counted as one bonded pair	Trigonal planar	Trigonal planar	
Carbon dioxide (CO_2)		Carbon has two double bonds, which are counted as two bonded pairs	Linear	Linear	

Steric Number		Number of Lone Pairs on Central Atom			
		None	1	2	3
2	$\text{:}\ddot{\text{Cl}}=\text{Be}=\ddot{\text{Cl}}\text{:}$				
3					
4					
5					
6					

hybridization of Atomic Orbitals:

In VBT (Valence Bond Theory), covalent bond is the result of overlap of atomic orbitals having unpaired electron. Thus according to this theory ${}_4\text{Be}$, ${}_5\text{B}$ and ${}_6\text{C}$ which have respectively 0, 1 and 2 unpaired electrons in their valence-shell should be expected to form no covalent bond, one covalent bond and two covalent bonds but experiments show that Be, B and C form two (i.e. divalency), three (i.e. trivalency), and four (i.e. tetravalency) covalent bonds respectively. VBT says these elements show divalency, trivalency and tetravalency, one of the paired 2s-electrons promoted to vacant 2p-orbital, the promotion of a 2s electron to 2p level, requires some energy which is available from heat of reaction taking place when covalent bonds formed provided that no change of principle quantum number during the promotion of the electron. Thus in Be, B

and C the promotion of 2s to 2p orbital and gives 2, 3 and 4 unpaired electrons respectively.

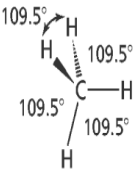
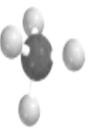
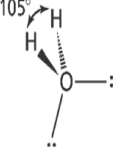
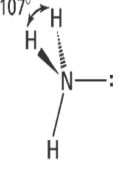
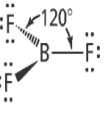
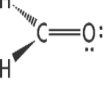
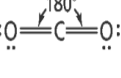
Compound	Structural Formula	Repulsive Electron Pairs	Arrangement of Electron Pairs	Molecular Shape	Molecular Model
Methane (CH ₄)		Carbon has four bonded pairs	Tetrahedral	Tetrahedral	
Water (H ₂ O)		Oxygen has two bonded pairs + two unshared pairs	Tetrahedral	Bent	
Ammonia (NH ₃)		Nitrogen has three bonded pairs + one unshared pair	Tetrahedral	Trigonal pyramidal	
Boron trifluoride (BF ₃)		Boron has three bonded pairs	Trigonal planar	Trigonal planar	
Formaldehyde (H ₂ CO)		Carbon has two bonded pairs + one double bond, which is counted as one bonded pair	Trigonal planar	Trigonal planar	
Carbon dioxide (CO ₂)		Carbon has two double bonds, which are counted as two bonded pairs	Linear	Linear	

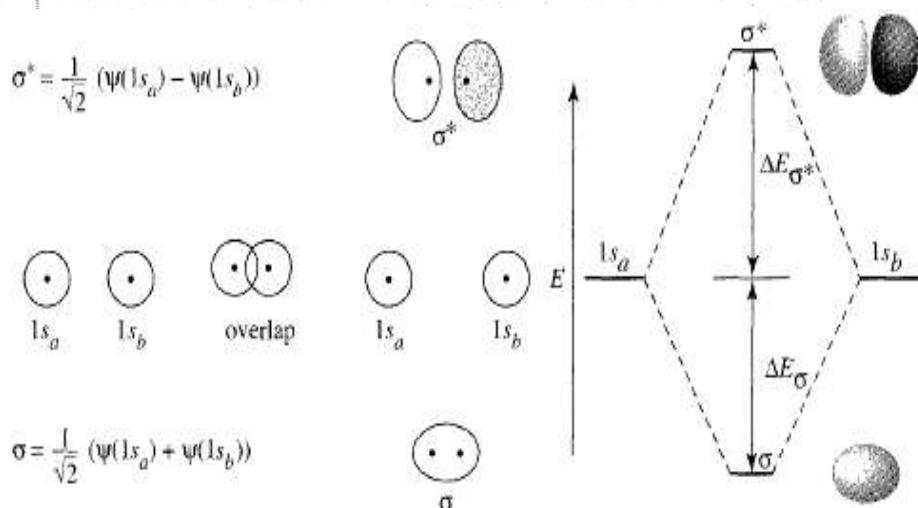
Figure showing Hybrid orbitals, each hybrid shape  The figures here show all the resulting hybrids combined, omitting the smaller lobe in: the *sp*³ and higher orbitals.

<i>Coordination number</i>	<i>Shape</i>	<i>Hybridization</i>
2	Linear	sp, pd, sd
	Angular	sd
3	Trigonal planar	sp ² , p ² d
	Unsymmetrical planar	spd
	Trigonal pyramidal	pd ²
4	Tetrahedral	sp ³ , sd ³
	Irregular tetrahedral	spd ² , p ³ d, pd ³
	Square planar	p ² d ² , sp ² d
5	Trigonal bipyramidal	sp ³ d, spd ³
	Tetragonal pyramidal	sp ² d ² , sd ⁴ , pd ⁴ , p ³ d ²
	Pentagonal planar	p ² d ³
6	Octahedral	sp ³ d ²
	Trigonal prismatic	spd ⁴ , pd ⁵

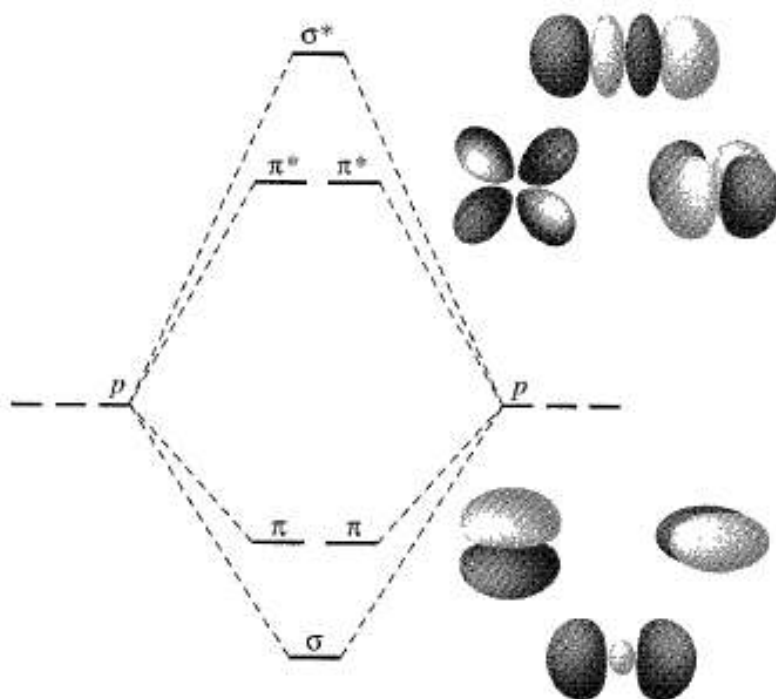
3.6 MOLECULAR ORBITAL THEORY (MOT)

According to this theory all atomic orbitals of the participating atoms mix up and give rise to an equivalent number of new orbitals belonging to the molecule. These new orbitals are called molecular orbitals. These are of two types.

- (i) **Bonding Molecular orbital:** They formed by the addition of wave functions of atomic orbitals. It lowers the energy and is responsible for the stability in the system.
- (ii) **Anti-Bonding Molecular orbital:** They formed by the subtraction of wave function of atomic orbitals. It has net disruptive effect.



Molecular orbitals from Hydrogen 1s orbital



Molecular orbitals from p-orbitals

Since we are concerned with the only molecular orbitals which need to be considered are

Bonding MOs = $\sigma(1s)$, $\sigma(2s)$, $\sigma(2p_z)$, $2p_y$, $\pi(2p_x)$, $\pi(2p_y)$,.....

Antibonding MOs = $\sigma^*(1s)$, $\sigma^*(2s)$, $\sigma^*(2p_z)$, $\pi^*(2p_x)$, $\pi^*(2p_y)$,.....

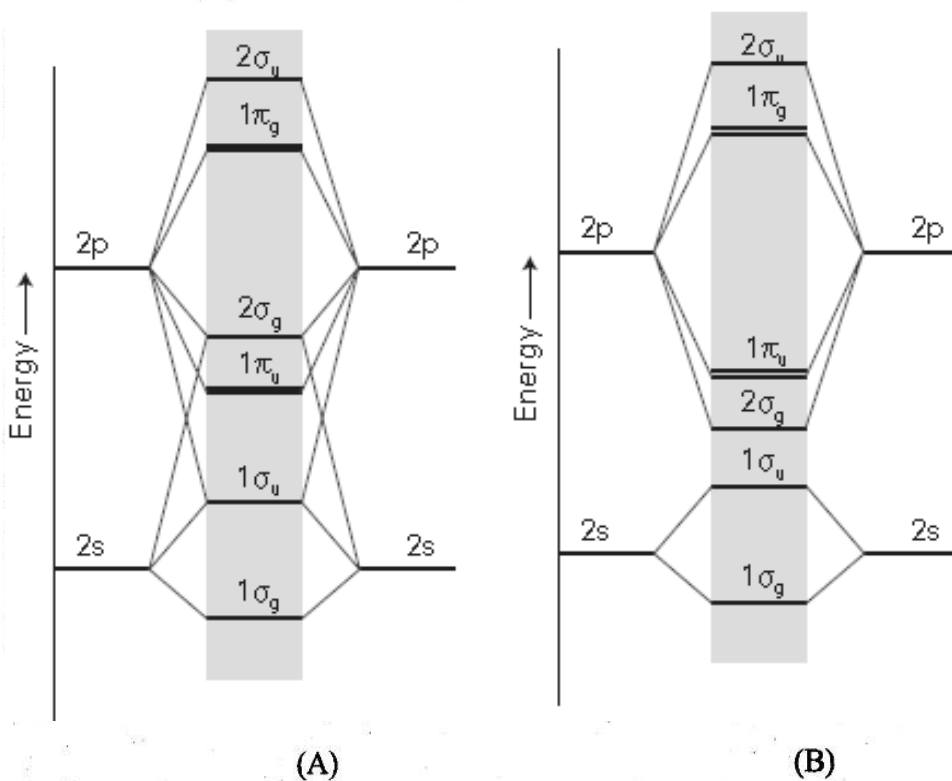
These are arranged in their increasing order of energy as determined by spectroscopic measurements as follows:

For up to 14 electron in molecule

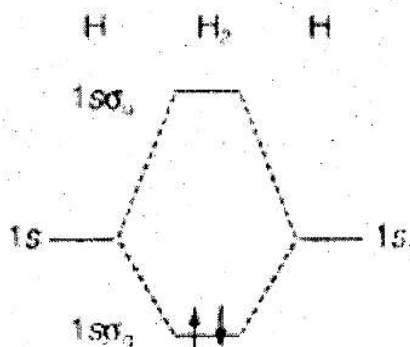
$\sigma(1s), \sigma^*(1s), \sigma(2s), \sigma^*(2s), \pi(2p_y) = \pi(2p_x), \sigma(2p_z), \pi^*(2p_y) = \sigma^*(2p_x),$
 $\sigma^*(2p_z),$ and so on.

For above 14 electron in molecule

$\sigma(1s), \sigma^*(1s), \sigma(2s), \sigma^*(2s), \sigma(2p_z), \pi(2p_y) = \pi(2p_x), \pi^*(2p_y) = \pi^*(2p_x),$
 $\sigma^*(2p_z),$ and so on.



In figure A is for up to 14 electron in molecule Li_2, N_2 and in figure B is for above 14 electron in molecule O_2, F_2 .



MO diagram for H_2 showing the bonding MO occupied by two electrons with paired spins

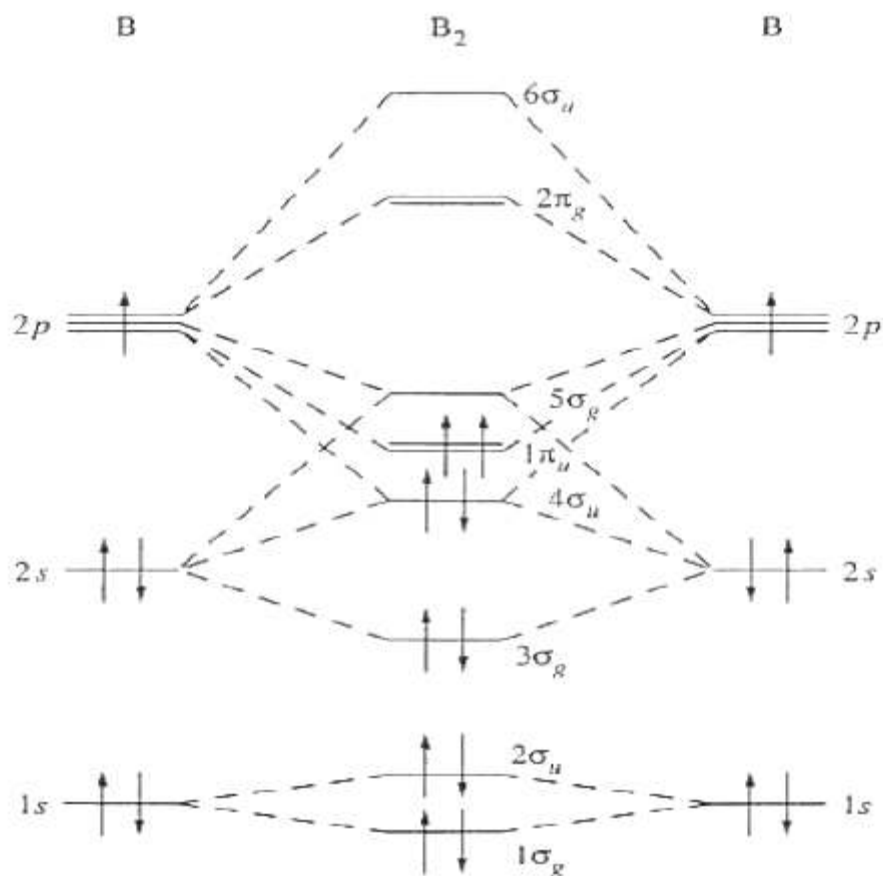
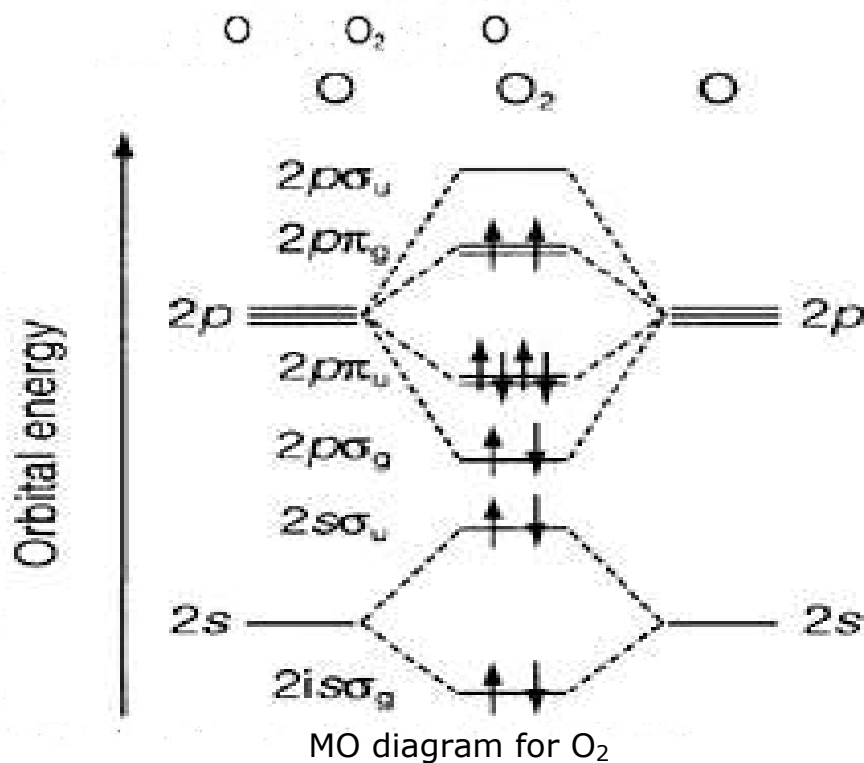


Figure: MOT diagram for B_2 molecule orbitals



MO diagram for O_2

MOT of Heteroatomic molecule of CO

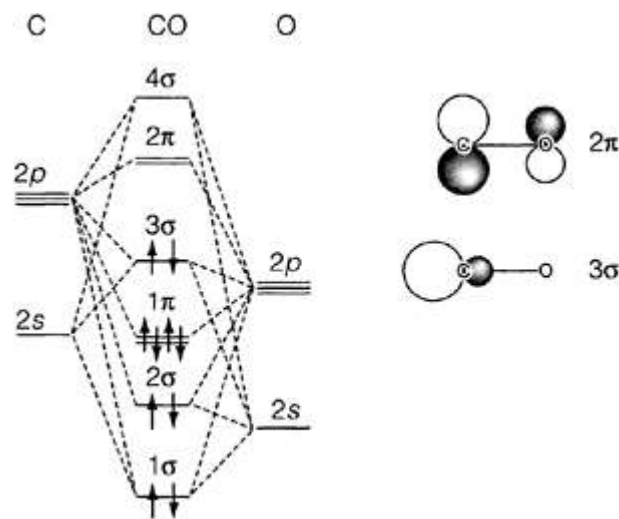
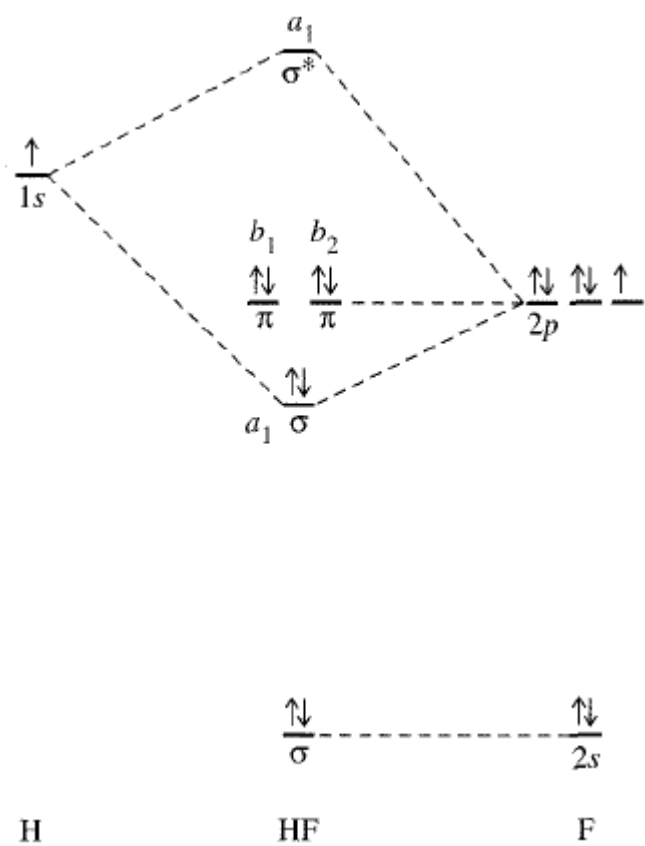


Figure: MOT diagram of molecular orbitals of CO molecule

MOT of Heteroatomic molecule of HF



BOND ORDER

The term bond order refers to the number of bonds that exist between two atoms. In molecular orbital theory the bond order is one half of the difference of the number of electrons in the bonding molecular orbitals and the number of electrons in the antibonding molecular orbitals.

Mathematically,

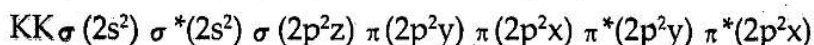
$$\text{Bond Order} = \frac{N_b - N_a}{2}$$

Where,

N_b is the number of electrons in Bonding Molecular Orbitals (BMOs). and N_a is the number of electrons in Anti-bonding Molecular Orbitals (ABMOs).

Example: Write the electronic configuration of O_2^{2-} molecule on the basis of M.O. Theory and calculate its bond order.

Solution: (i) Electronic Configuration



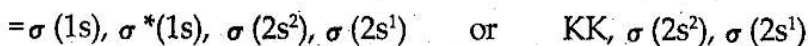
(ii) To calculate bond order formula used

$$\text{Bond Order} = \frac{N_b - N_a}{2} = \frac{8 - 6}{2} = 1 \quad \text{where, } N_b = 8 \text{ and } N_a = 6$$

Answer: The Bond Order for the O_2^{2-} ion is 1.

Example: Calculate the bond order in He^+ on the basis of M.O. theory.

Solution: The electronic configuration of He^+ is

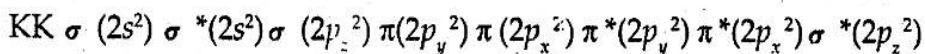


$$\text{Bond Order} = \frac{N_b - N_a}{2} = \frac{2 - 1}{2} = 0.5$$

Answer: The Bond Order for the He^+ ion is 0.5.

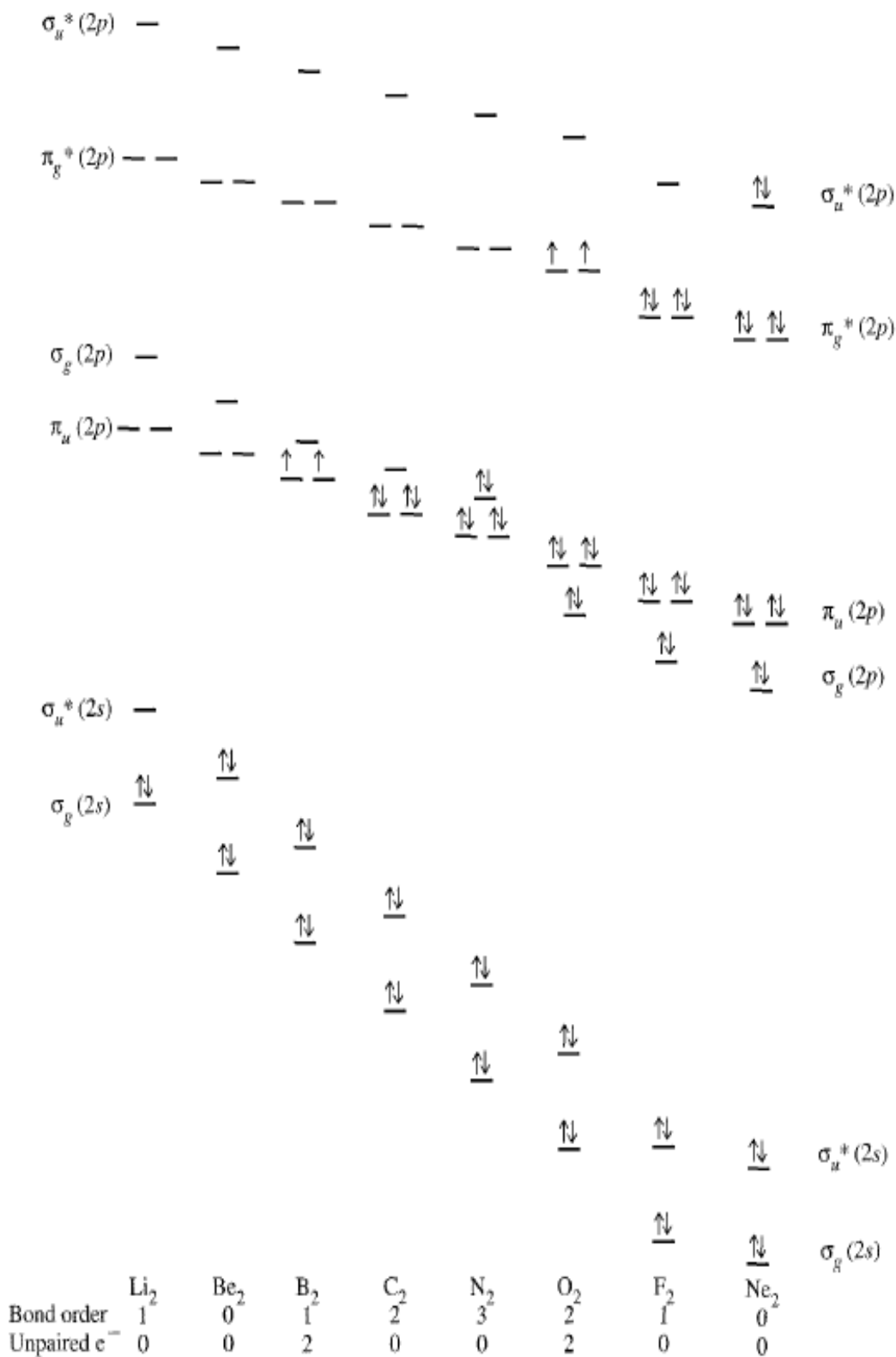
Example: Why does the molecule Ne_2 not exist?

Solution: Two electronic configuration of Ne_2 molecule is



$$\text{Bond Order} = \frac{N_b - N_a}{2} = \frac{8 - 8}{2} = 0$$

Answer: Since the bond order is Ne_2 is zero, thus it does not exist.



Energy Levels of the Homonuclear Diatomic molecules of the Second Period

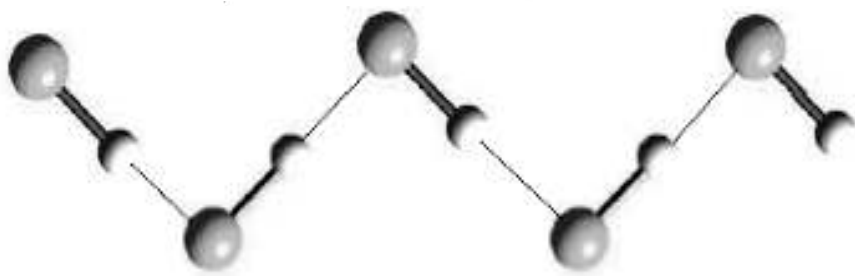
The electronic configuration and bond order of various molecules have been summarized in table given below:

Molecules	Electronic configurations	Bond Order
H_2	$\sigma(1s^2) \sigma^*(1s^0)$	$\frac{2-0}{2} = 1$
He_2	$\sigma(1s^2) \sigma^*(1s^2)$	$\frac{2-2}{2} = 0$
Li_2	$KK\sigma(2s^2) \sigma^*(2s^0)$	$\frac{2-0}{2} = 1$
Be_2	$KK\sigma(2s^2) \sigma^*(2s^2)$	$\frac{2-2}{2} = 0$
N_2	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_x^2) \pi(2p_y^2)$	$\frac{8-2}{2} = 3$
O_2	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_x^2) \pi(2p_y^2) \pi^*(2p_x^1) \pi^*(2p_y^1)$	$\frac{8-4}{2} = 2$
O_2^+	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_x^2) \pi(2p_y^2) \pi^*(2p_x^1)$	$\frac{8-3}{2} = 2.5$
O_2^-	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_x^2) \pi(2p_y^2) \pi^*(2p_x^2) \pi^*(2p_y^1)$	$\frac{8-5}{2} = 1.5$
O_2^{2-}	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_x^2) \pi(2p_y^2) \pi^*(2p_x^2) \pi^*(2p_y^2)$	$\frac{8-6}{2} = 1$
F_2	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_x^2) \pi(2p_y^2) \pi^*(2p_x^2) \pi^*(2p_y^2)$	$\frac{8-6}{2} = 1$
Ne_2	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_x^2) \pi(2p_y^2) \pi^*(2p_x^2) \pi^*(2p_y^2) \pi^*(2p_x^2) \pi^*(2p_y^2)$	$\frac{8-8}{2} = 0$
NO	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_x^2) \pi(2p_y^2) \pi^*(2p_x^1)$	$\frac{8-3}{2} = 2.5$
CO	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_x^2) \pi(2p_y^2)$	$\frac{8-2}{2} = 3$

3.7 HYDROGEN BONDING

Compounds and functionalities containing H atoms attached to electronegative elements with at least one lone pair often associate through hydrogen bonds. An E-H bond between an electronegative element E and hydrogen is highly polar, $--E-H--$, and the partially positively charged H atom can interact with a lone pair on the E atom of another molecule, forming a bridge that is known as a **hydrogen bond**. Although hydrogen bonds are usually much weaker than conventional bonds, their collective action is responsible for stabilizing complex

structures such as the open network structure of ice. Similarly, solid HF consists of chain structures that survive partially even in the vapour (5).



They are also responsible for the recognition between specific DNA bases, adenine/thymine and guanine/cytosine, that underlies gene replication. Ammonia, water, and hydrogen fluoride all have much higher boiling points than other similar molecules. Striking evidence for hydrogen bonding is provided by the trends in normal boiling points, which are unusually high for the strongly hydrogen-bonded molecules water (in which there are O-H-O bonds), ammonia (containing N-H-N bonds), and hydrogen fluoride (containing F-H-F bonds). The relatively low boiling points of PH_3 , H_2S , HCl and the heavier p-block molecular hydrides indicate that these molecules do not form strong hydrogen bonds.

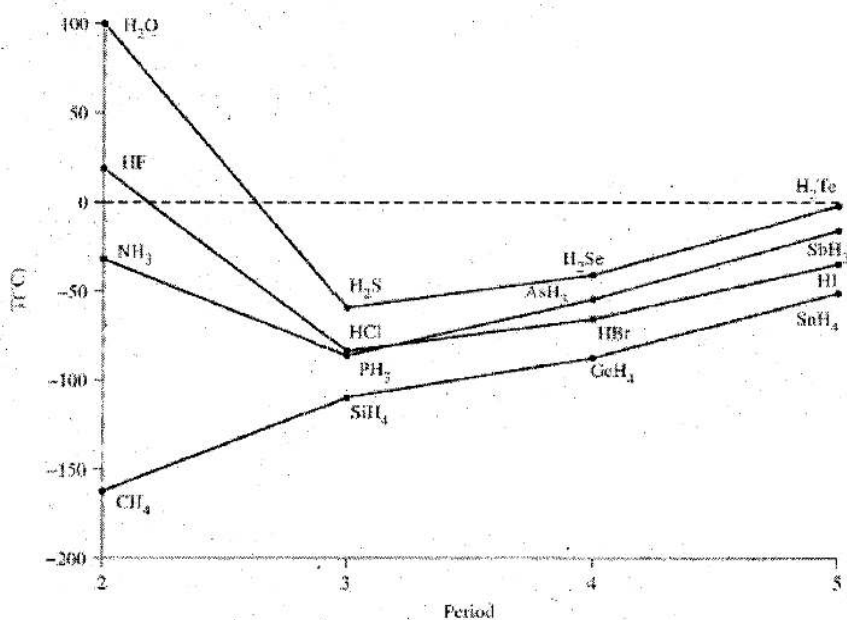


Figure showing Boiling points (B.P.) of hydrogen compounds.

Water has other unusual properties because of hydrogen bonding. For example, the freezing point of water is much higher than that of similar molecules. An even more striking feature is the decrease in density as water freezes. The tetrahedral structure around each oxygen atom with two regular bonds to hydrogen and two hydrogen bonds to other molecules requires a very open structure with large spaces between ice molecules (Figure). This makes the solid less dense than the more random liquid water surrounding it, so ice floats. Life on earth would be very different if this were not so. Lakes, rivers, and oceans would freeze from the bottom up, ice cubes would sink, and ice fishing would be impossible.

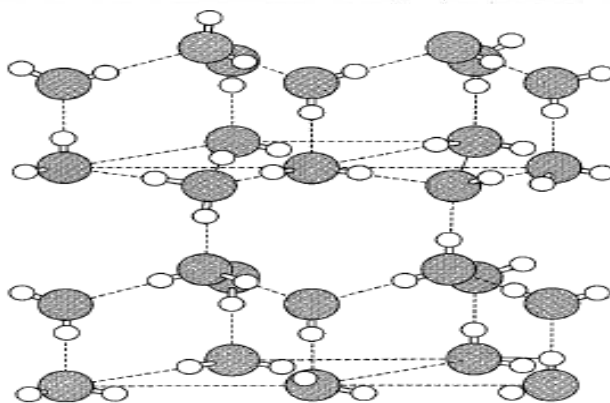


Figure of Ice. (From T. L. Brown and H. E. LeMay, Jr., *Chemistry, The Central Science*, Prentice Hall, Englewood Cliffs, NJ, 1988, (p.628).

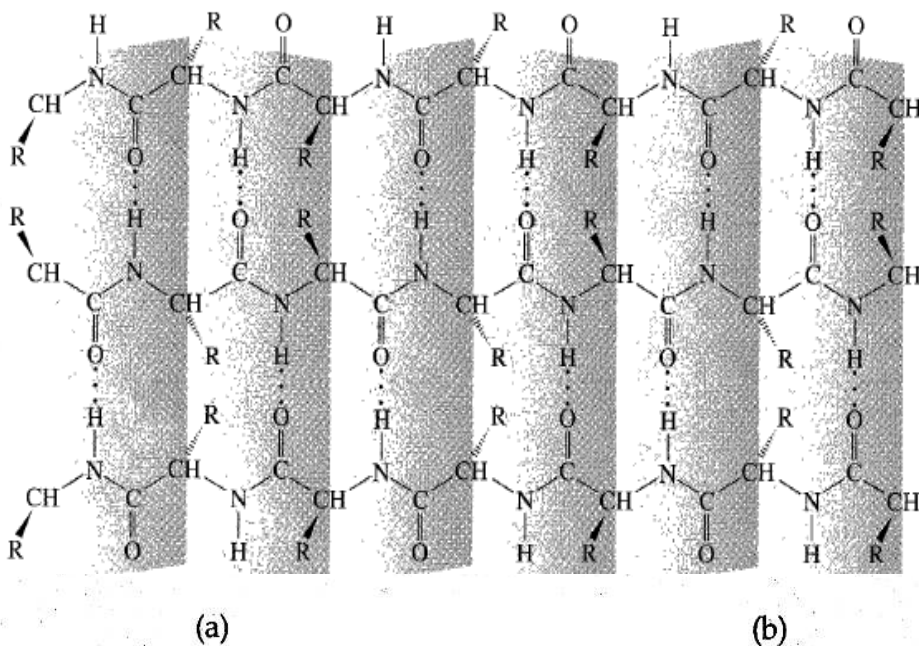


Figure showing Hydrogen-Bonded Protein Structures. (a) A protein α -helix. Peptide carbonyls and N-H

hydrogens on adjacent turns of the helix are hydrogen-bonded. (From T. L. Brown and H. E. LeMay, Jr., Chemistry, the Central Science, Prentice Hall, Englewood Cliffs, NJ, 1988, p. 946.)

(b) The pleated sheet arrangement. Each peptide carbonyl group is hydrogen-bonded to a N - H hydrogen on an adjacent peptide chain. (From L. G. Wade, Jr., Organic Chemistry, Prentice Hall, Englewood Cliffs, NJ, 1988, pp. 1255)

3.8 METALLIC BONDS

A metallic conductor is a substance with an electric conductivity that decreases with increasing temperature; a semiconductor is a substance with an electric conductivity that increases with increasing temperature.

The molecular orbital theory of small molecules can be extended to account for the properties of solids, which are aggregations of an almost infinite number of atoms. This approach is strikingly successful for the description of metals; it can be used to explain their characteristic lustre, their good electrical and thermal conductivity, and their malleability. All these properties arise from the ability of the atoms to contribute electrons to a common 'sea'. The lustre and electrical conductivities stem from the mobility of these electrons in response to either the oscillating electric field of an incident ray of light or to a potential difference. The high thermal conductivity is also a consequence of electron mobility because an electron can collide with a vibrating atom, pick up its energy, and transfer it to another atom elsewhere in the solid. The ease with which metals can be mechanically deformed is another aspect of electron mobility because the electron sea can quickly readjust to a deformation of the solid and continue to bind the atoms together.

Electronic conduction is also a characteristic of semiconductors. The criterion for distinguishing between a metallic conductor and a semiconductor is the temperature dependence of the electric conductivity.

Properties of metals

The single property that best distinguishes metals from nonmetals is conductivity. Metals have high conductivity, or low resistance, to the passage of electricity and of heat; nonmetals have low conductivity or high resistance. One exception is diamond, which has low electrical conductivity and high heat conductivity. Conductivity is discussed the

electronic structure of metals and semiconductors. Aside from conductivity, metals have quite varied properties. Some are soft and easily deformed by pressure or impact, or malleable (Cu, fcc structure), whereas others are hard and brittle, more likely to break rather than bend (Zn, hcp). However, most can be shaped by hammering or bending. This is possible because the bonding is nondirectional; each atom is rather weakly bonded to all neighboring atoms, rather than to individual atoms, as is the case in discrete molecules.

A **metallic conductor** is a substance with an electric conductivity that *decreases* with increasing temperature.

A **semiconductor** is a substance with an electric conductivity that *increases* with increasing temperature.

A **Superconductors** are a special class of materials that have zero electrical resistance below a critical temperature.

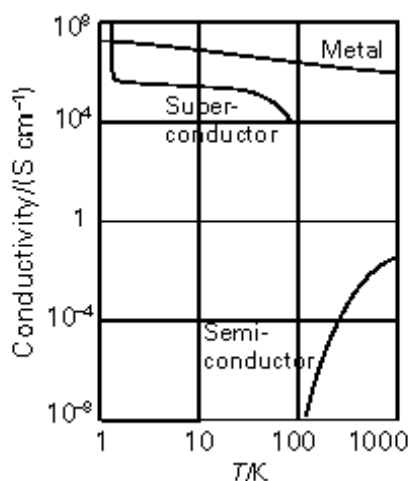


Figure shows the electrical conductivity of a substance with temperature is the basis of the classification of the substance as a metallic conductor, a semiconductor, or a superconductor.

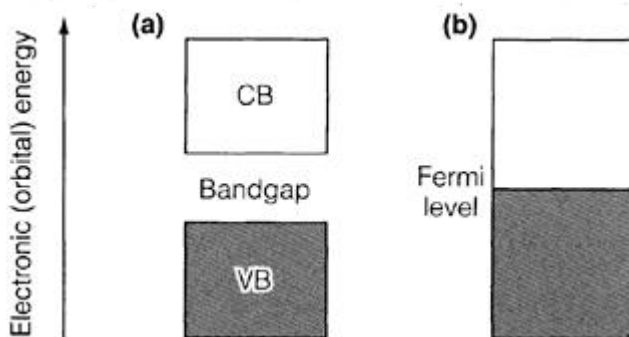
The band model

Bands formed from overlapping atomic orbitals. The central idea underlying the description of the electronic structure of solids is that the valence electrons supplied by the atoms spread through the entire structure. This concept is expressed more formally by making a simple extension of MO theory in which the solid is treated like an indefinitely large molecule. In solid-state physics, this approach is called the **tight-binding approximation**. The description in terms of delocalized

electrons can also be used to describe nonmetallic solids. We therefore begin by showing how metals are described in terms of molecular orbitals.

The **band model** of solids is an extension of the molecular orbital (MO) method. The overlap of atomic orbitals in an extended solid gives rise to continuous bands of electronic energy levels associated with different degrees of bonding. In a simple monatomic solid the bottom of the band is made up of orbitals bonding between all neighboring atoms; orbitals at the top of the band are antibonding, and levels in the middle have an intermediate bonding character. Different atomic orbitals can, in principle, give rise to different bands, although they may overlap in energy. The fundamental distinction between **metallic** and **nonmetallic** solids arises from the way in which orbitals are filled. Metallic behavior results from a band partially occupied by electrons, so that there is no energy gap between the top filled level (known as the **Fermi level**) and the lowest empty one. On the other hand, a nonmetallic solid has a **bandgap** between a completely filled band (the **valence band VB**) and a completely empty one (the **conduction band CB**). In a filled band the motion of any electron is matched by another one moving in the opposite direction, so that there is no net motion of electric charge. For conduction to occur in a nonmetallic solid, therefore, some electrons must be excited from the VB to the CB. This gives rise to an **activation energy**, and conductivity increases with rise in temperature approximately in accordance with the **Arrhenius equation** used in chemical kinetics.

Nonmetallic solids include ionic and covalent compounds. In the former case, the VB is made up of the top filled anion levels (e.g. the $3p$ orbitals of Cl^- , which are filled in making the ion) and the CB of the lowest empty cation levels (e.g. in Na^+ the $3s$ level from which an electron has been removed to make the cation). In covalent solids such as diamond the VB consists of bonding orbitals (e.g. $\text{C}-\text{C}$) and the CB of antibonding orbitals. Simple metallic solids are elements or alloys with close-packed structures where the large number of interatomic overlaps gives rise to wide bands with no gaps between levels from different atomic orbitals. Metallic properties can arise, however, in other contexts. In transition metal compounds a partially occupied d shell can give rise to a partly filled band



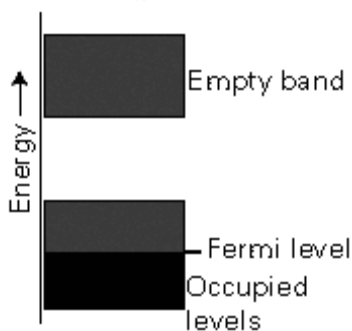
Band picture for (a) nonmetallic and (b) metallic solid; occupied electronic levels are shown shaded.

Bandgap

The bandgap in a nonmetallic solid is important for electrical and optical properties. A solid with a small bandgap is a **semiconductor** with a conductivity that (unlike the case with a metal) increases as temperature is raised. The bandgap also determines the minimum photon energy required to excite an electron from the VB to the CB, and hence the threshold for **optical absorption** by a solid.

The Fermi level

The Fermi level is the highest occupied energy level in a solid at $T=0$. Electrons occupy the individual molecular orbitals of the bands in accordance with the building-up principle. If each atom supplies one s electron, then at $T=0$ the lowest $1/2 N$ orbitals are occupied. The highest occupied orbital at $T=0$ is called the **Fermi level**; it lies near the centre of the band. When the band is not completely full, the electrons close to the Fermi level can easily be promoted to nearby empty levels. As a result, they are mobile and can move relatively freely through the solid, and the substance is an electrical conductor.



The solid is in fact a *metallic* conductor. We have seen that the criterion of metallic conduction is the decrease of electrical conductivity with increasing temperature. This behaviour is the opposite of what we

might expect if the conductivity were governed by thermal promotion of electrons above the Fermi level. The competing effect can be identified once we recognize that the ability of an electron to travel smoothly through the solid in a conduction band depends on the uniformity of the arrangement of the atoms. An atom vibrating vigorously at a site is equivalent to an impurity that disrupts the orderliness of the orbitals. This decrease in uniformity reduces the ability of the electron to travel from one edge of the solid to the other, so the conductivity of the solid is less than at $T=0$. If we think of the electron as moving through the solid, then we would say that it was 'scattered' by the atomic vibration. This carrier scattering increases with increasing temperature as the lattice vibrations increase, and the increase accounts for the observed inverse temperature dependence of the conductivity of metals

Some typical band gaps at 298 K

Material	E_g/eV
Carbon (diamond)	5.47
Silicon carbide	3.00
Silicon	1.11
Germanium	0.66
Gallium arsenide	1.35
Indium arsenide	0.36

Semiconduction

The characteristic physical property of a semiconductor is that its electrical conductivity increases with increasing temperature. At room temperature, the conductivities of semiconductors are typically intermediate between those of metals and insulators. The dividing line between insulators and semiconductors is a matter of the size of the band gap. The conductivity itself is an unreliable criterion because, as the temperature is increased, a given substance may have in succession a low, intermediate, and high conductivity. The values of the band gap and conductivity that are taken as indicating semiconduction rather than insulation depend on the application being considered.

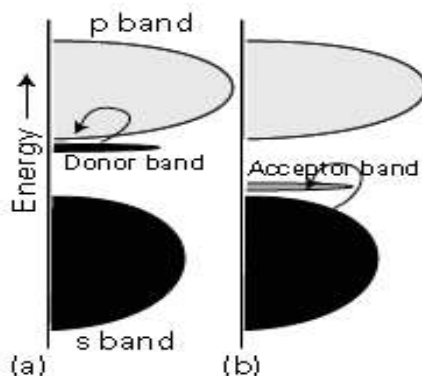
a) Intrinsic semiconductors

In an intrinsic semiconductor, the band gap is so small that the energy of thermal motion results in some electrons from the valence band

populating the empty upper band. This occupation of the conduction band introduces positive holes, equivalent to an absence of electrons, into the lower band, and as a result the solid is conducting because both the holes and the promoted electrons can move. A semiconductor at room temperature generally has a much lower conductivity than a metallic conductor because only very few electrons and holes can act as charge carriers.

(b) Extrinsic semiconductors

p-Type semiconductors are solids doped with atoms that remove electrons from the valence band; n-type semiconductors are solids doped with atoms that supply electrons to the conduction band. An **extrinsic semiconductor** is a substance that is a semiconductor on account of the presence of intentionally added impurities. The number of electron carriers can be increased if atoms with more electrons than the parent element can be introduced by the process called **doping**.



The band structure in (a) an n-type semiconductor and (b) a p-type semiconductor.

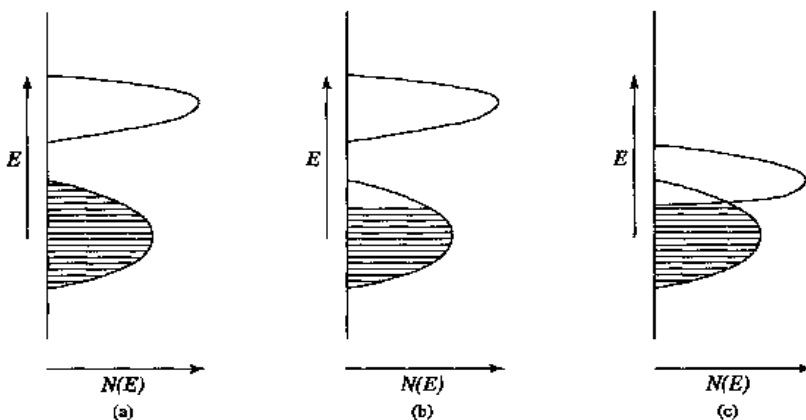


Figure of Energy Bands and Density of States. (a) An insulator, with a filled valence band. (b) A metal, with a partly filled valence band and a separate empty band. (c) A metal with overlapping bands caused by similar energies of the initial atomic orbitals.

3.9 SUMMARY

Form the above unit you come to know about types of bonds and their properties. Many of the atoms combine to the other or same atoms and what extent they may combine with other atom. You also learner what types of bonding takes place between the atoms and how extent the theory is applicable in the formation of molecules. Also learn the types of bonds as ionic, covalent, coordinate, metallic, non-metallic, etc.

3.10 TERMINAL QUESTIONS

- Find out the lattice packing structure for the followings:
 - Radius of Na^+ ion is $0.95 \text{ \AA}$ and Cl^- ion is $1.81 \text{ \AA}$, find packing structure with the help of radius ratio rule.
 - Radius of Zn^{2+} ion is $0.75 \text{ \AA}$ and S^{2-} ion is $1.84 \text{ \AA}$, find packing structure with the help of radius ratio rule.
 - Radius of B^{3+} ion is $0.23 \text{ \AA}$ and O^{2-} ion is $1.40 \text{ \AA}$, find packing structure with the help of radius ratio rule.
 - Radius of Cs^+ ion is $1.69 \text{ \AA}$ and Cl^- ion is $1.8 \text{ \AA}$, find packing structure with the help of radius ratio rule.
- Calculate the bond order and shortest bond length of the following molecule:
 $\text{NO}, \text{NO}^+, \text{NO}^{2+}, \text{NO}^-$
- Calculate the bond order, bond length and magnetic character of the CN and CN^- molecules.
- Molecules of CH_4 , NH_3 and H_2O involves sp^3 hybridization but bond angles of these molecules are 109.5° , 107° and 104.5° respectively and why?
- Predict molecules shape of CH_4 , NH_3 and H_2O ?
- Discuss band model of sodium metal, an insulator and semi conductor?

3.11 ANSWERS

- a. 0.524, this ratio lies between 0.414 and 0.732, hence Na^+ ions prefer to occupy octahedral sites having coordination number 6 in the closed pack lattice of Cl^- ions.

- b. 0.40, this ratio lies between 0.225 and 0.414, hence Zn^{2+} ions prefer to occupy tetrahedral sites having coordination number 4 in the closed pack lattice of S^{2-} ions.
- c. 0.164, this ratio lies between 0.155 and 0.225, hence boron oxide would prefer to occupy plane trigonal structure.
- d. 0.93, this ratio lies between 0.732 and 1, hence Cs^+ ions prefer to occupy cubic sites having coordination number 8.
2. Bond Orders are 2.5, 3, 2.5 and 2 respectively and obviously NO^+ has the highest bond order, thus has the shortest bond length.
3. Bond order of CN and CN^- is 2.5 and 3 respectively; hence CN^- has smaller bond length. Further, since in CN there is one unpaired electron in σ ($2p_x$) MO, it will be paramagnetic where as in CN^- have no unpaired electron evidently diamagnetic.
4. Due to lone pair–bond pair interaction ($\text{lp-lp} > \text{lp-bp} > \text{bp-bp}$).
5. Molecular shapes of CH_4 , NH_3 and H_2O are tetrahedral, pyramidal and 'V'-shape respectively.
6. See 3.8.

SUGGESTED READINGS:

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UGCHE-101

Inorganic Chemistry-I

Block 2

INORGANIC CHEMISTRY-I (Basic Inorganic Chemistry)

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Structure

- 4.1 Introduction
 - Objectives
- 4.2 s-Block Elements
 - 4.2.1 Competitive study and diagonal relationships
- 4.3 Salient features of s-block elements (hydrides, solvation and complexation tendencies including their function in bio-systems, an introduction to alkyls and aryls)
- 4.4 Chemical reactivity of alkali and earth alkaline metals
- 4.5 Uses of s-block elements and their compounds (Li, Na and K only)
- 4.6 Organometallic compounds of Li, Na, K, Be and Mg
- 4.7 Polyether complexes (Crown ether complexes) of alkali metals
- 4.8 Extraction and isolation of Li, Be and Ra from their minerals
- 4.9 Summary
- 4.10 Terminal Questions
- 4.11 Answers

4.1 INTRODUCTION

s-block elements have the important place in the main group elements. Most appropriate position of hydrogen in the periodic table has been a matter of some dispute among chemists. Its electron configuration is $1s^1$, is similar to the valence electron configurations of the alkali metals (ns^1). Hence, hydrogen is most commonly listed in the periodic table at the top of Group 1. However, it has little chemical similarity to the alkali metals. Hydrogen is also one electron short of a noble gas configuration and could conceivably be classified with the halogens. Although hydrogen has some similarities with the halogens for example, in forming a diatomic molecule and an ion of -1 charge, these similarities are limited. A third possibility is to place hydrogen in

Group 14 above carbon: both elements have filled valence electron shells, are of similar electronegativity, and usually form covalent rather than ionic bonds. We prefer not to attempt to fit hydrogen into any particular group in the periodic table because it is a unique element in many ways and deserves separate consideration. The elements having electronic configuration ns^1 for last electron the metals form Group 1 called alkali metals and elements having electronic configuration ns^2 for last electron metals form Group 2 are called alkali earth metals.

Objective:

After studying this unit, you should be able to know

- Properties of s-block elements
- Hydrogen properties
- Chemical reactivity of alkali and earth alkaline metals.
- s-block elements and their compounds
- Organometallic compounds of Li, Na, K, Be and Mg
- Polyether complexes or Crown ether complexes.
- Extraction and isolation of Li, Be and Ra

4.2 s-Block Elements

In the previous studies in the introduction, hydrogen having different properties as usual in ns^1 block elements. Thus hydrogen not studies into any particular group in the periodic table because it is a unique element in many ways and deserves separate concern. In general the elements except hydrogen in Group 1, they form closely related group and probably have least complicated chemistry than other group. The physical and chemical properties of the elements are closely related to their electronic configurations and sizes. The elements are all metal, excellent conductor of electricity, typically soft and highly reactive. They have loosely held one valence electron and form univalent ionic and colourless compounds. Their hydroxides and oxides are very strong bases and oxosalts are very stable.

HYDROGEN

Hydrogen is the most abundant element in the universe and is also common on earth, being the third most abundant element after

oxygen and silicon on the surface of the globe. The gradual recognition of hydrogen as an element during the sixteenth and seventeenth centuries forms part of the obscure and tangled web of experiments that were carried out as chemistry emerged from alchemy to become a modern science. Despite its very simple electronic configuration ($1s^1$) hydrogen can, paradoxically, exist in over 50 different forms most of which have been well characterized. This multiplicity of forms arises firstly from the existence of atomic, molecular and ionized species in the gas phase: H , H_2 , H^+ , H^- , H_2^+ , H_3^+ , H_{11}^+ ; secondly, from the existence of three isotopes, ${}_1H^1$, ${}_1H^2$ (D) and ${}_1H^3$ (T), and correspondingly of D , D_2 , HD , DT , etc., and finally, from the existence of nuclear spin isomers for the homonuclear diatomic species. The discovery of ortho- and para-hydrogen in 1924, closely followed by the discovery of heavy hydrogen (deuterium) and tritium in the 1930s.

Hydrogen is a colourless, tasteless, odourless gas which has only low solubility in liquid solvents. It is comparatively unreactive at room temperature though it combines with fluorine even in the dark and readily reduces aqueous solutions of palladium (II) chloride. This reaction can be used as a sensitive test for the presence of hydrogen.



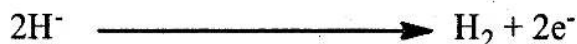
At higher temperatures hydrogen reacts vigorously even explosively, with many metals and non-metals to give the corresponding hydrides. Activation means of homogeneous hydrogenation catalysts. Industrially important processes include the hydrogenation of many organic compounds and the use of cobalt compounds as catalysts in the hydroformylation of olefins to aldehydes and alcohols at high temperatures and pressures

Deuterium as D_2O is separated from water by fractional distillation or electrolysis and by utilization of very small differences in the free energies of the H and D forms of different compounds, the H_2O - H_2S system being particularly favorable in large scale.

Tritium is formed continuously in the upper atmosphere in nuclear reaction induced by cosmic rays.

Properties Hydrogen can gain an electron to achieve a noble gas configuration in forming the hydride ion, H^- . Many metals, such as the

alkali metals and alkaline earths, form hydrides that are essentially ionic and contain discrete H^- ions. The hydride ion is a powerful reducing agent. it reacts, for example, with water and other protic solvents to generate H_2



Hydride ions may also act as ligands in bonding to metals, Many complex hydrides, such as BH_4^- and AlH_4^- serve as important reagents in organic and inorganic synthesis, their bonding is essentially covalent. Lithium aluminum hydride can be prepared by the treatment of lithium hydride with a solution of aluminum chloride in ether.



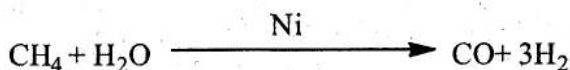
LiAlH_4 is a versatile reducing agent for many organic compounds such as ketones, aldehydes, nitriles and nitro compounds.

Hydrogen ion " H^+ ", is also common. However, in the presence of solvent, the extremely small size of the proton (radius approximately $1.5 \times 10^{-3}\text{pm}$) requires that it be associated with solvent molecules or other dissolved species. In aqueous solution, a more correct description is H_3O^+ (aq) although larger species such as H_9O_4^+ are also likely. Another important characteristic of H^+ that is a consequence of its small size is its ability to form hydrogen bonds. The ready combustibility of hydrogen, together with the lack of potentially polluting byproducts, has led to the proposal to use hydrogen as a fuel. For example, as a potential fuel for automobiles, H_2 can provide a greater amount of energy per unit mass than gasoline without producing such environmentally damaging byproducts as carbon monoxide, sulfur dioxide, and unburned hydrocarbons. A challenge for chemists is to develop practical thermal or photochemical processes for generating hydrogen from its most abundant source, water.

Small amounts of H_2 can be generated in the laboratory by reacting "active" metals such as zinc, magnesium, or aluminum with acid.



Commercially, H_2 is frequently prepared by cracking petroleum hydrocarbons with solid catalysts, also forming alkenes or by steam reforming of natural gas, typically using a nickel catalyst.



Molecular hydrogen is also an important reagent, especially in the industrial hydrogenation of unsaturated organic molecules.

Ortho and para hydrogen

A molecule of dihydrogen contains two atoms, in which the nuclei of both the atoms are spinning. Depending upon the direction of the spin of the nuclei, the hydrogens are of two types:

Ortho hydrogen molecules are those in which the spins of both the nuclei are in the same direction. Molecules of hydrogen in which the spins of both the nuclei are in the opposite direction are called **para** hydrogen. Ordinary dihydrogen is an equilibrium mixture of ortho and para hydrogen. The amount of ortho and para hydrogen varies with temperature as:

- i. At $0^\circ K$, hydrogen contains mainly para hydrogen which is more stable.
- ii. At the temperature of liquefaction of air, the ratio of ortho and para hydrogen is 1 : 1.
- iii. At the room temperature, the ratio of ortho to para hydrogen is 3 : 1.
- iv. Even at very high temperatures, the ratio of ortho to para hydrogen can never be more than 3 : 1.

Thus to get pure para hydrogen by cooling ordinary hydrogen gas to a very low temperature about 20 K but it is never possible to get a sample of hydrogen containing more than 75% of ortho hydrogen.

s-block elements electronic structure

Group 1 elements having electronic configuration is ns^1 for outer orbit. The single valence electron is a long distance from the nucleus, is

weakly held and is readily removed. In contrast the rest electrons are closer to the nucleus and more tightly held and are removed only with great difficulty. Group 1 elements are also called Alkali Metals due to their strong basic hydroxides. Group 1 element's electronic configurations are given in table 1. Group 2 elements having electronic configuration is ns^2 for outer orbit. The two valence electrons is a long distance from the nucleus, is weakly held and is readily removed. In contrast the rest electrons are closer to the nucleus and more tightly held and are removed only with great difficulty. Group 2 element's electronic configurations are given in table 2.

Table 1: Electronic structures of Group 1 (Alkali Metals):

Element	Symbol	Electronic configuration	
Hydrogen	H	$1s^1$	
Lithium	Li	$1s^2 2s^1$	or [He] $2s^1$
Sodium	Na	$1s^2 2s^2 2p^6 3s^1$	or [Ne] $3s^1$
Potassium	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	or [Ar] $4s^1$
Rubidium	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$	or [Kr] $5s^1$
Casesium	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$	or [Xe] $6s^1$
Francium	Fr		[Rn] $7s^1$

Table 2: Electronic structures of Group 2 (Alkali Earth Metals):

Element	Symbol	Electronic configuration	
Beryllium	Be	$1s^2 2s^2$	or [He] $2s^2$
Magnesium	Mg	$1s^2 2s^2 2p^6 3s^2$	or [Ne] $3s^2$
Calcium	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	or [Ar] $4s^2$
Strontium	Sr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$	or [Kr] $5s^2$
Barium	Ba	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$	or [Xe] $6s^2$
Radium	Ra		[Rn] $7s^2$

Group 1 atoms are the largest in their horizontal periods in the periodic table. When electron is removed to give a positive ion, the size decreases considerably.

However, because of the difficulty of reducing the alkali metal ions, the elements were not isolated easily till date. Two of the alkali metals, sodium and potassium are essential for human life, their careful regulation is often important in treating a variety of medical conditions.

The alkali metals are silvery except for cesium, which has a golden appearance, are highly reactive solids having low melting points. They are ordinarily stored under nonreactive oil to prevent air oxidation and are soft enough to be easily cut with a knife. Their melting points decrease with increasing atomic number because metallic bonding between the atoms becomes weaker with increasing atomic size. Physical properties of the alkali metals are summarized in table given below.

Table: Physical properties of Alkali Metals

Property	Li	Na	K	Rb	Cs
Atomic number	3	11	19	37	55
Molar mass (g mol ⁻¹)	6.94	22.99	39.10	85.48	132.91
Density (g cm ⁻¹)	0.534	0.972	0.859	1.530	1.903
Atomic radius (Å)	1.34	1.54	1.96	2.11	2.25
Ionic radius (Å)	0.60	0.95	1.33	1.48	1.69
Melting point (°C)	180	97.8	64	38.9	28.7
Boiling point (°C)	1326	883	756	688	690
Ionization energy (kJ mol ⁻¹)	520.1	495.2	418.7	403	375.7
Electronegativity	1.0	0.9	0.8	0.8	0.7
Flame coloration	Crimson red	Golden yellow	Violet	Violet	Violet

The elements calcium, strontium, barium, and radium are known as the alkaline earth metals, but the term is often applied to the whole of Group 2. All the elements are silvery white metals and the bonding in their compounds is normally described in terms of the ionic model. Some aspects of the chemical properties of beryllium are more like those of a metalloid with a degree of covalence in its bonding. The elements are denser, harder, and less reactive than the elements of Group 1 but are still

more reactive than many typical metals. The lighter elements beryllium and magnesium form a number of complexes and organometallic compounds.

Table: Physical properties of Alkali Earth Metals

Property	Be	Mg	Ca	Sr	Ba	Ra
Atomic number	4	12	20	38	56	88
Molar mass (g mol ⁻¹)	9.01	24.31	40.08	87.67	137.34	26.05
Density (g cm ⁻¹)	1.84	1.74	1.55	2.54	3.75	6.00
Atomic radius (Å)	0.90	1.36	1.74	1.92	1.98	-
Ionic radius (Å)	0.30	0.65	0.94	1.10	1.29	1.32
Melting point (°C)	1277	650	838	768	714	700
Boiling point (°C)	2770	1107	1440	1380	1640	1140
Ionization energy (kJ mol ⁻¹)	899	737	590	549	503	509
Electronegativity	1.5	1.0	1.2	1.0	0.9	0.9
Flame coloration	None	None	Brick	Crimson red	Grassy green	Crimson

4.2.1 COMPARATIVE STUDY AND DIAGONAL RELATIONSHIPS

In periodic table it is observed that the first element of a group shows similarities with the second element in the next higher group in the next period is called **diagonal relationship**. The diagonal relationship is due to similar polarization powers of Li⁺ and Mg²⁺ ions despite occurrence of different charges on these ions. Relationship of elements with their electronegativity:

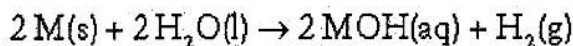
Group I	Group II	Group III	Group IV
Li 1.0 Na 0.9	Be 1.5 Mg 1.2	B 2.0 Al 1.5	C 2.5 Si 1.8

The diagonal relationship arises because of the effects of both size and charge. On descending a group, the atoms and ions increase in size. On moving from left to right in the periodic table, the size decreases. Thus on moving diagonally, the size remains nearly the same. For example, lithium is smaller than sodium, and magnesium is also smaller than sodium, and hence lithium and magnesium are similar in size. The size of $\text{Li}^+ = 0.76 \text{ \AA}$ and $\text{Mg}^{2+} = 0.72 \text{ \AA}$ are close and so in situations where size is important for their behavior should be similar.

4.3 SALIENT FEATURES OF s-BLOCK ELEMENTS

Properties of the alkali metals

Lithium is the smallest element in the group and has the highest ionization energy, mp and heat of atomization; it also has the lowest density of any solid at room temperature. All the alkali metals have characteristic flame colorations due to the ready excitation of the outermost electron, and this is the basis of their analytical The alkali metals reaction with water

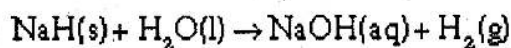


Their reaction trends with water are as follows:

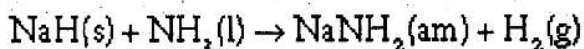
Li	Na	K	Rb	Cs
gently	vigorously	vigorously with ignition	explosively	explosively

Hydrides

The Group 1 elements react with hydrogen to form ionic hydrides with the rock-salt structure and the anion present is the hydride ion, H^- . The hydrides react violently with water.



Finely divided sodium hydride can ignite if it is left exposed to humid air. Such fires are difficult to extinguish because even carbon dioxide is reduced when it comes into contact with hot metal hydrides. Hydrides are useful as non-nucleophilic bases and reductants.



Solubility and hydration

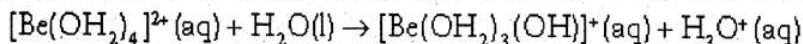
All the common salts of the Group 1 elements are soluble in water. The solubilities cover a wide range of values, some of the most soluble being those for which there is the greatest difference between the radii of the cation and anion. Thus, the solubilities of the Li halides increase from the fluoride to the bromide whereas for Cs the trend is reversed.

Compounds of the Group 2 elements are generally much less soluble in water than those of Group 1 elements even though the hydration enthalpies are more negative ($\Delta H = \text{kJ mol}^{-1}$).

Na^+	K^+	Mg^{2+}	Ca^{2+}
-406	-322	-1920	-1650

With the exception of the fluorides, the salts of singly charged anions are usually soluble in water and those of doubly charged anions (such as oxides) are usually only sparingly soluble. These trends in solubility and hydrolysis can also be explained in hard/soft acid–base (HSAB) terms. As the group is descended the ions become less hard; the fluorides and hydroxides (small, hard anions) are insoluble for the harder Be^{2+} and Mg^{2+} but more soluble for Ba^{2+} . Be^{2+} is most strongly hydrated by the hard O atom in H_2O and the relatively soft Ba^{2+} much more weakly. The amphoteric nature of Be leading to the formation of $[\text{Be}(\text{OH})_4]^{2-}$ under strongly basic conditions means that the element forms an extensive series of beryllates that are built from BeO_4 tetrahedra.

The H_2O molecules directly coordinated to Be^{2+} are very strongly held in aqueous solution, exchanging only very slowly with free water. The hydrated Be^{2+} cation, $[\text{Be}(\text{OH}_2)_4]^{2+}$, acts as an acid in water.

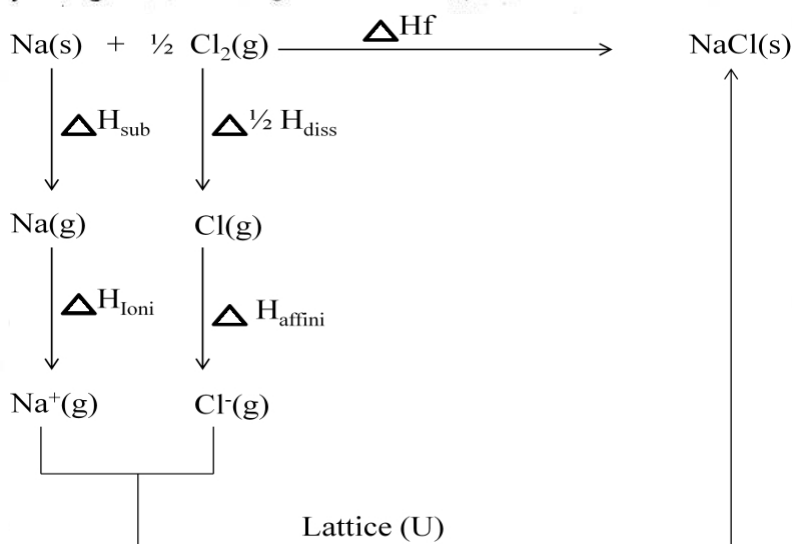


Halides

All the Group 1 elements form halides, MX, by direct combination of the elements. Most of the halides have the (6,6)-coordinate rock-salt structure, but CsCl , CsBr , and CsI have the (8,8)-coordinate caesium-chloride structure. The enthalpies of formation of all the halides are large and negative, becoming less negative from the fluoride to iodide for each element. The enthalpies of formation become less negative for the fluorides

on descending the group but become more negative for the chlorides, bromides, and iodides. These trends can be rationalized by considering a Born-Haber cycle for formation of the halides from the elements shown in figure below. These calculations treat the bonding in alkali metal compounds as purely ionic; however, for the heavier metal ions there is increasing contribution from covalence as the ions become larger, more polarizable, and less hard. As we saw in the requirement that the sum of enthalpy changes round a Born-Haber cycle be zero implies that the enthalpy of formation of a compound.

The lattice energy cannot be calculated directly. It is evaluated by using a series cyclic operations e.g. the lattice energy for NaCl can be calculated by using the following Born-Habercycle.



Where, The cycle when completed

U = Lattice energy

H_{ioni} = ionization potential of Na H_{sub} = heat of sublimation of Na

H_{affin} = electron affinity of Cl H_{diss} = heat of dissociation Cl_2

would result to zero energy change i.e. H_f = heat of formation of NaCl

$$U - H_{\text{ion}} + H_{\text{affin}} - \frac{1}{2} H_{\text{diss}} + H_{\text{sub}} - H_f = 0$$

$$U = H_{\text{ion}} - H_{\text{affin}} + \frac{1}{2} H_{\text{diss}} - H_{\text{sub}} + H_f = 0$$

From the above equation, the lattice energy of NaCl can be determined experimentally. Born- Haber cycle is also used to determine electron affinities which cannot be determined directly for endothermic reactions.

For various salts that the lattice energies determined experimentally (Born- Haber cycle) with the calculated values (Born- Lande cycle) given below:

Salt	Experimental U(kJ/mole)	Calculated U(kJ/mole)
LiCl	840.1	811.2
NaCl	770.3	755.2
KCl	701.3	687.4
RbCl	682	661.6
CsCl	629.7	622.6

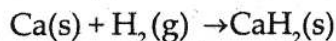
4.4 CHEMICAL REACTIVITY OF ALKALI AND EARTH ALKALINE METALS

As we discussed in above section about the reactivity of the alkaline metals now we compare them with Group 2 elements. In the Group 2 (earth alkaline metals) contains soft, silver metals that are less metallic in character than the Group 1 elements. Although many characteristics are common throughout the group, the heavier metals such as Ca, Sr, Ba, and Ra are almost as reactive as the Group 1 Alkali Metals. All the elements in Group 2 have two electrons in their valence shells, giving them an oxidation state of +2 were as in alkaline metals have one electron gives +1 oxidation state. This enables the metals to easily lose electrons, which increases their stability and allows them to form compounds via ionic bonds.

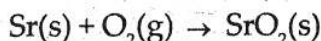
Beryllium is the very first element in Group 2, and has the highest melting point about 1560 K of any element in the group. It is very rare on Earth as well as in the universe and is not considered important for plant or animal life. In nature it can only be found in compounds with other elements.

Beryllium forms compounds with most non-metals. The most common compound is beryllium oxide (BeO) which does not react with water and dissolves in strongly basic solutions. Because of its high melting point, BeO is a good heat conductor in electrical insulators. It is also an amphoteric oxide, meaning it can react with both strong acids and bases. The most important applications of beryllium is the production of radiation windows. As beryllium is almost transparent to x-rays, it can be used in windows for x-ray tubes. The reactions of the alkaline earth metals differ from those of the Group 1 metals. Radium is radioactive and is not considered in this section. **Reactions with Hydrogen:** All

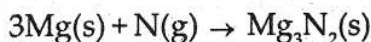
the alkaline earth metals react with hydrogen to create metallic hydrides. Below is an example of a reaction of this type:



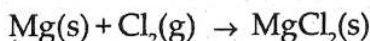
Reactions with Oxygen: The alkaline earth metals react with oxygen to produce metal oxides. An oxide is a compound containing oxygen in a -2 oxidation state. The following is an example reaction of an alkaline earth metal with oxygen (beryllium does not react with oxygen, but the other metals react in this manner:



Reactions with Nitrogen: These reactions cannot occur in ordinary condition; extremely high temperatures are required. A theoretical reaction of an alkaline earth metal with nitrogen would proceed in the following manner:



Reactions with Halogens: Alkaline earth metals react with halogens to form metal halides. A halide is a compound containing an ionic halogen. A reaction of this type between magnesium and chlorine is given below:



Reactions with Water: Beryllium does not react with water; however, magnesium, calcium, strontium, and barium do react to form metal hydroxides and hydrogen gas. The reaction of barium and water is illustrated in the following equation:



4.5 USES OF s-BLOCK ELEMENTS AND THEIR COMPOUNDS (Li, Na AND K ONLY)

Use of Lithium and their compounds: Lithium stearate $\text{C}_{17}\text{H}_{35}\text{COOLi}$ is used in making automobile grease. Li_2CO_3 is added to bauxite in the electrolytic production of aluminium, as it lowers the melting point. LiCO_3 is also used to toughen glass. It also has uses in medicine, as it affects the balance between Na^+ and K^+ and Mg^{2+} and Ca^{2+} in the body. Lithium metal is used to make alloys, for example with lead to make 'white metal' bearings for motor engines with aluminium

to make aircraft parts which are light and strong and with magnesium to make armor plate. There is great interest in lithium for thermonuclear purposes, since when bombarded with neutrons it produces tritium.

Lithium is also used to make electrochemical cells (both primary and secondary batteries). Primary batteries produce electricity by a chemical change and are discarded when they 'run down'. These have Li anodes, carbon cathodes and SOCl_2 as the electrolyte. There is interest in Li/S batteries which could power battery cars in the future and in secondary cells, which may provide a practical way of storing off-peak electricity, LiH is used to generate hydrogen, and LiOH to absorb CO_2 .

Use of Sodium and their compounds: Caustic soda (NaOH) is the most important alkali used in industry and is used for a wide variety of purposes including making many inorganic and organic compounds, paper making, neutralizations, and making alumina, soap and rayon.

Soda ash Na_2CO_3 may be used interchangeably with NaOH in many applications such as making paper, soap and detergents. Large amounts are used in making glass, phosphates, silicates and cleaning preparations and removing SO_2 pollution from the flue gases at coal-fired electricity generating stations.

Large amounts of Na_2SO_4 are used to make paper, detergents and glass. NaOCl is used as bleach and a disinfectant.

NaHCO_3 is used in baking powder. Sodium metal is used in large quantities.

Na produced is used to make a Na/Pb alloy which is used to make PbEt_4 and PbMe_4 which are used as anti-knock additives to petrol, but this will decrease with the increasing use of lead free petrol. About 20% is used to reduce TiCl_4 and ZrCl_4 to the metals and the remainder is used to make compounds such as Na_2O_2 and NaH.

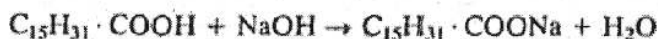
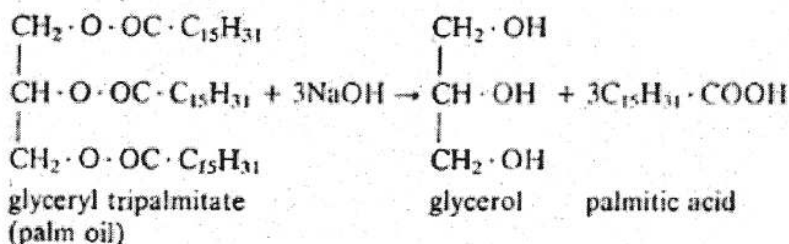
Liquid sodium metal is used as a coolant in one type of nuclear reactor. It is used to transfer heat from the reactor to turbines where it produces steam which is used to generate electricity. Fast breeder nuclear reactors, metal sodium conducts heat very well, and as its boiling point is 881°C it is ideal for this purpose. Small amounts of the metal are used in inorganic synthesis, and for drying organic solvents.

Use of Potassium and their compounds: Potassium is an essential element for life. Roughly 95% of potassium compounds are used

as fertilizers for plants - KCl 90%, K_2SO_4 9%, KNO_3 1%. Potassium salts are always more expensive than sodium salts, usually by a factor of 10 or more. KOH (which is prepared by electrolysis of aqueous KCl) is used to make potassium phosphates and also soft soap, e.g. potassium stearate, both of which are used in liquid detergents. KNO_3 is used in explosives. $KMnO_4$ is used in the manufacture of saccharin, as an oxidizing agent and for titrations. K_2CO_3 is used in ceramics, colour - TV tubes and fluorescent light tubes. Potassium superoxide KO_2 is used in breathing apparatus in submarines and KBr is used in photography. Potassium metal most of it is used to making KO_2 .

4.6 ORGANOMETALLIC COMPOUNDS

The alkali metals replace hydrogen in organic acids, form salts such as sodium acetate (sodium ethanoate) CH_3COONa . Soap is a mixture of the sodium salts of palmitic, oleic and stearic acids. Soap is made by the saponification (hydrolysis) of naturally occurring fats and oils. These fats and oils are esters of glycerol and their hydrolysis with NaOH first breaks the ester to glycerol and fatty acids, neutralizing the fatty acid to give the sodium salts.



Lithium stearate is also a 'soap', and is made from LiOH and some natural fat such as tallow. It is widely used to thicken hydrocarbon oils used as lubricants (the so-called detergent oils) and it is also used to make greases for motor vehicles.

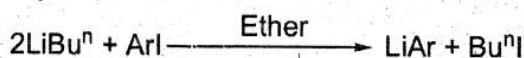
Exciting developments have occurred in the coordination chemistry of the alkali metals during the last few years that have completely revived what appeared to be a largely predictable and worked-out area of chemistry. Conventional beliefs had reinforced the predominant impression of very weak coordinating ability and had rationalized this in terms of the relatively large size and low charge of the cations M^+ . On this view, stability of coordination complexes should diminish in the sequence $Li > Na > K > Rb > Cs$ and this is frequently

observed, though the reverse sequence is also known for the formation constants for example, the weak complexes with sulfate, peroxosulfate, thiosulfate and the hexacyanoferrates in aqueous solutions. It was also known that the alkali metal cations formed numerous hydrates, or aqua-complexes, as discussed in the preceding section, and there is a definite, though smaller tendency to form ammine complexes such as $[\text{Li}(\text{NH}_3)_4]^+$. Other well-defined complexes include the extremely stable adducts $\text{LiX} \cdot 5\text{Ph}_3\text{PO}$, $\text{LiX} \cdot 4\text{Ph}_3\text{PO}$ and $\text{NaX} \cdot 5\text{Ph}_3\text{PO}$, where X is a large anion such as I, NO_3^- , ClO_4^- , BPh_4^- , SbF_6^- , AuCu , etc.; these compounds melt in the range $200\text{--}315^\circ$ and are stable to air and water (in which they are insoluble). In recent years this simple picture has been completely transformed and it is now recognized that the alkali metals have a rich and extremely varied coordination chemistry which frequently transcends even that of the transition metals. The efflorescence is due to several factors such as the emerging molecular chemistry of lithium in particular, the imaginative use of bulky ligands, the burgeoning numbers of metal amides, alkoxides, enolates and organometallic compounds, and the exploitation of multidentate crown and cryptand ligands. Lithium is now known in at least 20 coordination geometries with coordination numbers ranging from 1-12.

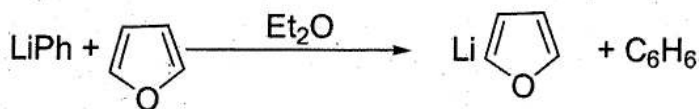
Organolithium compounds can readily be prepared from metallic Li and this is one of the major uses of the metal. Because of the great reactivity both of the reactants and the products, air and moisture must be rigorously excluded by use of an inert atmosphere. Lithium can be reacted directly with alkyl halides in light petroleum, cyclohexane, benzene or ether, the chlorides generally being preferred:



Lithium aryls are best prepared by metal-halogen exchange using LiBu^n and an aryl iodide, and transmetalation is the most convenient route to vinyl, allyl and other unsaturated derivatives:



Similar reactions are available for the other alkali metals. Metalation (metal-hydrogen exchange) and metal addition to alkenes provide further routes, e.g.



Compounds of Be show properties consistent with a greater covalent character than those of its group, and some of its complexes with ordinary ligands are stable. The complexes are usually tetrahedral, although the coordination number of Be can fall to 3 or 2 if the ligands are bulky. For example, basic beryllium acetate (beryllium oxoethanoate, $\text{Be}_4\text{O}(\text{O}_2\text{CCH}_3)_6$) consists of a central O atom surrounded by a tetrahedron of four Be atoms, which in turn are bridged by ethanoate ions shown in X-ray structure below.

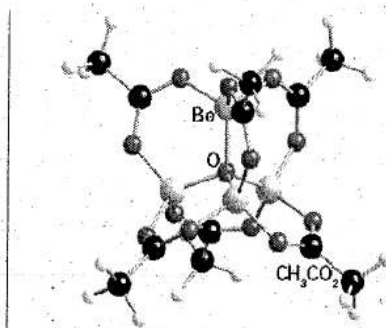


Figure of X-ray structure of beryllium oxoethanoate, $\text{Be}_4\text{O}(\text{O}_2\text{CCH}_3)_6$

Group 2 cations form complexes with crown and crypt ligands. The least labile of these complexes are formed with the larger Sr^{2+} and Ba^{2+} cations. All the complexes are more stable than those of the smaller Group 1 cations. The most stable complexes are formed with charged polydentate ligands, such as the analytically important ethylenediaminetetraacetate ion (EDTA). The formation constants of edta complexes lie in the order $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$.

In the solid state, the structure of the Mg^{2+} edta complex is seven-coordinate, with H_2O at one coordination site. The Ca^{2+} complex is either seven- or eight coordinate, depending on the counter ion, with one or two H_2O molecules serving as ligands shown in x-ray structure below.

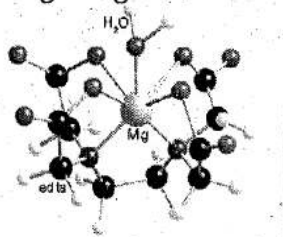


Figure : X-ray structure of $[\text{Mg}(\text{EDTA})(\text{OH}_2)]^{2-}$

Many complexes of Ca^{2+} and Mg^{2+} occur naturally. The most important macrocyclic complexes are the chlorophylls, which are porphyrin complexes of Mg and are central to photosynthesis.

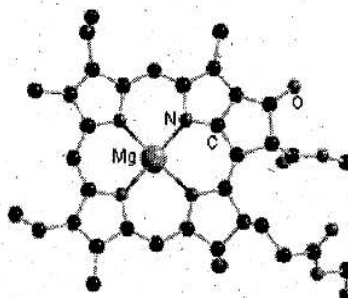
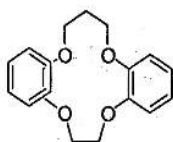
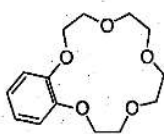


Figure: X-ray structure of Chlorophyll fragment with skeleton MgCNO .

4.7 POLYETHER COMPLEXES (CROWN ETHER COMPLEXES) OF ALKALI METALS

In 1967 when C. J. Pedersen announced the synthesis of several macrocyclic polyethers which were shown to form stable complexes with alkali metal and other cations. The stability of the complexes was found to depend on the number and geometrical disposition of the ether oxygen atoms and in particular on the size and shape of potential coordination polyhedra relative to the size of the cation.

Such "crown" ethers are given in the numerical prefix indicating the number of atoms in the heterocycle and the suffix the number of ether oxygens. The "hole size" for coordination depends on the number of atoms in the ring and is compared with conventional ionic diameters. The best complexing agents are rings of 15-24 atoms including 5 to eight oxygen atoms. Nitrogen and sulfur can also serve as the donor atoms in analogous macroheterocycles. The X-ray crystal structures of many of these complexes have now been determined from which it is clear that, at least for the larger cations, coordinative saturation and bond directionality are far less significant factors than in many transition element complexes.

Dibenzo-14-crown-4
crown-6

Benzo-15-crown-5



Dibenzo-18-

Figure: Schematic representation of the (non-planar) structure of some typical crown ethers.

Table: Comparison of ionic diameters and crown ether "hole sizes"

Ionic diam/pm	Ionic diam/pm	Ionic diam/pm	Ionic diam/pm	Polyether ring	"Hole size" (pm)
Li^+	152	Mg^{2+}	144	14-crown-4	120-150
Na^+	204	Ca^{2+}	200	15-crown-5	170-220
K^+	276	Sr^{2+}	236	18-crown-6	260-320
Rb^+	304	Ba^{2+}	270	21-crown-7	340-430
Cs^+	334	Ra^{2+}	296		

Another group of very effective ligands that have recently been employed to coordinate alkali metal cations are the macrobicyclic polydentate ligands that J. M. Lehn has termed "**Cryptands**". Such complexes are finding increasing use in solvent extraction, phase-transfer catalysis. The crystal structure of $[\text{Cs}(18\text{-crown-6})_2]^+ \text{e}^-$ shown in figure given below.

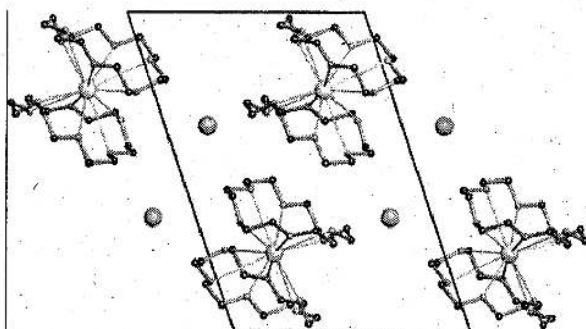


Figure of the crystal structure of $[\text{Cs}(18\text{-crown-6})_2]^+ \text{e}^-$. The pink spheres mark the sites of highest electron density and so indicate the locations of the 'anion' e^- . (From S.B. Dawes, D.L. Ward, R.H. Huang, and J.J. Dye, *J. Am. Chem. Soc.*, 1986, 108, 3534.)

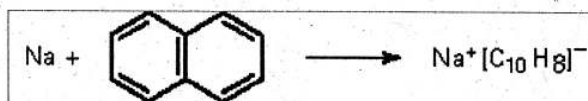
4.6 ORGANOMETALLIC COMPOUNDS OF Li, Na, K, Be and Mg

Organometallic chemistry developed slowly from the discovery of Zeise's salt in 1827 until around 1950. Some organometallic compounds such as Grignard reagents found utility in organic synthesis but there was little systematic study of compounds Fulvalene containing metal-carbon bonds.

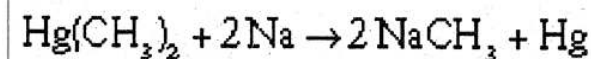
Group 1 elements form a number of organometallic compounds that are unstable in the presence of water and are pyrophoric in air. They are prepared in organic solvents such as tetrahydrofuran (THF). Protic (proton-donating) organic compounds form ionic organometallic compounds with the Group 1 metals. For example, cyclopentadiene reacts with sodium metal in THF.



The resulting cyclopentadienide anion is an important intermediate in the synthesis of d-block organometallic compounds. Lithium, sodium, and potassium form intensely coloured compounds with aromatic species. The oxidation of the metal results in transfer of an electron to the aromatic system to produce a **radical anion**, an anion that possesses an unpaired electron.

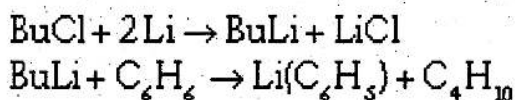


Sodium and potassium alkyls are colourless solids that are insoluble in organic solvents and, when stable, have fairly high melting temperatures. They are produced by a **transmetallation reaction**, which involves breaking a metal-carbon bond and forming a metal-carbon bond to a different metal. Alkylmercury compounds are often the starting materials in these reactions. For example, methylsodium is produced in the reaction between sodium metal and dimethylmercury in a hydrocarbon solvent.



Organolithiums are by far the most important Group 1 organometallic compounds. They are liquids or low melting solids, are the most thermally stable of the entire group, and are soluble in organic and nonpolar solvents such as THF. They can be synthesized from an

alkyl halide and lithium metal or by reacting the organic species with butyllithium, $\text{Li}(\text{C}_4\text{H}_9)$, commonly abbreviated to BuLi.



A feature of many main-group organometallic compounds is the presence of bridging alkyl groups. When ethers are the solvent, methyl lithium exists as $\text{Li}_4(\text{CH}_3)_4$, with a tetrahedron of Li atoms and bridging CH_3 groups. In hydrocarbon solvents, $\text{Li}_6(\text{CH}_3)_6$ is formed; its structure is based on an octahedral arrangement of Li atoms shown in figure below. Other alkyllithiums adopt similar structures except when the alkyl groups become very bulky, as in the case of *t*-butyl, $-\text{C}(\text{CH}_3)_3$, when tetramers are the largest species formed. Many of these alkyllithiums are electrondeficient compounds and contain the 3c, 2e bonds characteristic of such compounds.

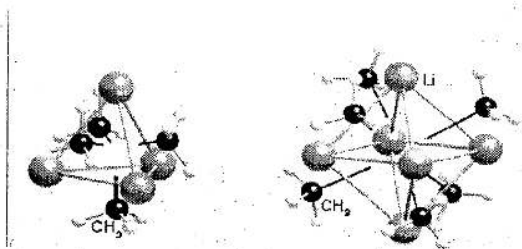
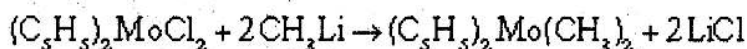


Figure of X-ray structure of a- $\text{Li}_4(\text{CH}_3)_4$ and b- $\text{Li}_6(\text{CH}_3)_6$

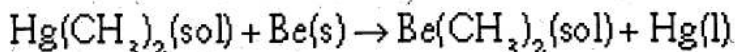
Alkyllithiums are important industrially in the stereospecific polymerization of alkenes to form synthetic rubber. Butyllithium is used as an initiator in solution polymerization to produce a wide range of elastomers and polymers. Organolithium compounds are also used in the synthesis of a range of pharmaceuticals, including vitamins A and D, analgesics, antihistamines, antidepressants, and anticoagulants. Alkyllithiums can be used in the synthesis of other organometallic compounds. For example to introduce alkyl groups into d-metal organometallic compounds.



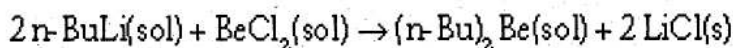
The reactivity and solubility of alkyllithium is enhanced by adding a chelating ligand such as tetramethylethylenediamine, TMEDA, which breaks up any tetramers to give complexes such as $[\text{BuLi}(\text{TMEDA})]_2$.



Organometallic compounds of Be are pyrophoric in air and unstable in water. Methylberyllium can be prepared by transmetallation from methylmercury in a hydrocarbon solvent:



Another synthetic route is by halogen exchange or metathesis reactions in which a beryllium halide reacts with an alkyllithium compound. The products are the lithium halide and an alkylberyllium compound. In this way, the halogen and organic groups are transferred between the two metal atoms. The driving force for this and similar reactions is the formation of the halide of the more electropositive metal.



Methylberyllium, $\text{Be}(\text{CH}_3)_2$, is predominantly a monomer in the vapour phase and in hydrocarbon solvents, where it adopts a linear structure, as expected from the VSEPR model. In the solid it forms polymeric chains in which the bridging CH_3 groups form $3c, 2e$ bridging bonds. Bulkier alkyl groups lead to a lower degree of polymerization; ethylberyllium is a dimer and *t*-butylberyllium is a monomer shown in figure below.

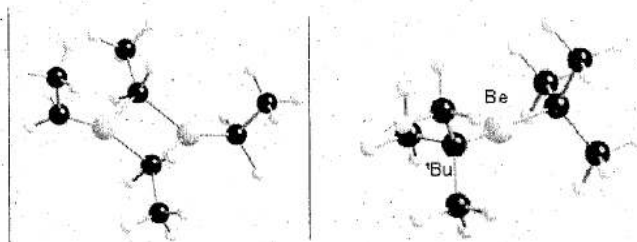


Figure: X-ray structure of $(\text{BeEt}_2)_2$ and Be^tBu_2 , $^t\text{Bu} = (\text{CH}_3)_3\text{C}$

An interesting organoberyllium compound is beryllocene, $(\text{C}_5\text{H}_5)_2\text{Be}$, which, although the formula suggests an analogy with ferrocene, in fact has a different structure in the crystalline state, with the Be atom positioned directly above the centre of one cyclopentadienyl ring and below a single C atom on the other ring. However, the low-temperature (-135°C) NMR spectrum of this compound in solution suggests that the two rings are equivalent, indicating that even at this low temperature the Be atom and the C_5H_5 rings are rearranging rapidly.

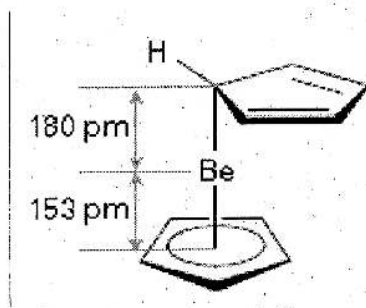


Figure of Representing the BeCp_2 , $\text{Cp} = \text{C}_5\text{H}_5$

Alkyl- and arylmagnesium halides are very well known as **Grignard reagents** and are widely used in synthetic organic chemistry where they behave as a source of R^- . They are prepared from magnesium metal and an organohalide. As the surface of magnesium is covered by a passivating oxide film, it has to be activated before the reaction can proceed. A trace of iodine is usually added to the reactants, forming magnesium iodide; this compound is soluble in the solvent used and dissolves to expose an activated magnesium surface. Alternatively a highly active, finely powdered form of magnesium can be generated by reducing MgCl_2 with potassium in THF. The reaction to produce the Grignard reagents is carried out in ether or tetrahydrofuran. The structures of Grignard reagents are far from simple. The metal atom has a coordination number of 2 only in solution and when the alkyl group is bulky, it is solvated with a tetrahedral arrangement of solvent molecules around the Mg atom shown in figure below.

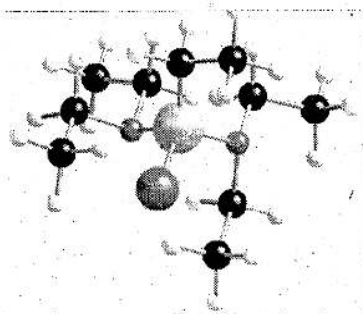


Figure: X-ray structure of $\text{MgBr}(\text{OEt})_2$

The organometallic compounds of Ca, Sr, and Ba are generally ionic and very unstable. They all form analogues of Grignard reagents by direct interaction of the finely divided metal with organohalide. Finally, although the members of the group occur almost exclusively in oxidation state +2 in their compounds, the reduction of $\text{Mg}(\text{II})$ to $\text{Mg}(\text{I})$ by potassium

has been achieved in the synthesis of the compounds LMg-MgL where L is $[\text{Ar}(\text{NC})(\text{NPr}_2)\text{N}(\text{Ar})]^-$ and $\text{Ar} = 2,6\text{-diisopropylphenyl}$.

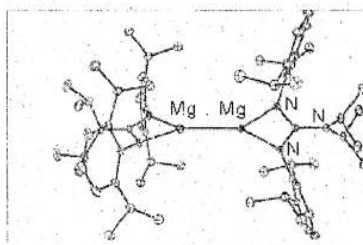


Figure: X-ray structure of LMgMgL , $\text{L} = [\text{Ar}(\text{NC})(\text{NPr}_2)\text{NAr}]^-$, $\text{iPr} = (\text{CH}_3)_2\text{CH}$

Organometallic chemistry the compounds containing metal-carbon bonds, has grown a lot as a field of study during the past four decades. It covers a wide variety of chemical compounds and their reactions including compounds containing both σ and δ bonds between metal atoms and carbon. In the many cluster compounds containing one or more metal-metal bonds and molecules of structural types unusual or unknown in organic chemistry. In some cases, reactions of organometallic compounds bear similarities to known organic reactions and in other cases they are significantly different. Aside from their inherently interesting nature, many organometallic compounds form useful catalysts and consequently are of significantly industrial interest.

4.8 EXTRACTION AND ISOLATION OF Li, Be and Ra FROM THEIR MINERALS

Extraction and isolation of Lithium (Li): Lithium is fairly widely distributed in nature and is about twice as lead. However, the amount present in any mineral is always small and the extraction is not easy task. Lithium salt also occur in certain spring waters and in some plants as tobacco, beet and sugar cane. The lithium bearing minerals are

1. **Lepidolite or Lithia mica** $(\text{Li}, \text{Na}, \text{K})_2\text{Al}_2(\text{SiO}_3)_3(\text{F}, \text{OH})_2$ containing about 1.5% of Lithium.
2. **Petalite**, $\text{LiAl}(\text{Si}_2\text{O}_5)_4$, containing about 2.7-3.7% of lithium.
3. **Spodumene**, $\text{LiAl}(\text{SiO}_3)_2$, containing about 4-6% of lithium.
4. **Triphylite**, $(\text{Li}, \text{Na})_3\text{PO}_4(\text{Fe}, \text{Mn})_3(\text{PO}_4)_2$, containing upto 4% of lithium.

Extraction of lithium from their ores involve following steps

1. Preparation of lithium chloride
 - a) Acid treatment method b) Fusion method

2. Electrolysis of lithium chloride

1. *Preparation of lithium chloride,*

- a) *Acid treatment method-*

Lithium mineral is finely powdered and boiled with sulphuric acid, the insoluble silica is formed is filtered off. The solution is treated with sodium carbonate to precipitate aluminum and iron, then excess sodium carbonate is added to precipitate lithium as the carbonate. This is filtered and dissolved in HCl to obtained lithium chloride which is purified by alcohol.

- b) *Fusion method-*

The powdered mineral is fused with a mixture of barium carbonate and barium/sodium sulphate, the fused mass separated into two layers, the upper layer contain the sulphate of alkali metals and lower layer contain barium sulphate along with alumina and silica.

Extraction and isolation of Beryllium (Be): The extraction of beryllium from its compounds is a difficult process due to its high affinity for oxygen at elevated temperatures and its ability to reduce water when its oxide film is removed. The United States, China and Kazakhstan are the only three countries involved in the industrial-scale extraction of beryllium.

Beryllium is most commonly extracted from the mineral **beryl**, which is either sintered using an extraction agent or melted into a soluble mixture. The sintering process involves mixing beryl with sodium fluorosilicate and soda at 770 °C to form sodium fluoroberyllate, aluminium oxide and silicon dioxide. Beryllium hydroxide is precipitated from a solution of sodium fluoroberyllate and sodium hydroxide in water. Extraction of beryllium using the melt method involves grinding beryl into a powder and heating it to 1,650 °C. The melt is quickly cooled with water and then reheated 250 to 300 °C in concentrated sulfuric acid, mostly yielding beryllium sulfate and aluminium sulfate. Aqueous ammonia is then used to remove the aluminium and sulfur, leaving beryllium hydroxide.

Beryllium hydroxide created using either the sinter or melt method is then converted into beryllium fluoride or beryllium chloride. To form the fluoride, aqueous ammonium hydrogen fluoride is added to beryllium hydroxide to yield a precipitate of ammonium tetrafluoroberyllate, which is heated to $1,000\text{ }^{\circ}\text{C}$ to form beryllium fluoride. Heating the fluoride to $900\text{ }^{\circ}\text{C}$ with magnesium forms finely divided beryllium, and additional heating to $1,300\text{ }^{\circ}\text{C}$ creates the compact metal. Heating beryllium hydroxide forms the oxide, which becomes beryllium chloride when combined with carbon and chlorine. Electrolysis of molten beryllium chloride is then used to obtain the metal.

The low weight and high rigidity of beryllium make it useful as a material for high-frequency speaker drivers. Because beryllium is expensive (many times more than titanium), hard to shape due to its brittleness, and toxic if mishandled.

Extraction and isolation of Radium (Ra):

In the first extraction of Radium, Curie used the residues after extraction of uranium from pitchblende. The uranium had been extracted by dissolution in sulphuric acid (H_2SO_4) leaving radium sulphate, which is similar to barium sulphate (BaSO_4) but even less soluble in the residues. The residues also contained rather substantial amounts of barium sulphate which thus acted as a carrier for the radium sulphate. The first steps of the radium extraction process involved boiling with sodium hydroxide (NaOH) followed by hydrochloric acid (HCl) treatment to remove as much as possible of other compounds. The remaining residue was then treated with sodium carbonate (Na_2CO_3) to convert the barium sulphate into barium carbonate carrying the radium, thus making it soluble in hydrochloric acid. After dissolution the barium and radium are re-precipitated as sulphates and this was repeated one or few times, for further purification of the mixed sulphate. Some impurities that form insoluble sulphides, were removed by treating the chloride solution with hydrogen sulphide (H_2S) followed by filtering. When the mixed sulphate were pure enough they were once more converted to mixed chloride and barium and radium were separated by fractional crystallisation while monitoring the progress using a spectroscope (radium gives characteristic red lines in contrast to the green barium lines) and the electroscope. A similar process was still used for industrial radium extraction in 1940, but mixed bromides were then used for the fractionation. If the barium

content of the uranium ore is not high enough it is easy to add some to carry the radium. These processes were applied to high grade uranium ores but may not work well with low grade ores.

4.9 SUMMARY

As the objective of the unit you may be able to explain the properties of s-block elements, Hydrogen and their isotopes and properties, Chemical reactivity of alkali and earth alkaline metals, some of the s-block elements and their compounds, Organometallic compounds of Li, Na, K, Be and Mg, Polyether complexes or Crown ether complexes and their properties, and extraction and isolation of Li, Be and Ra.

4.10 TERMINAL QUESTIONS

1. In group 1, values of the first ionization energies order among the Li Na and K?
2. In group 1, values of the metallic radii in the order among Na, K and Rb?
3. In group 1, Which ion liberates the most energy on hydration?
4. Give the formula of Peroxide, superoxide and ozonide ions are, respectively?
5. Peroxide and superoxide ions are, respectively?
6. What happens when Al dissolves in aqueous NaOH?
7. When alkali metal ions are complexed with the cyclic ether 18-crown-6, the most stable complex is formed with?
8. Sodium amalgam is used as?
9. Which is the safest way to dispose of Na metal?
10. Na_2O reacts with water to give?
11. In CaF_2 lattice, Ca is coordinated by number of F^- atoms?
12. Suitable hybridization schemes for Be in $\text{BeCl}_2(\text{g})$ and $\text{BeCl}_2(\text{s})$ are, respectively?
13. Formula of Soda lime consists of?
14. Formula of Quicklime and slaked lime are, respectively?
15. In chlorophyll, the coordination environment of Mg^{2+} is approximately?

16. The charge density of an Mg^{2+} ion is most similar to which element?
 17. Mg^{2+} , Ca^{2+} and Sr^{2+} ions form stable complexes with crown ethers. This involves which type of interactions between them?
 18. BeCl_2 is an example of ?
-

4.11 ANSWERS

1. $\text{Li} > \text{Na} > \text{K}$
2. $\text{Na} < \text{K} < \text{Rb}$
3. Na^+
4. $[\text{O}_2]^{2-}$, $[\text{O}_2]^-$, $[\text{O}_3]^-$
5. Diamagnetic and paramagnetic
6. Forms soluble $\text{NaAl}(\text{OH})_4$.
7. K^+
8. A reducing agent
9. Add small amounts of Na to propan-2-ol
10. Only NaOH product.
11. F^- ions are 8-coordinate
12. sp and sp^3 hybridization.
13. NaOH and $\text{Ca}(\text{OH})_2$
14. CaO and $\text{Ca}(\text{OH})_2$
15. Square Planer
16. Li^+
17. Hard Acid and Hard Base
18. Lewis acid

SUGGESTED READINGS:

1. **Advance Inorganic Chemistry**, F. A. Cotton and G. Wilkinson, Interscience Publishers, J. Wiley and Sons.
2. **Inorganic Chemistry**, Shriver and Atkins, W. H. Freeman and Company New York
3. **Inorganic Chemistry**, P.A.Cox, Taylor and Francis Group.

4. **Inorganic Chemistry**, G.L. Miessler and D.A Tarr, Pearson Press International
5. **Concise Inorganic Chemistry**, J D Lee, Oxford University Press
6. **Chemistry of the Elements**, N.N.Greenwood, Butterworth and Hinemann, Oxford
7. **Principles of Inorganic Chemistry**, B. R. Puri, Sharma and Kalia, Milestone publishers & distributors.

UNIT 5 GENERAL STUDIES OF p- BLOCK ELEMENTS

- 5.1 Introduction
 - Objectives
- 5.2 Group wise discussion with respect to electronic configuration, ionisation potential, electron affinity, electronegativity, atomic radii and oxidation states
- 5.3 Catenation and inert pair effect
- 5.4 Preparation, properties and structures of diborane, borazine and hydrazine
- 5.5 Interhalogens and polyhalides and fluorides of Xenon
- 5.6 Structure and basicities of oxyacids of B, P and S
- 5.7 Structural features of hydrides, halides, oxides and oxyacids
- 5.8 Summary
- 5.9 Terminal Questions
- 5.10 Answers

5.1 INTRODUCTION

In the previous units, you studied the main features of the chemistry of s-block (Group 1 and Group 2) elements, i.e. the alkali and the alkaline earth metals. In this unit you - will study the elements of p-block elements (Group 13 to 18). While studying the alkali and alkaline earth metals, you have seen that all the elements of these two groups are highly reactive metals and the first element of each group shows some differences from the rest. In Group 13, the differences between the first element and the remaining elements become so pronounced that the first member of the group, i.e. boron is a nonmetal whereas the rest of the elements are distinctly metallic in nature. In a way, this is the first group of the periodic table in which you observe a marked change in the nature of the elements down the group. describe the chemistry of hydrides, halides and oxides of boron and aluminium, elucidate the structures of hydrides of boron.

- Student can able to define as follows:
- The electronic configuration of p-block elements, oxidation state and properties of p-block elements.
- Compounds of p-block elements, preparation and properties.

5.2 GROUP WISE DISCUSSION WITH RESPECT TO ELECTRONIC CONFIGURATION, IONISATION POTENTIAL, ELECTRON AFFINITY, ELECTRONEGATIVITY, ATOMIC RADII AND OXIDATION STATES

The valence electron configuration of the Group 3 elements is ns^2np^1 (Table 1) and as this configuration suggests all the elements adopt the +3 oxidation state in their compounds. However, the heavier elements of the group also form compounds with the metal in the -1 oxidation state and this state increases in stability down the group.

Table 1: Electronic structures of Group 3 elements:

Element	Symbol	Electronic configuration	
Boron	B	$1s^2 2s^2 2p^1$	or [He] $2p^1$
Aluminium	Al	$1s^2 2s^2 2p^6 3s^2 3p^1$	or [Ne] $3p^1$
Gallium	Ga	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$	or [Ar] $4p^1$
Indium	In	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^1$	or [Kr] $5p^1$
Thallium	Tl	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^1$	or [Xe] $6p^1$

Table 2: Physical properties of Group III elements

Property	B	Al	Ga	In	Tl
Atomic number	5	13	31	49	81
Molar mass (g mol ⁻¹)	10.81	26.98	69.72	114.82	204.37
Density (g cm ⁻³)	3.3	2.7	5.91	7.31	11.90
Atomic radius (Å)	0.82	1.18	1.26	1.44	1.48
Melting point (°C)	2030	659	29.8	156.4	303
Boiling point (°C)	2550	2450	2237	2000	1457
Ionization energy (kJ mol ⁻¹)	800	577	579	558	589
Electronegativity	2.0	1.5	1.6	1.7	1.8

The valence electron configuration of the Group 4 elements is ns^2np^2 (Table 2). The elements of Group 4, carbon, silicon germanium, tin, and lead, show considerable diversity in their chemical and physical properties.

Table 3: Electronic structures of Group 4 elements

Element	Symbol	Electronic configuration	
Carbon	C	$1s^2 2s^2 2p^2$	or [He] $2p^2$
Silicon	Si	$1s^2 2s^2 2p^6 3s^2 3p^2$	or [Ne] $3p^2$
Germanium	Ge	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$	or [Ar] $4p^2$
Tin	Sn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$	or [Kr] $5p^2$
Lead	Pb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14}$ $5s^2 5p^6 5d^{10} 6s^2 6p^2$	or [Xe] $6p^2$

Table 4: Physical properties of Group IV elements

Property	C	Si	Ge	Sn	Pb
Atomic number	6	14	32	50	82
Molar mass (g mol ⁻¹)	12	28.08	72.59	118.89	207.19
Density (g cm ⁻³)	3.52	2.49	5.35	7.30	11.34
Atomic radius (Å)	0.77	1.11	1.22	1.41	1.44
Melting point (°C)	3727	1410	937.5	231.8	327.4
Boiling point (°C)	4833	2680	2830	2270	1725
Ionization energy (kJ mol ⁻¹)	1086	786	761	708	718
Electronegativity	2.5	1.8	1.8	1.8	1.8

The wide variety of possible oxidation states of the Group 5 elements can be understood to a large extent by considering the valence electron configuration of the elements which is ns^2np^3 . This configuration suggests that the highest oxidation state should be +5, as is indeed the case. Nitrogen has a very high electronegativity (exceeded by only O, F, and Cl) and in many compounds, for example the nitrides, which contain the N_3^- ion, and ammonia, NH_3 , nitrogen is in a negative oxidation state.

Table 5: Electronic structures of Group 5 elements

Element	Symbol	Electronic configuration	
Nitrogen	N	$1s^2 2s^2 2p^3$	or [He] $2p^3$
Phosphorus	P	$1s^2 2s^2 2p^6 3s^2 3p^3$	or [Ne] $3p^3$
Arsenic	As	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$	or [Ar] $4p^3$
Antimony	Sb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^3$	or [Kr] $5p^3$
Bismuth	Bi	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14}$ $5s^2 5p^6 5d^{10} 6s^2 6p^3$	or [Xe] $6p^3$

Table 6: Physical properties of Group V elements

Property	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Molar mass (g mol ⁻¹)	14.007	30.97	74.922	121.75	208.98
Density (g cm ⁻³)	17.3	17	13.1	18.4	21.3
Atomic radius (Å)	0.75	1.06	1.19	1.38	1.46
Melting point (°C)	-210	44.1 (white)	817 (at 36 atm)	630.5	271.3
Boiling point (°C)	-195.8	280	713	1380	1470
Ionization energy (kJ mol ⁻¹)	1402	1012	946	840	703
Electronegativity	3	2.1	2.0	1.8	1.7

The Group 6 electron configuration of ns^2np^4 suggests a group maximum oxidation number of +6. Oxygen, sulfur, and selenium are nonmetals, tellurium is a metalloid, and polonium is a metal. Allotropy and polymorphism are important features of Group 6 and sulfur occurs in more natural allotropes and polymorphs than any other element. The electron configuration also suggests that stability may be achieved with an oxidation number of -2, which is overwhelmingly. The electron configuration also suggests that stability may be achieved with an oxidation number of -2, which is overwhelmingly common for O. The most remarkable feature of S is that it forms stable compounds with oxidation numbers between -2 and +6. In addition to its distinctive physical properties, O is significantly different chemically from the other members of the group.

Table 7: Electronic structures of Group 6 elements:

Element	Symbol	Electronic configuration	
Oxygen	O	$1s^2 2s^2 2p^4$	or [He] $2p^4$
Sulphur	S	$1s^2 2s^2 2p^6 3s^2 3p^4$	or [Ne] $3p^4$
Selenium	Se	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$	or [Ar] $4p^4$
Tellurium	Te	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ $4d^{10} 5s^2 5p^4$	or [Kr] $5p^4$
Polonium	Po	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}$ $4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^4$	or [Xe] $6p^4$

Table 8: Physical properties of Group VI elements

Property	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Molar mass (g mol ⁻¹)	15.99	32.06	78.96	127.6	210
Density (g cm ⁻³)	1.14	2.07	4.79	6.23	9.2
Atomic radius (Å)	0.73	1.09	1.16	1.35	-
Melting point (°C)	-218.8	114.0	217.0	449.5	254
Boiling point (°C)	-183	444.6	685	989.8	962
Ionization energy (kJ mol ⁻¹)	1313.7	999.4	940.9	869.5	813.5
Electronegativity	3.5	2.5	2.4	2.1	2.0

The Group 7 elements, fluorine, chlorine, bromine, iodine and astatine, are known as the **halogens** from the Greek for 'salt giver'. Fluorine and chlorine are poisonous gases, bromine is a toxic, volatile liquid, and iodine is a sublimable solid. They are among the most reactive nonmetallic elements. The atomic properties of the halogens are listed in Table they all have the valence electron configuration $ns2np5$. The features to note include their high ionization energies and their high electronegativities and electron affinities. Their electron affinities are high because the incoming electron can occupy an orbital of an incomplete valence shell and experience a strong nuclear attraction: recall that Z_{eff} increases progressively across the period.

Table 9: Electronic structures of Group 7 elements (Halogens):

Element	Symbol	Electronic configuration	
Fluorine	F	$1s^2 2s^2 2p^5$	or [He] $2p^5$
Chlorine	Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$	or [Ne] $3p^5$
Bromine	Br	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$	or [Ar] $4p^5$
Iodine	I	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$	or [Kr] $5p^5$
Astatine	At	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^4$ $5s^2 5p^6 5d^{10} 6s^2 6p^5$	or [Xe] $6p^5$

Table 10: Physical properties of Group VII elements

Property	F	Cl	Br	I
Atomic number	9	17	35	53
Molar mass (g mol ⁻¹)	18.99	35.45	79.90	126.90
Density (g cm ⁻³)	1.1	1.155	2.948	3.76
Atomic radius (Å)	0.72	0.99	1.14	1.33
Colour of liquid	Yellow	Yellow	Reddish brown	Violet shining solid
Melting point (°C)	-218	-101	-7.2	113.9
Boiling point (°C)	1.11	1.16	2.95	3.76(solid)
Ionization energy (kJ mol ⁻¹)	1680	1255	1142	1008
Electronegativity	4	3	2.8	2.5

The Group 8 elements are very unreactive. Their unreactivity can be understood in terms of their atomic properties and in particular their ground-state valence electron configurations, $ns^2 np^6$. The features to note include their high ionization energies and negative electron affinities. The first ionization energy is high because the effective nuclear charge is high at the far right of the period. The Group 8 elements, helium, neon, argon, krypton, xenon, and radon, are all monatomic gases. They are the least reactive elements and have been given and their properties have been identified and then disproved. Thus they have been called the *rare gases* and the *inert gases*, and are currently called the **noble gases**.

Helium makes up 23 per cent by mass of the Universe and the Sun, and is the second most abundant element after hydrogen; it is rare in the atmosphere because its atoms travel fast enough to escape from the Earth.

Table 11: Electronic structures of Group 8 elements or Zero group (Noble Gases):

Element	Symbol	Electronic configuration
Helium	He	$1s^2$
Neon	Ne	$1s^2 2s^2 2p^6$
Argon	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$
Krypton	Kr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
Xenon	Xe	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
Radon	Rn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6$ $5d^{10} 6s^2 6p^6$

The percentage by volume of the various elements of Zero Group is given below

Gas	He	Ne	Ar	Kr	Xe
Percentage by volume	5.24×10^{-4}	1.82×10^{-3}	9.34×10^{-1}	1.45×10^{-3}	8.7×10^{-6}

Table 12: Physical properties of Zero group (Noble Gases)

Property	He	Ne	Ar	Kr	Xe	Rn
Atomic number	2	10	18	36	54	86
Molar mass (g mol^{-1})	4	20.1	39.95	83.3	131.3	222
Density (g cm^{-3})						
Atomic radius ($\text{\AA}$)	1.4	1.54	1.88	2.02	2.16	-
Melting point ($^{\circ}\text{C}$)	-272.1	-246.6	-189.4	-157.2	-111.8	-71
Boiling point ($^{\circ}\text{C}$)	-268.9	-246.1	-185.86	-153.35	-108.1	-62
Ionization energy (kJ mol^{-1})	2372	2080	1520	1350	1170	1037
Critical pressure(atm)	2.26	26.9	50	54.3	58.2	62.4

5.3 CATENATION AND INERT PAIR EFFECT

The chemical properties of the first member of each group in the p-block are significantly different from its congeners. These anomalies are attributable to the small atomic radius and its correlates, high ionization energies, high electronegativities, and low coordination numbers. For example, in Group 4 carbon forms an enormous number of catenated hydrocarbons with strong C-C bonds. Carbon also forms strong multiple bonds in the alkenes and alkynes. This tendency to catenation is much reduced for its congeners and the longest silane formed contains just four Si atoms.

The E-E bond enthalpy decreases on descending the group. As a result, the tendency to catenation decreases from C to Pb. As C-C, 348; Si-Si, 326; Ge-Ge, 186; Sn-Sn, 150; and Pb-Pb, 87 kJmol⁻¹. Silicon forms a series of compounds analogous to the alkanes, the *silanes*, but the longest chain contains just seven Si atoms, as heptasilane, Si₇H₁₆. The silanes, with their greater number of electrons and stronger intermolecular forces, are less volatile than their hydrocarbon analogues. Thus, whereas propane, C₃H₈, is a gas under normal conditions, its silicon analogue trisilane Si₃H₈ is a liquid that boils at 53°C.

Inert pair effect

The group oxidation number can be predicted from the electron configuration of an element. The inert pair effect leads to an increasing stability of an oxidation state that is 2 less than the group oxidation number for the heavier elements. d-Block elements exhibit a variety of oxidation states.

The trends in stable oxidation states within the periodic table can be understood to some extent by considering electron configurations. A complete or half-full valence shell imparts greater stability than a partially filled shell. Therefore, there is a tendency for atoms to gain or lose electrons until they acquire that configuration. A noble-gas configuration is achieved in the s and p blocks when eight electrons occupy the s and p subshells of the valence shell. In Groups 1, 2, and 13 the loss of electrons to leave the inner complete shell can be achieved with a relatively small input of energy. Thus, for these elements the oxidation numbers typical of the groups are +1, +2 and +3, respectively. From Group 4 to Group 7 it becomes increasingly energetically favourable for the atoms to accept

electrons in order to complete the valence shell. Consequently, the group oxidation numbers are -4, -3, -2, -1 with more electronegative elements. Group 8 elements already have a complete octet of electrons and are neither readily oxidized nor reduced.

The heavier elements of the p block also form compounds with the element with an oxidation number 2 less than the group oxidation number. The relative stability of an oxidation state in which the oxidation number is 2 less than the group oxidation number is an example of the *inert pair effect* and it is a recurring theme within the p block. For example, in Group 3 whereas the group oxidation number is -3, the -1 oxidation state increases in stability down the group. In fact, the most common oxidation state of thallium is Tl(I). There is no simple explanation for this effect: it is often ascribed to the large energy that is needed to remove the ns^2 electrons after the np^1 electron has been removed. However, the sum of the first three ionization energies of Tl-5438 kJ mol⁻¹, is not higher than the value for Ga -5521 kJ mol⁻¹ and only slightly higher than the value for In-5083 kJ mol⁻¹. Another contribution to the effect may be the low M-X bond enthalpies for the heavier p-block elements and the decreasing lattice energy as the atomic radii increase down a group.

5.4 PREPARATION, PROPERTIES AND STRUCTURES OF DIBORANE, BORAZINE AND HYDRAZINE

A most striking feature of the lighter Group 3 elements is their ns^2np^1 electron configuration, which contributes up to a maximum of six electrons in the valence shell when three covalent bonds are formed by electron sharing. As a result, many of their compounds have an incomplete octet and act as Lewis acids, being able to complete their octet by accepting a pair of electrons from a donor. The electron deficiency from the possession of an incomplete octet. The former refers to the lack of sufficient electrons to be able to account for the connections between atoms as normal covalent bonds; the latter is the possession of less than eight electrons in a valence shell.

The binary hydrogen compounds of B are called **boranes**. The simplest member of the series, **diborane**, B₂H₆ is electron deficient and its structure is commonly described in terms of 2c, 2e (two center two electrons) and 3c, 2e (three center two electrons) bonds, bridging 3c, 2e

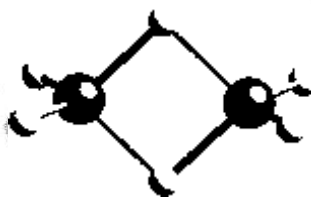
bonds are a recurring theme in borane chemistry. All the boron hydrides burn with a characteristic green flame and several of them ignite explosively on contact with air. The valence orbitals of each boron atom in B_2H_6 are sp^3 hybridized. The two terminal BH_2 groups are present in one plane and the bridged $B \begin{array}{c} H \\ \diagup \quad \diagdown \\ B \end{array} H$ part of the molecule is present in a perpendicular plane containing the two BH_2 groups. Thus the valence electrons of the two boron atoms can be counted as follows:

Total number of valence electrons of boron = 6

Electrons used up in two $B \begin{array}{c} H \\ \diagup \quad \diagdown \\ B \end{array} H$ bridges = 2

Electrons used up in the four terminal BH bonds = 4

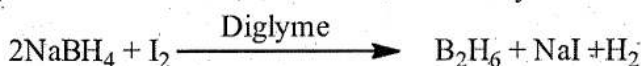
Thus total number of valence electrons of 2 boron and 6 hydrogen atoms = 12



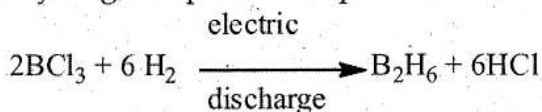
Diborane, B_2H_6

Preparation

1. By the reaction of iodine on sodium borohydride in diglyme.



2. By passing electric discharge through a mixture of boron trichloride and hydrogen vapors at low pressure.



3. By the reduction of boron trihalide with lithium aluminium hydride.



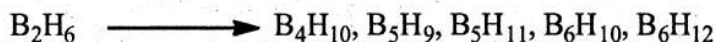
4. By reducing gaseous boron trifluoride with sodium hydride at $180^\circ C$.



Properties

1. **Physical state:** Diborane is colourless gas with a foul smell.
2. **Stability:** It is stable only at low temperature. When heated at $100^\circ C$ to $250^\circ C$ temperature it changes to higher number of higher

hydrides. This process involves a series of decomposition and polymerizations.



3. **Action of oxygen:** Diborane and other boranes releases large amount of energies during combustion. This phenomenon increases attention of technologists for energy resources. $\Delta H = -2165 \text{ kJ mol}^{-1}$



4. **Hydrolysis:** It yields boric acid with water.



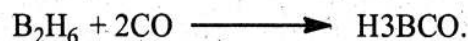
5. **Action with alkalis:** It dissolves in strong alkali solution gives metaborates and evolves hydrogen.



6. **Action with metals:** It reacts with active metals such as Na, K, Ca etc.



7. **Action with carbon monoxide:** With carbon monoxide at 100°C and 20 atmospheric pressure forms H_3BCO .



8. **Action with halogens:** With halogens forms halodiboranes.



Where $\text{X}_2 = \text{Cl}_2, \text{Br}_2$ etc.

9. **Action with halogen acids:** It reacts with halogen acids to give halodiborane and hydrogen.



Where, $\text{X} = \text{Cl}, \text{Br}, \text{I}$.

9. **Action with alkenes and alkynes:** It adds alkenes and alkynes and forms organoboranes called hydroboration reaction, which is applicable in organic synthetic chemistry.



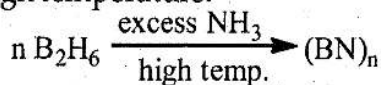
10. **Action with ammonia:** It reacts with ammonia, the products depend upon conditions of experiment.

- a. At low temperature



The Diammoniate of diborane is ionic and exist as $[\text{H}_3\text{N}^+\text{BH}_2][\text{NH}_3]^-$ $[\text{BH}_4]^-$. On heating it forms borazine.

b. In excess at high temperature.



Boron nitride

The thermodynamically stable phase of boron nitride, BN, consists of planar sheets of atoms like those in graphite. The planar sheets of alternating B and N atoms consist of edge shared hexagons and, as in graphite, the B-N distance within the sheet (145 pm) is much shorter than the distance between the sheets 333 pm. The difference between the structures of graphite and boron nitride, however, lies in the register of the atoms of neighbouring sheets: in BN, the hexagonal rings are stacked directly over each other, with B and N atoms alternating in successive layers; in graphite, the hexagons are staggered.

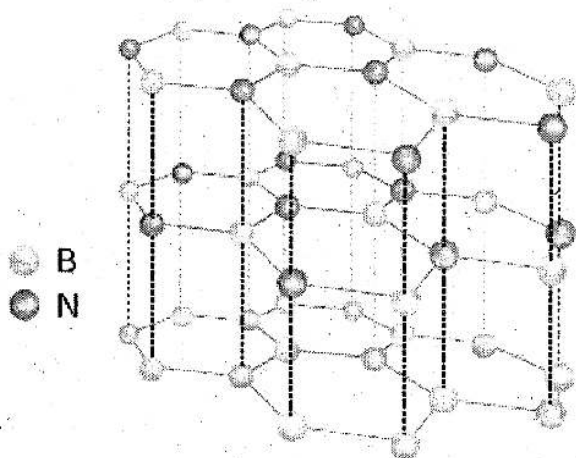


Figure: The structure of layered hexagonal boron nitride.

Boron nitride is stable in air up to 1000°C , making it a useful refractory material. Layered boron nitride changes into a denser cubic phase at high pressures and temperatures (60 kbar and 2000°C).

Carborane

A carborane is a clusters composed of boron, carbon and hydrogen atoms. Like many of the related boranes, these clusters are polyhedra and are similarly classified as closo-, nido-, arachno-, hypho-, etc. based on whether they represent a complete (closo-) polyhedron, or a polyhedron that is missing one (nido-), two (arachno-), or more vertices. Carboranes are a notable example of heteroboranes.

Interesting examples of carboranes are the extremely stable icosahedral closo-carboranes. These boron-rich clusters exhibit unique organomimetic properties with chemical reactivity matching classical organic molecules, yet structurally similar to metal-based inorganic and organometallic species.

$C_2B_{10}H_{12}$ or *o*-Carborane or Dicarbadodecaborane with the prefix *o*- derived from ortho, which has been explored for use in a wide range of applications from heat-resistant polymers to medical applications.

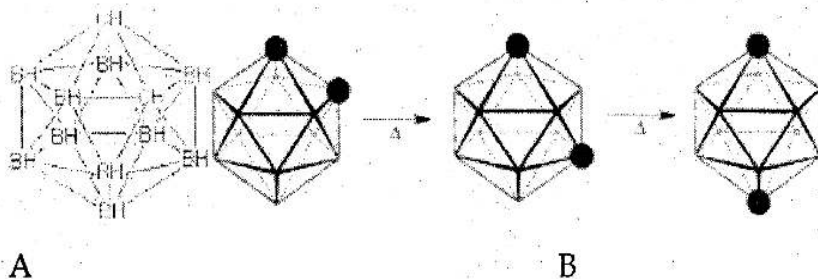


Figure A: Skeletal formula of *o*-carborane and in Figure B: Thermal rearrangement of *o*-dicarborane to its meta- and para-isomers [closo- $B_{10}C_2H_{12}$].

Ortho dicarborane is the kinetic product from the addition of acetylenes to decarborane precursors. Upon heating at 420 °C, the ortho dicarborane rearranges to the meta isomer. Upon further heating, one obtains para-carborane. Like arenes, carboranes also undergo electrophilic aromatic substitution.

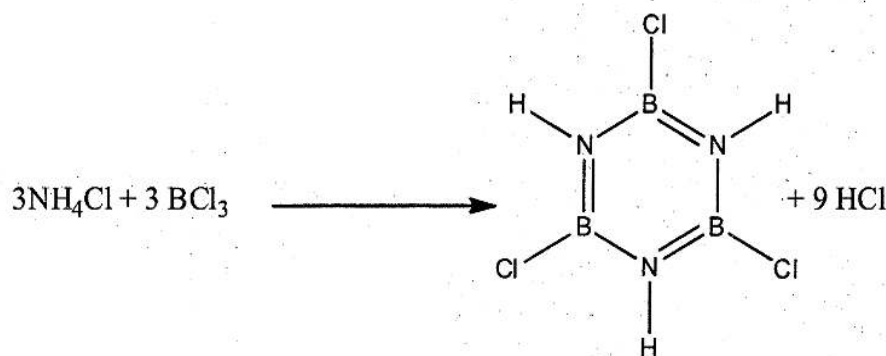
Carboryne, or 1,2-dehydro-*o*-carborane, is an unstable derivative of ortho-carborane with the formula $B_{10}C_2H_{10}$. The hydrogen atoms on the C2 unit in the parent *o*-carborane are missing. The compound resembles and is isolobal with benzyne. A carboryne compound was first generated in 1990 starting from *o*-carborane.

The strongest Bronsted–Lowry acid is the boron-based carborane acid, also known simply as carborane acid. This superacid is known to be one million times stronger than sulfuric acid whose pK_a value is 1.92. Carborane acids differ from classic superacids by giving high superacidity to weakly basic organic solvents.

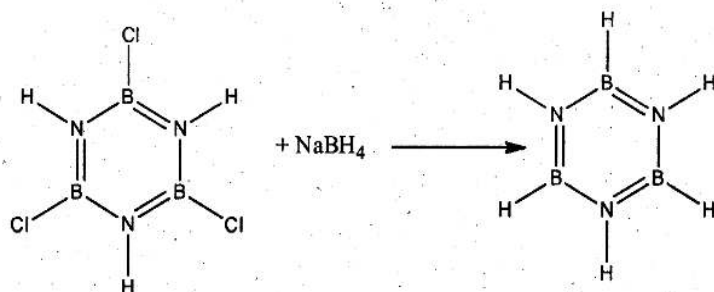
Borazine

Apart from layered boron nitride, the best known unsaturated compound of boron and nitrogen is borazine, $B_3N_3H_6$, which is isoelectronic and isostructural with benzene. Borazine was first prepared by Alfred Stock in 1921

by the reaction between diborane and ammonia. Since then, many symmetrically trisubstituted derivatives have been made by procedures that depend on the protolysis of BCl bonds of BCl_3 by an ammonium salt. The trichloroborazine which on reduction with NaBH_4 yields borazine.



Trichloroborazine



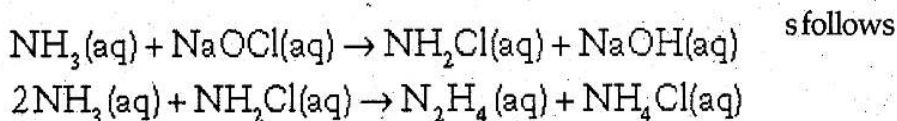
Borazine

The structure of borazine is similar to the structure of benzene, due to similar structure of borazine and benzene, borazine is also known as **inorganic benzene**. In this structure the valence shell orbitals of both boron and nitrogen atoms are sp^3 hybridization. Each nitrogen atom has one lone pair of electrons while each boron atom has an empty p orbital. The bonding in borazine is dative and it arises from the sidewise overlapping of fully filled p orbitals of nitrogen and empty p orbitals of boron.

Hydrazine (N_2H_4)

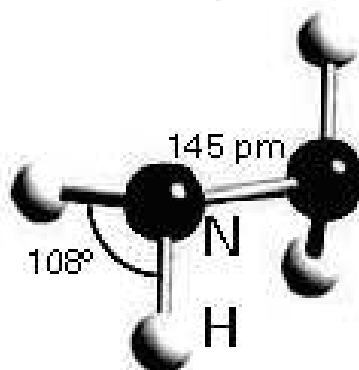
In the Group 5 elements form binary compounds with hydrogen. All the EH_3 hydrides are toxic. Nitrogen also forms a catenated hydride, hydrazine, N_2H_4 . Hydrazine, N_2H_4 , is a fuming, colourless liquid with an odour like that of ammonia. It has a liquid range similar to that of water (-114°C), indicating the presence of hydrogen bonding. In the

liquid phase hydrazine adopts a *gauche* conformation around the N-N bond. Hydrazine is manufactured by the **Raschig process**, in which ammonia and sodium hypochlorite react in dilute aqueous solution. The



Gelatine is added to the reaction mixture to trap the d-metal ions by forming a complex with them. The dilute aqueous solution of hydrazine so produced is converted to a concentrated solution of hydrazine hydrate, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, by distillation. This product is often preferred commercially as it is cheaper than hydrazine and has a wider liquid range. Hydrazine is produced by distillation of the hydrate in the presence of a drying agent such as solid NaOH or KOH.

Hydrazine is a weaker base than ammonia.

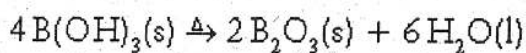


Hydrazine, N_2H_4

The major use of hydrazine and its methyl derivatives as CH_3NHNH_2 and $(\text{CH}_3)_2\text{NNH}_2$, are as rocket fuels. Hydrazine is also used as a foam-blowing agent and as a treatment in boiler water to scavenge by dissolved oxygen and prevent oxidation of pipes. Both N_2H_4 and N_2H_5^+ are reducing agents and are used in the recovery of precious metals.

Boron trihalides consist of trigonal-planar BX_3 molecules. Unlike the halides of the other elements in the group they are monomeric in the gas, liquid, and solid states. Boron trifluoride and boron trichloride are gases, the tribromide is a volatile liquid, and the triiodide is a solid. Boron trihalides have an incomplete octet and are Lewis acids. The order of Lewis acidity is $\text{BF}_3 > \text{BCl}_3 \geq \text{BBr}_3$ and contrary to the order of electronegativity of the attached halogens. The elements Al, Ga, In, and Tl are metals with many similarities in their chemical properties. Like B, they form electron-deficient compounds that act as Lewis acids.

Aluminium forms alloys with many other metals and produces light, corrosion-resistant materials. When Al is alloyed with Ga, the Ga prevents the formation of the tightly held passivating oxide film on the Al. When the alloy is dropped in water the Al reacts with the water forming aluminium oxide and liberating hydrogen. This reaction has been suggested as a solution to the problem of storing hydrogen for use in fuel cells. Aluminium hydride, AlH_3 , is a solid that is best regarded as saline, like the hydrides of the s-block metals. Unlike CaH_2 and NaH , which are more readily available commercially, AlH_3 has few applications in the laboratory. The most important oxide of B, B_2O_3 , is prepared by dehydration of boric acid.



Crystalline B_2O_3 consists of an ordered network of BO_3 units joined through O atoms. Metal oxides dissolve in molten B_2O_3 to give coloured glasses. Boron oxides and silica are the main constituents of borosilicate glass, which, because of the low thermal expansivity of the glass due to the strong B-O bonds, is used to make heat-resistant laboratory glassware.

The valence electron configuration of the Group 4 elements is ns^2np^2 (Table 2). The elements of Group 4, carbon, silicon, germanium, tin, and lead, show considerable diversity in their chemical and physical properties. Carbon, of course, is the building block of life and central to organic chemistry. In this unit, our focus with carbon is on its inorganic chemistry. The lightest members of the group, carbon and silicon, are nonmetals, germanium is a metalloid, and tin and lead are metals. This increase in metallic properties on descending a group is a striking feature of the periodic table and can be understood in terms of the increasing atomic radius and associated decrease in ionization energy down the group. Because the ionization energies of the heavier elements are low, the metals form cations increasingly readily down the group. As the valence configuration ns^2np^2 suggests, the +4 oxidation state is dominant in the compounds of the elements. The major exception is lead, for which the most common oxidation state is +2, two less than the group maximum. The electronegativities of carbon and silicon are similar to that of hydrogen and they form many covalent hydrogen and alkyl compounds. Carbon and silicon are strong **oxophiles** and **fluorophiles**. Their oxophilic character is evident in the existence of an extensive series of oxoanions, carbonates and silicates. Two almost pure forms of carbon, *diamond*

and *graphite*, are mined. There are many less pure forms, such as *coke*, which is made by the pyrolysis of coal, and *lamp black*, which is the product of incomplete combustion of hydrocarbons. Silicon occurs widely distributed in the natural environment and makes up 26 per cent by mass of the Earth's crust. It occurs as sand, quartz, amethyst, agate, and opal, and is also found in asbestos, feldspar, clays, and micas. Germanium is low in abundance and occurs naturally in the ore *germanite*, $\text{Cu}_{13}\text{Fe}_2\text{Ge}_2\text{S}_{16}$, in zinc ores and in coal. Tin occurs as the mineral cassiterite, SnO_2 and lead occurs as *galena*, PbS . Diamond and graphite, the two common crystalline forms of elemental carbon, are strikingly different. Diamond is effectively an electrical insulator; graphite is a good conductor. Diamond is the hardest known natural substance and hence the ultimate abrasive; impure or partially oxidized graphite is slippery and frequently used as a lubricant. In diamond, each C atom forms single bonds of length 154 pm with four adjacent C atoms at the corners of a regular tetrahedron.

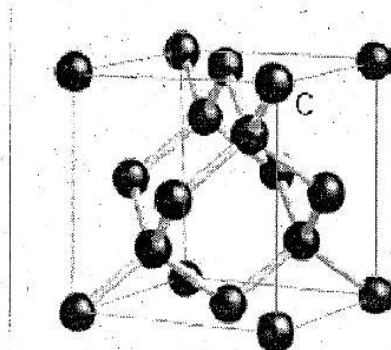


Figure of the cubic diamond structure.

5.5 INTERHALOGENS AND POLYHALIDES AND FLUORIDES OF XENON

Interhalogens: The halogens react with each other to form interhalogen compounds. The general formula of most interhalogen compounds is XY_n , where $n = 1, 3, 5$ or 7 , and X is the less electronegative of the two halogens. The compounds which are formed by the union of two different halogens are called inter halogen compounds.

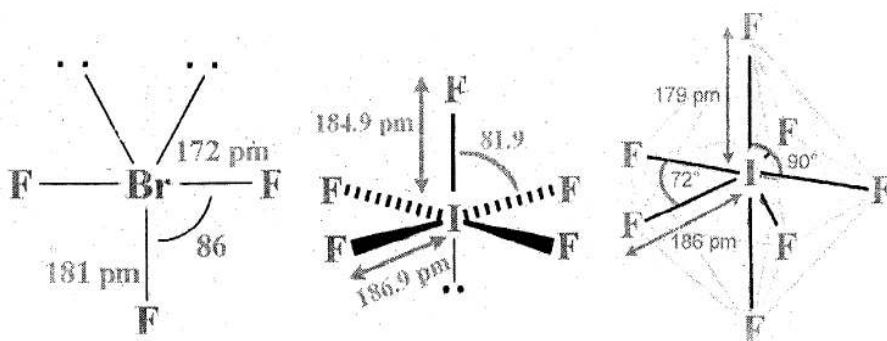
Types of interhalogens:

1. AX-type : ClF , BrF , BrCl , ICl , IBr ,

2. AX_3 -type: ClF_3 , BrF_3 , $(ICl_3)_2$
3. AX_5 -type: ClF_5 , BrF_5 , IF_5
4. AX_7 -type: IF_7

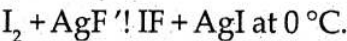
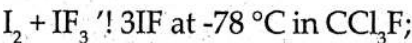
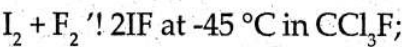
The interhalogen compounds of type AX and AX_3 are formed between the halogen having very low electronegative difference (e.g., ClF , ClF_3). The inter halogen compounds of type AX_5 and AX_7 are formed by larger atoms having low electronegativity with the smaller atoms having high electronegativity. This is because it is possible to fit the greater number of smaller atom around a larger one (e.g. BrF_5 , IF_7)

Properties: They are all prepared by direct combination of the elements although since in some cases more than one product is possible the conditions may vary by altering the temperature and relative proportions. For example under the same conditions difluorine reacts with dichlorine to give ClF with dibromine to give BrF_3 but with diiodine to give IF_5 . The VSEPR theory thus provides a simple model for predicting the shapes of such species, in particular for main group compounds. The structures found for the various interhalogens conform to what would be expected based on the VSEPR model. For XY_3 the shape can be described as T-shaped with 2 lone pairs sitting in equatorial positions of a trigonal bipyramid. For XY_5 the shape is a square pyramid with the unpaired electrons sitting in an axial position of an octahedral and XY_7 is a pentagonal bipyramid.



The interhalogens with formula XY have physical properties intermediate between those of the two parent halogens. The covalent bond between the two atoms has some ionic character, the larger element, X , becoming oxidised and having a partial positive charge. Most combinations of F , Cl , Br and I are known, but not all are stable.

They can be generated, by the following reactions:

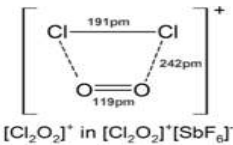


Polyhalogens: Polyhalogen ions are a group of polyatomic cations and anions containing halogens only. The ions can be classified into two classes, isopolyhalogen ions which contain one type of halogen only, and heteropolyhalogen ions with more than one type of halogen. In general, a large counter cation or anion (such as Cs^+ , $[\text{SbF}_6]^-$) can help stabilize the polyhalogen ions formed in the solid state from lattice energy considerations, as the packing efficiency was increased. The polyhalogen cations are strong oxidizing agents, as indicated by the fact that they can only be prepared in oxidative liquids as a solvent, such as oleum. The most oxidizing and therefore most unstable ones are the species $[\text{X}_2]^+$ and $[\text{XF}_6]^+$ ($\text{X} = \text{Cl}, \text{Br}$), followed by $[\text{X}_3]^+$ and $[\text{IF}_6]^+$. Stability of the anions decrease in the order:

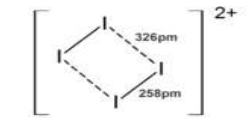
Some of the polyhalogens are illustrated below

Isopolyhalogen cations		Isopolyhalogen anions	
Diatomic species	$[\text{Cl}_2]^+, [\text{Br}_2]^+, [\text{I}_2]^+$	Triatomic species	$[\text{Cl}_3]^-, [\text{Br}_3]^-, [\text{I}_3]^-$
Triatomic species	$[\text{Cl}_3]^+, [\text{Br}_3]^+, [\text{I}_3]^+$	Tetraatomic species	$[\text{Br}_4]^{2-}, [\text{I}_4]^{2-}$
Tetraatomic species	$[\text{Cl}_4]^+, [\text{I}_4]^{2+}$	Pentaatomic species	$[\text{I}_5]^-$
Pentaatomic species	$[\text{Br}_5]^+, [\text{I}_5]^+$	Heptaatomic species	$[\text{I}_7]^-$
Heptaatomic species	$[\text{I}_7]^+$	Octaatomic species	$[\text{Br}_8]^{2-}, [\text{I}_8]^{2-}$
Higher species	$[\text{I}_{15}]^{3+}$	Higher species	$[\text{I}_9]^{2-}, [\text{I}_{10}]^{2-}$

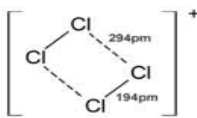
Structures of some isopolyhalogen cations



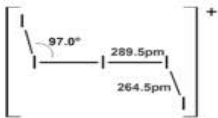
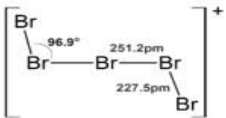
$[\text{Cl}_2\text{O}_2]^+$ in $[\text{Cl}_2\text{O}_2]^+[\text{SbF}_6]^-$



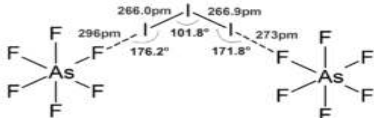
$[\text{I}_4]^{2+}$ in $[\text{I}_4]^{2+}[\text{Sb}_3\text{F}_{14}][\text{SbF}_6]^-$



$[\text{Cl}_4]^+$ in $[\text{Cl}_4]^+[\text{IrF}_6]^-$



The centrosymmetric $[\text{Br}_5]^+$ and $[\text{I}_5]^+$ ions in their $[\text{AsF}_6]^-$ salts



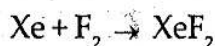
Solid state structure of $[\text{I}_3]^+$ in $[\text{I}_3]^+[\text{AsF}_6]^-$

Fluorides of Xenon:

Three different xenon fluorides are known, Xenon difluoride (XeF_2), Xenon tetrafluoride (XeF_4) and Xenon hexafluoride (XeF_6).

Xenon difluoride is a powerful fluorinating agent with the chemical formula XeF_2 , and one of the most stable xenon compounds. Like most covalent inorganic fluorides it is moisture-sensitive. It decomposes on contact with light or water vapor. Xenon difluoride is a dense, white crystalline solid. It has a nauseating odour and low vapor pressure.

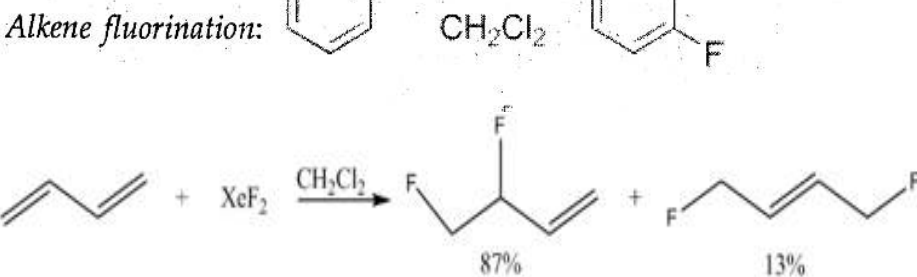
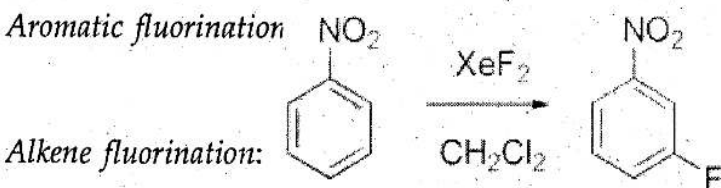
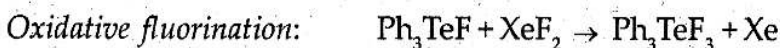
Synthesis proceeds by the simple reaction:



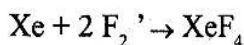
The reaction needs heat, irradiation, or an electrical discharge. The product is a solid. It is purified by fractional distillation or selective condensation using a vacuum line

Applications as a fluorinating agent Xenon difluoride is a strong fluorinating and oxidising agent. With fluoride ion acceptors, it forms XeF^+ and Xe_2F_3^+ species which are even more powerful fluorinators.

Among the fluorination reactions that xenon difluoride undergoes are:



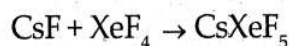
Xenon tetrafluoride is a chemical compound with chemical formula XeF_4 . It was the first discovered binary compound of a noble gas. It is produced by the chemical reaction of xenon with fluorine, F_2 , according to the chemical equation:



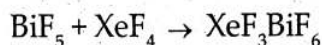
This reaction is exothermic, releasing an energy of 251 kJ/mol of xenon

Xenon tetrafluoride is hydrolyzed by water at low temperatures to form elemental xenon, oxygen, hydrofluoric acid and aqueous xenon trioxide.

Reaction with tetramethylammonium fluoride forms tetramethylammonium pentafluoroxenate, which contains the pentagonal XeF_5^- anion. The XeF_5^- anion is also formed by reaction with caesium fluoride:



Reaction with bismuth pentafluoride (BiF_5) forms the XeF_3^+ cation:



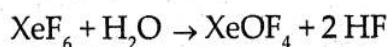
Xenon tetrafluoride is used as a decomposition agent of silicone rubber for analysing trace metal impurities in the rubber. XeF_4 reacts with the silicone structure that makes up the backbone of silicone rubber to form simple gaseous products, leaving behind any content of metal impurities.

Xenon Hexafluoride (XeF_6) is the strongest fluorinating agent of the series. At room temperature, it is a colorless solid that readily sublimates into intensely yellow vapors. Xenon hexafluoride can be prepared by long-term heating of XeF_2 at about 300 °C and pressure 6 MPa (60 atmospheres).

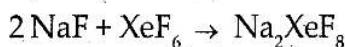
The structure of XeF_6 required several years to establish in contrast to the cases of XeF_2 and XeF_4 . In the gas phase the compound is monomeric. VSEPR theory predicts that due to the presence of six fluoride ligands and one lone pair of electrons the structure lacks perfect octahedral symmetry, and indeed electron diffraction combined with high-level calculations indicate that the compound's point group is C_{3v} .

^{129}Xe and ^{19}F NMR spectroscopy indicates that in solution the compound assumes a tetrameric structure where four equivalent xenon atoms are arranged in a tetrahedron surrounded by a fluctuating array of 24 fluorine atoms that interchange positions in a "cogwheel mechanism".

Xenon hexafluoride hydrolyzes stepwise, ultimately affording xenon trioxide



Salts of the octafluoroxenate(VI) anion (XeF_8^{2-}) are very stable, decomposing only above 400 °C



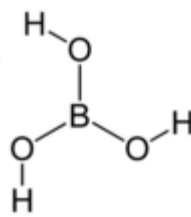
5.6 STRUCTURE AND BASICITIES OF OXYACIDS OF B, P and S

Many inorganic oxoacids are traditionally called with names ending with the word *acid* and which also contain, in a somewhat modified form, the name of the element they contain in addition to hydrogen and oxygen. Well-known examples of such acids are sulfuric acid, nitric acid and phosphoric acid.

IUPAC, however, recommends against calling future compounds not yet discovered with a name ending with the word acid. Indeed, acids can be called with names formed by adding the word hydrogen in front of the corresponding anion; for example, sulfuric acid could just as well be called hydrogen sulfate (or dihydrogen sulfate).

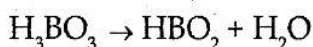
Boric acid, also called hydrogen borate, boracic acid, orthoboric acid and *acidum boricum*, is a weak, mono basic Lewis acid of boron often used as an antiseptic, insecticide, flame retardant, neutron absorber, or precursor to other chemical compounds. It has the chemical formula H_3BO_3 (sometimes written $\text{B}(\text{OH})_3$), and exists in the form of colorless crystals or a white powder that dissolves in water. When occurring as a mineral, it is called sassolite.

Boric acid may be prepared by reacting borax (sodium tetraborate decahydrate) with a mineral acid, such as hydrochloric acid:



Crystalline boric acid consists of layers of $\text{B}(\text{OH})_3$ molecules held together by hydrogen bonds. The B-O bond length is 136 pm and the O-H is 97 pm with a hydrogen bond of 272pm.

Boric acid is soluble in boiling water. When heated above 170 °C, it dehydrates, forming *metaboric acid* (HBO_2):



Long term exposure to boric acid may be of more concern, causing kidney damage and eventually kidney failure. Although it does not appear

to be carcinogenic, studies in dogs have reported testicular atrophy after exposure.

Boric acid was first registered in the US as an insecticide in 1948 for control of cockroaches, termites, fire ants, fleas, silverfish, and many other insects.

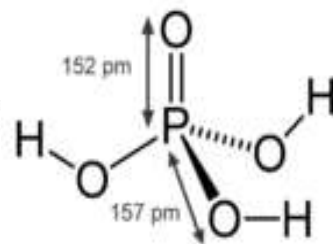
Colloidal suspensions of nanoparticles of boric acid dissolved in petroleum or vegetable oil can form a remarkable lubricant on ceramic or metal surfaces.

Boric acid is used in some nuclear power plants as a neutron poison. The boron in boric acid reduces the probability of thermal fission by absorbing some thermal neutrons.

Phosphoric acid is a mineral (inorganic) acid having the chemical formula H_3PO_4 . Orthophosphoric acid refers to *phosphoric acid*, which is the IUPAC name for this compound. The prefix *ortho* is used to distinguish the acid from related phosphoric acids, called polyphosphoric acids. Phosphoric acid, H_3PO_4 , has sometimes been called *orthophosphoric acid*, in order to distinguish it from

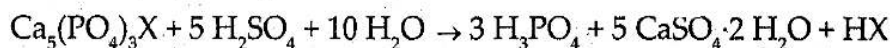
metaphosphoric acid, HPO_3 .

Orthophosphoric acid is a non-toxic acid, which, when pure, is a solid at room temperature and pressure.



Phosphoric acid is produced industrially by two general routes – the thermal process and the wet process. The wet process dominates in the commercial sector. The more expensive thermal process produces a purer product that is used for applications in the food industry.

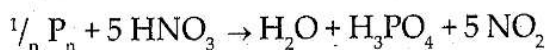
Wet process phosphoric acid is prepared by adding sulfuric acid to tricalcium phosphate rock, typically found in nature as apatite. The reaction is:



where X may include OH, F, Cl, and Br

Very pure phosphoric acid is obtained by burning elemental phosphorus to produce phosphorus pentoxide, which is subsequently dissolved in dilute phosphoric acid. This route produces a very pure phosphoric acid, since most impurities present in the rock have been removed when extracting phosphorus from the rock in a furnace.

A demonstrative process consists in the oxidation of red phosphorus by nitric acid.



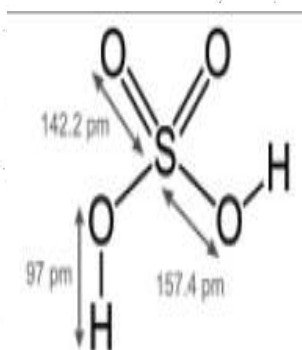
The dominant use of phosphoric acid is for fertilizers, consuming approximately 90% of production.

Food-grade phosphoric acid (additive E338) is used to acidify foods and beverages such as various colas and jams. It provides a tangy or sour taste.

Phosphoric acid may be used to remove rust by direct application to rusted iron, steel tools, or other surfaces.

Phosphoric acid is used in dentistry and orthodontics as an etching solution, to clean and roughen the surfaces of teeth where dental appliances or fillings will be placed.

Sulfuric acid is a diprotic acid and shows different properties depending upon its concentration. Its corrosiveness on other materials, like metals, living tissues or even stones, can be mainly ascribed to its strong acidic nature and, if concentrated, strong dehydrating and oxidizing properties. Sulfuric

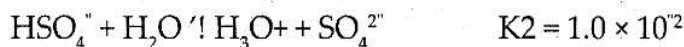


acid at a high concentration can cause very serious damage upon contact, since not only does it cause chemical burns via hydrolysis, but also secondary thermal burns through dehydration. Accordingly, safety precautions should be strictly observed when handling it. Moreover, it is hygroscopic, readily absorbing water vapour from the air.

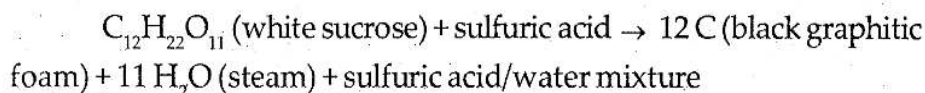
Sulfuric acid/sulphuric acid is a highly corrosive strong mineral acid with the molecular formula H_2SO_4 and molecular weight 98 g/mol. It is a strong ethereal, colorless to slightly yellow viscous liquid that is soluble in water at all concentrations. Sometimes, it is dyed dark brown during production to alert people to its hazards. Sulfuric acid is a diprotic acid and shows different properties depending upon its concentration. Its corrosiveness on materials, like metals, living tissues or even stones, can be mainly ascribed to its strong acidic nature. High concentrated sulphuric acid is strong dehydrating and oxidizing properties.

Because the hydration reaction of sulfuric acid is highly exothermic, dilution should always be performed by adding the acid to

the water rather than the water to the acid. Because the reaction is in an equilibrium that favors the rapid protonation of water, addition of acid to the water ensures that the acid is the limiting reagent. This reaction is best thought of as the formation of hydronium ions



Because the hydration of sulfuric acid is thermodynamically favorable and the affinity of it for water is sufficiently strong, sulfuric acid is an excellent dehydrating agent.



List given below having some of the Oxoacids of B, P and S

Boron +3	H_3BO_3	Boric acid (formerly <i>orthoboric acid</i>)	BO_3^{3-}	Borate (formerly <i>orthoboric</i>)
	$(\text{HBO}_2)_n$	Metaboric acid Phosphorus	BO_2^-	Metaborate
	H_3PO_4	Phosphoric acid (formerly <i>ortho-phosphoric acid</i>)	PO_4^{3-}	Phosphate (orthophosphate)
Phosphorus +5	HPO_3	Metaphoric acid	PO_3^{3-}	Meta Phosphate
		Pyrophosphoric acid		Pyrophosphate
	$\text{H}_3\text{P}_2\text{O}_7$		$\text{P}_2\text{O}_7^{4-}$	
Sulfur +6	H_2SO_4	Sulfuric acid	SO_4^{2-}	Sulfate
	$\text{H}_2\text{S}_2\text{O}_7$	Disulfuric acid	$\text{S}_2\text{O}_7^{2-}$	Disulfate
	H_2SO_5	Peroxomono sulfuric acid	SO_5^{2-}	Peroxomonosulfate

5.8 SUMMARY

Form the above unit you studied studied the elements of p-block (Group 13 to 18). In Group 13, the differences between the first element and the remaining elements become so pronounced that the first member

of the group, i.e. boron is a nonmetal whereas the rest of the elements are distinctly metallic in nature. In a way, this is the first group of the periodic table in which you observe a marked change in the nature of the elements down the group. You learn the chemistry of hydrides, halides and oxides of boron and aluminium, and also elucidate the structures of hydrides of boron. You also understand the electronic configuration, oxidation state and properties of p-block elements. Synthesis of compounds of p-block elements and properties you come to know.

5.9 TERMINAL QUESTIONS

1. In which reaction does the cluster core undergo a significant change in shape?
2. Is $[\text{CO}_3]^{2-}$ and $[\text{BO}_3]^{3-}$ the following species are isoelectronic?
3. In aqueous solution, H_3BO_3 behaves as a Brønsted acid?
4. TlI_3 is isotypic with CsI_3 . This suggests?
5. To which point group does Al_2Cl_6 belong?
6. A low temperature bath for use in the laboratory is required to maintain a temperature of 195 K. You would use?
7. Which of the following orderings gives the correct sequence of bond enthalpy terms for covalent bonds involving group 14 elements?
8. Which of the tin(IV) halides is the strongest halide acceptor?
9. Which shape *correctly* describes the stated for PCl_3 molecule?
10. When heated, which metal nitrate would give the respective metal, NO_2 and O_2 ?
11. To which point group does the SbF_5 molecule belong?
12. Which of the following is a greenhouse gas under the 1997 Kyoto Protocol?
13. The reaction of SF_4 with CsF would produce?
14. Formula of thiosulfuric acid is?
15. Consider $[\text{IF}_5]^{2-}$. With which arrangement of atoms is the VSEPR model consistent?
16. $[\text{BrF}_4]^-$ molecules or ions to their shapes?

5.10 ANSWERS

1. $B_{10}H_{14} + C_2H_2 \rightarrow 1,2-C_2B_{10}H_{12} + 2H_2$
2. Yes.
3. No
4. The presence of Tl^+ ions in TlI_3
5. D_{2h}
6. Solid CO_2 and acetone
7. $C-C > Si-Si > Ge-Ge > Sn-Sn$
8. SnF_4
9. Trigonal Pyramidal
10. $AgNO_3$
11. D_{3h}
12. SF_6
13. $[SF_5]^-$
14. $H_2S_2O_3$
15. Pentagonal Planer
16. Square planar
17. $HOCl$ and $HClO_4$

SUGGESTED READINGS:

1. Advance Inorganic Chemistry, F. A. Cotton and G. Wilkinson, Interscience Publishers, J. Wiley and Sons.
2. Inorganic Chemistry, Shriver and Atkins, W. H. Freeman and Company New York
3. Inorganic Chemistry, P.A. Cox, Taylor and Francis Group.
4. Inorganic Chemistry, G.L. Miessler and D.A Tarr, Pearson Press International
5. Concise Inorganic Chemistry, J D Lee, Oxford University Press
6. Chemistry of the Elements, N.N. Greenwood, Butterworth and Hinemann, Oxford
7. Principles of Inorganic Chemistry, B. R. Puri, Sharma and Kalia, Milestone publishers & distributors.

- 6.1 Introduction
 - Objectives
 - 6.2 Electrode potential
 - 6.3 Electrochemical series and its applications
 - 6.4 EMF and their utility
 - 6.5 Principle involved in the extraction of the elements
 - 6.6 Summary
 - 6.7 Terminal Questions
 - 6.8 Answers
-

6.1 INTRODUCTION

In this unit you should learn definitions of oxidation and reduction is commonly called redox, in terms of the transfer of oxygen, hydrogen and electrons. It also explains in the terms oxidizing agent and reducing agent. The origin of the electrochemical series and shows how it can be used to work out the ability of the various substances included in it to act as oxidizing or reducing agents. How oxidation-reduction is important for the metal extraction processes.

Objective

After studying this unit you should learn about

- How the oxidation and reduction occur
- Importance of oxidation and reduction potential
- Electrochemical series
- EMF and utility
- Principal of extraction process of metals

6.2 ELECTRODE POTENTIAL

In term of oxygen transfer oxidation and reduction, the oxidation is gain of oxygen and reduction is loss of oxygen (Figure 1). In terms of hydrogen transfer oxidation and reduction, the oxidation is loss of hydrogen and reduction is gain of hydrogen (Figure 2). In terms of electron transfer the electron gain is called **reduction** and electron loss is called **oxidation**; the joint

6.2 ELECTRODE POTENTIAL

In term of oxygen transfer oxidation and reduction, the oxidation is gain of oxygen and reduction is loss of oxygen (Figure 1). In terms of hydrogen transfer oxidation and reduction, the oxidation is loss of hydrogen and reduction is gain of hydrogen (Figure 2). In terms of electron transfer the electron gain is called **reduction** and electron loss is called **oxidation**; the joint process is called a **redox reaction**. The species that supplies electrons is the **reducing agent** (or 'reductant') and the species that removes electrons is the **oxidizing agent** (or 'oxidant') (Figure 3).

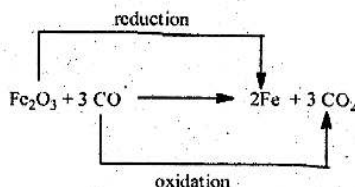


Figure 1: The oxidation is gain of oxygen and reduction is loss of oxygen

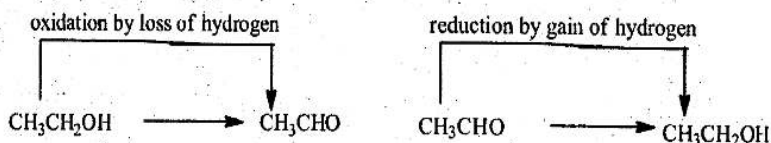


Figure 2: The oxidation is loss of hydrogen and reduction is gain of hydrogen

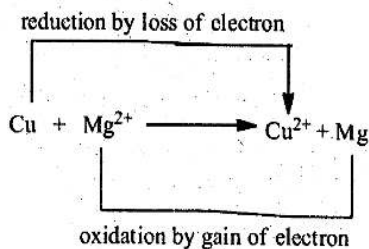


Figure 3: The oxidation is loss of electrons and reduction is gain of electrons

The ability of gain or loss of oxygen/hydrogen/electron depends upon the properties of element.

Electrode potential (E) in electrochemistry, the definition of the electromotive force of a cell built of two electrodes (i) on the left-hand side is the standard hydrogen electrode and (ii) on the right-hand side is the electrode the potential of which is being defined.

6.2 ELECTRODE POTENTIALS

An electrode potential is a measure of the thermodynamics of a redox reaction. It may be expressed as the difference between two half-cell potentials, which by convention are measured against a hydrogen electrode (This comprises a platinized platinum electrode, which is saturated with hydrogen at one atmosphere pressure and immersed in a solution of H_3O^+ at unit activity, 1M. The potential developed by this electrode is arbitrarily fixed as zero). If the elements are arranged in order of increasing standard electrode potentials of the series (Table-1) is called **electrochemical series**. **Standard electrode potentials** are the half-cell potentials measured against a **hydrogen electrode**, where the half-cell reaction is all reagents being under standard conditions (unit activity and pressure) in figure 4.

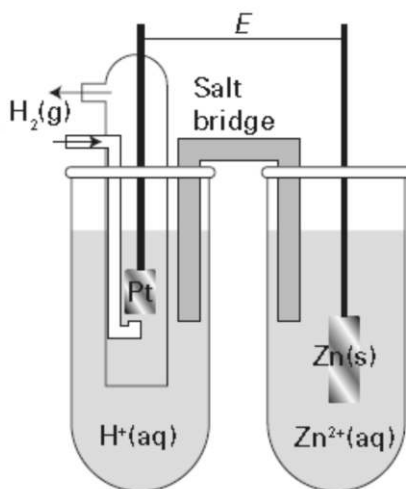


Figure 4: A schematic diagram of a galvanic cell. The standard potential (E_{cell}°) is the potential difference when the cell is not generating current and all the substances are in their standard states.

6.3 ELECTROCHEMICAL SERIES AND APPLICATION

Table 1: Electrochemical Series or standard reduction electrode potentials (Volts) at 25°C

Li^+	Li	-3.05
K^+	K	-2.93
Ca^{2+}	Ca	-2.84
Al^{3+}	Al	-1.66
Mn^{2+}	Mn	-1.08
Zn^{2+}	Zn	-0.76
Fe^{2+}	Fe	-0.44
Cd^{2+}	Cd	-0.40
Co^{2+}	Co	-0.27
Ni^{2+}	Ni	-0.23
Sn^{2+}	Sn	-0.14
Pb^{2+}	Pb	-0.13
H^+	H_2	0.0
Cu^{2+}	Cu	+0.35
Ag^+	Ag	+0.80
Au^{3+}	Au	+1.38

A negative standard potential signifies a couple in which the reduced species (the

Zn in Zn^{2+}/Zn) is a reducing agent for H^+ ions under standard conditions in aqueous solution. That is, if $E^\circ (\text{Ox, Red}) \hat{=} 0$, then the substance 'Red' is a strong enough reducing agent to reduce H^+ ions (in the sense that for the reaction). A short compilation of E° values at 25°C. The values of standard electrode potentials arranged in the decreasing order as shown is called the **electrochemical series**. Standard reaction Gibbs energies may be measured by setting up a **galvanic cell**, an electrochemical cell in which a chemical reaction is used to generate an electric current, in which the reaction driving the electric current through the external circuit is the reaction of interest.

Application

Suppose to know whether Zn and Ag would react with H_2SO_4 or not.

The reaction of Zn with H_2SO_4



The above reaction may be represented as into two half cell reaction

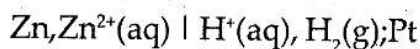
Oxidation half cell reaction



Reduction half cell reaction



Since, in a galvanic cell, oxidation occurs at the left hand electrode and reduction at the right hand. Thus the cell reaction is written as



Therefore, the EMF of the cell

$$E^\circ = E_R - E_L = 0 - (-0.76) \text{ V} = +0.76 \text{ V}$$

Since, E° is positive, $\Delta G^\circ (= -nFE^\circ)$ is negative. Hence, the reaction of zinc with sulphuric acid is feasible, i.e. **Zn will react with H_2SO_4 .**

Let us consider the silver (Ag) with H_2SO_4 .



The above reaction may be represented as into two half cell reaction

Thus the cell reaction is written as



Therefore, the EMF of the cell

$$E^\circ = E_R - E_L = 0 - (+0.80) \text{ V} = -0.80 \text{ V}$$

Since, E° is negative, $\Delta G^\circ (= -nFE^\circ)$ is positive. Hence, the reaction of Ag with sulphuric acid is not feasible, i.e. **Zn will not react with H_2SO_4 .**

Cu^{2+}/Cu is referred to as a redox couple and as written it refers to a half cell or reduction reaction.



In general redox couples are written ox/red where ox is the oxidation form and is written on the left hand side and red is the reduction form and is written on the right.

Standard electrode potentials values are determined relative to hydrogen electrode.

Thus Cu^{2+}/Cu $E^\circ = +0.35 \text{ V}$ really means that the reduction potential of reaction is 0.35 V.



$$E^\circ = +0.35 \text{ V} \dots\dots (\text{i})$$

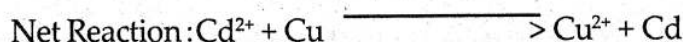
Similarly the standard electrode potential of Zn^{2+}/Zn E° is -0.76 V.



$$E^\circ \text{ is } -0.76 \text{ V} \dots\dots (\text{ii})$$

Problem-What will be the reaction in the cell which is made by combining standard Cd half cell with standard Cu half cell? Also calculate the emf of the cell. The standard oxidation potential of half cells is 0.453 and -0.337 V.

Solution- The cell reactions are



Formula used

$E_{\text{cell}} = \text{Reduction potential of cathode} - \text{Reduction potential of anode}$

Quantities given

Reduction potential of cathode = -0.337 V

Reduction potential of anode = 0.453 V

Substitution of values

$$\begin{aligned} E_{\text{cell}} &= -0.337 \text{ V} - 0.453 \text{ V} \\ &= -0.790 \text{ V} \end{aligned}$$

6.4 ELECTROMOTIVE FORCE (EMF) AND THEIR UTILITY

Any two suitable half cells can be combined to form a **galvanic cell**. A galvanic cell is a device in which the free energy of a physical or

chemical process is converted into electrical energy. Such a cell consists of two electrodes immersed in one or more suitable electrolytes. When the electrodes are connected externally a chemical reaction occurs in the cell involving oxidation at one electrode and reduction at another electrode. The electrode at which oxidation occurs is called a **negative electrode** or **cathode** while the electrode at which reduction occurs called a **positive electrode** or **anode**. The EMF of the cell and the feasible cell reaction can be easily determined with the help of the information given in the electrochemical series. For this purpose the following rules have been used:

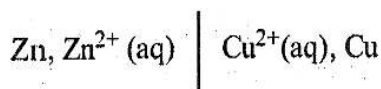
- **Writing the Cell Reaction:** The half cell reaction taking place at the left hand electrode is written as an oxidation reaction and the half cell reaction taking place at right hand electrode is written as a reduction reaction. The complete cell reaction is then given by the sum of these two half cell reactions.
- **Representation of the cell:** The electrode on the right is written in the order: ion, electrode, i.e. Cu^+, Cu (decr in oxidation number or reduction) and the electrode on the left is written in the order: electrode, ion, i.e. Zn, Zn^+ (increases in oxidation number or oxidation).
- **Determination of EMF:** The standard EMF of the cell (E°_{cell} or simply E°) is equal to standard electrode potential of the right electrode designated as E_R minus the standard electrode potential of the left hand electrode designated as E_L .

Thus

$$E^\circ_{\text{cell}} = E^\circ_R - E^\circ_L$$

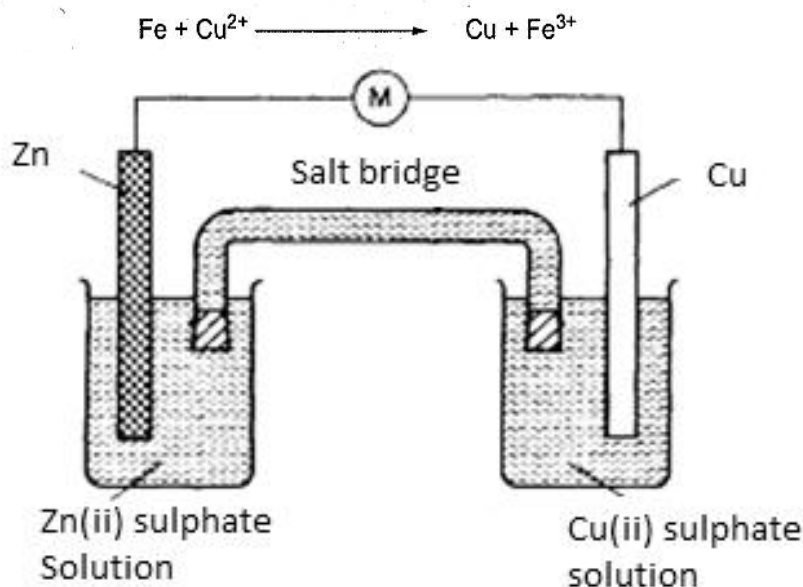
Both of the standard potentials are relative to the H^+/H_2 electrode (arbitrarily fixed as zero). When the Cu^{2+}/Cu couple is combined with Zn^{2+}/Zn couple then H^+ and H_2 disappear.

Thus



Since E° is positive, the reaction as written is spontaneous in forward direction.

In the electrochemical series the greater the negative value of the potential, the greater is the tendency for metal to ionize. Thus a metal high in electrochemical series will displace another metal lower down the series from solution. For example Iron (Fe) is above Copper (Cu) in electrochemical series, thus iron displaces copper ions from the solution of CuSO_4 in the recovery of metallic copper.



In an **electrochemical cell** a redox reaction occurs in two halves. Electrons are liberated by the oxidation half reaction at one **electrode** and pass through an electrical circuit to another electrode where they are used for the reduction. The **cell potential** E is the potential difference between the two electrodes required to balance the thermodynamic tendency for reaction, so that the cell is in equilibrium and no electrical current flows.

Thus we see that there will be a potential difference developed at the junction of the metal and the solution. However, the potential difference between the two phases cannot be readily measured. Therefore, instead of measuring the electrode potentials, we usually measure the total cell potential. The cell potential can be written & the sum of the two electrode potentials neglecting other effects which contribute to the potential difference between the phases. Thus,

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

The total cell potential is a measure of the driving force of a chemical reaction whereas E_{cathode} and E_{anode} representative of oxidizing and reducing capabilities of the concerned reactants,

respectively. Hence, in order to obtain a large cell potential, we must use a strong oxidizing agent along with a strong reducing agent. Now the question arises as to how we decide which a better oxidising agent is and which a better reducing agent is. To determine the comparative oxidizing or reducing capacity of any substance, we must use some standard against which all other electrode potentials are measured.

Relation between EMF and Free energy

When a cell produces a current, the currents can be used to do work. The maximum amount of work, W_{max} , obtainable from the cell by

$$W_{max} = - n F E$$

where n is the number of electrons transferred and is equal to the valence of the ion participating in the cell reaction, F stands for Faraday and is equal to 96500 coulombs and E is the EMF of the cell.

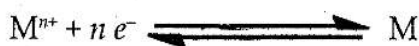
The Nernst Equation

Nernst derived a mathematical relationship which enables us to calculate the half cell, E from the standard electrode potential, E° , with the help of the following relation.

$$E = E^\circ - \frac{2.303RT}{nF} \log K$$

where K is the equilibrium constant for the half-cell reaction.

For the reaction



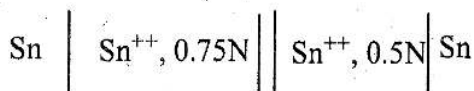
Nernst equation becomes

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[M^{n+}]}{[M]}$$

The concentration of solid metal $[M]$ is equal to zero.

Thus $E = E^\circ - \log [M^{n+}]$

Problem - Calculate the EMF of the given cell



Solution -

Formula used

$$E = \frac{2.303RT}{nF} \log \frac{C_2}{C_1}$$

Quantities given

$$n = 2$$

$$C_2 = 0.5N$$

$$C_1 = 0.75N$$

Substituting the values

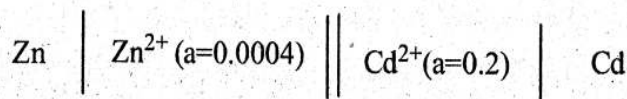
$$E_{cell} = \frac{2.303RT}{2} \log \frac{0.5}{0.75}$$

$$E_{cell} = \frac{2.303RT}{2} \log \frac{2}{3}$$

$$= \frac{0.0591}{2} \log X(-0.0176)$$

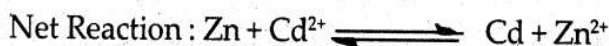
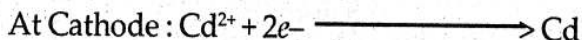
$$= 0.0052$$

PROBLEM- Calculate EMF of the following cell at 20 °C;



E° for Zinc and Cadmium electrodes are -0.76 and -0.40 volts respectively.

SOLUTION - The cell reactions are



(i) To calculate E° of the cell

Formula used

$$E^\circ_{cell} = E^\circ_{right} - E^\circ_{left}$$

Quantities given

$$E^\circ_{right} = -0.40 \quad E^\circ_{left} = -0.76$$

Substitution of values

$$E^\circ_{cell} = -0.40 - (-0.76 \text{ V})$$

$$= 0.36 \text{ V}$$

(ii) To calculate EMF of the cell

Formula used

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cd}^{2+}]}$$

Quantities given

$$E^\circ_{cell} = 0.36 \text{ V}, n = 2, [\text{Zn}^{2+}] = 0.0004, [\text{Cd}^{2+}] = 0.2$$

$$\begin{aligned}
 E_{\text{cell}} &= 0.36 - \frac{0.0591}{2} \log \frac{0.0004}{0.2} \\
 &= 0.36 - 0.02955 \log 0.0002 \\
 &= 0.36 - 0.02955 \times (-2.6989) \\
 &= 0.36 + 0.07975 \\
 &= 0.4397 \text{ V}
 \end{aligned}$$

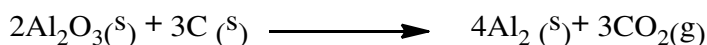
6.5 PRINCIPLE INVOLVED IN THE EXTRACTION OF THE ELEMENTS

Current industrial processes are varied in the strategies they adopt to ensure economical rates, exploit materials, and avoid environmental problems. We can explore these strategies by considering three important examples that reflect low, moderate, and extreme difficulty of reduction. The least difficult reductions include those of copper ores. Roasting and smelting are still widely used in the pyrometallurgical extraction of copper. However, some recent techniques seek to avoid the major environmental problems caused by the production of the large quantity of SO_2 , released to the atmosphere, that accompanies roasting. One promising development is the **hydrometallurgical extraction** of copper, the extraction of a metal by reduction of aqueous solutions of its ions, using H_2 or scrap iron as the reducing agent. In this process, Cu^{2+} ions, leached from low-grade ores by acid or bacterial action, are reduced by hydrogen in the reaction or by a similar reduction using iron. This process is less harmful to the environment provided the acid by-product is used or neutralized locally rather than contributing to acidic atmospheric pollutants. It also allows economic exploitation of lower grade ores.

The extraction of metals from ores electrochemically is confined mainly to the more electropositive elements, as discussed in the case of aluminium. For other metals produced in bulk quantities such as iron and copper, the more energy-efficient and cleaner routes used by industry in practice, using chemical methods of reduction. In some specialist cases, electrochemical reduction is used to isolate small quantities of platinum group metals. So, for example, treatment of spent catalytic converters with acids under oxidizing conditions produces a solution containing complexes of Pt(II) and other platinum group metals, which can then be reduced electrochemically.

The metals are deposited at the cathode with an overall 80 per cent efficient extraction from the ceramic catalytic converter. The reduction of Al_2O_3 with carbon becomes feasible only above 2400°C , which is uneconomical.

However, the reduction can be brought about **electrolytically** and all modern production uses the electrochemical **Hall-Heroult process**, which was invented in 1886 independently by Charles Hall and Paul Heroult. The process requires pure aluminium hydroxide that is extracted from aluminium ores using the **Bayer process**. In this process the bauxite ore used as a source of aluminium is a mixture of the acidic oxide SiO_2 and amphoteric oxides and hydroxides, such as Al_2O_3 , AlOOH , and Fe_2O_3 . The Al_2O_3 is dissolved in hot aqueous sodium hydroxide, which separates the aluminium from much of the less soluble Fe_2O_3 , although silicates are also rendered soluble in these strongly basic conditions. Cooling the sodium aluminate solution results in the precipitation of $\text{Al}(\text{OH})_3$, leaving the silicates in solution. For the final stage, in the Hall-Heroult process, the aluminium hydroxide is dissolved in molten cryolite (Na_3AlF_6) and the melt is reduced **electrolytically** at a steel cathode with graphite **anodes**. The latter participate in the electrochemical reaction by reacting with the evolved oxygen atoms so that the overall process is

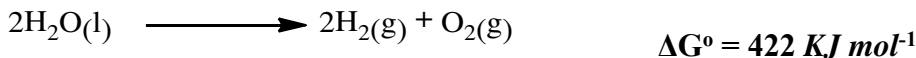


As the power consumption of a typical plant is huge, aluminium is often produced where electricity is cheap for example, from hydroelectric sources in Canada.

The lighter halogens are the most important elements extracted by electrochemical oxidation. The standard reaction Gibbs energy for the oxidation of Cl^- ions in water is strongly positive, which suggests that electrolysis is required. The minimum potential difference that can achieve the oxidation of Cl^- is about 2.2 V (from $\Delta G^\circ = -nFE^\circ$ and $n = 2$).



It may appear that there is a problem with the competing reaction which can be driven forwards by a potential difference of only 1.2 V, when $n = 4$.



However, the rate of oxidation of water is very slow at potentials at which it first becomes favorable thermodynamically.

Table 1: Reduction potentials and extraction methods

Elements	Reduction potentials E° (V)		Extraction method
Lithium	Li^+	Li -3.05	Electrolysis of fused salts, usually chlorides
Potassium	K^+	K -2.93	
Calcium	Ca^{2+}	Ca -2.84	

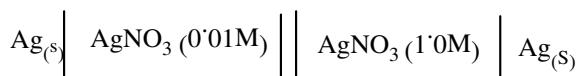
Sodium	Na ²⁺	Na	-2.71	Electrolysis of MgCl ₂ high temperature reduction with C
Magnesium	Mg ²⁺	Mg	-2.37	
Aluminum	Al ³⁺	Al	-1.66	Electrolysis of Al ₂ O ₃ dissolved in molten Na ₃ [AlF ₆]
Manganese	Mn ²⁺	Mn	-1.08	Reduction with Al Thermite process
Chromium	Cr	Cr ³⁺	-0.74	
Zinc	Zn ²⁺	Zn	-0.76	Chemical reduction of oxides by C sulphides are converted to oxides then reduced by C or sometimes H ₂
Iron	Fe ²⁺	Fe	-0.44	
Cobalt	Co ²⁺	Co	-0.27	
Nickel	Ni ²⁺	Ni	-0.23	
Tin	Sn ²⁺	Sn	-0.14	Found as native metal or a compound easily decomposes by heat. (Also cyanide extraction)
Lead	Pb ²⁺	Pb	-0.13	
Copper	Cu ²⁺	Cu	+0.35	
Silver	Ag ²⁺	Ag	+0.80	
Gold	Au ³⁺	Au	+1.38	

6.6 SUMMARY

From this unit you learn oxidation and reduction or redox reactions, in terms of the transfer of oxygen, hydrogen and electrons. The origin of the electrochemical series and ability of the various substances included in it to act as oxidizing or reducing agents. How the oxidation-reduction is important for the directing the metal extraction processes.

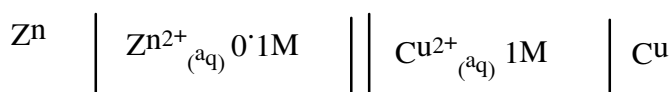
6.7 Terminal Questions

Question 1: For a Cell

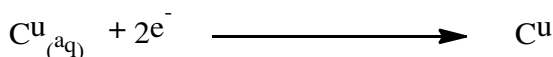


- (a) Calculate the emf at 25 °C
 (b) Will the cell generate emf when two concentrations become equal.

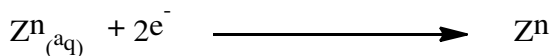
Question 2: Consider the cell



The standard reduction potentials are 0.35 V for

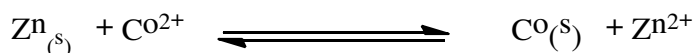


and – 0.763 V for



- (i) Write down the cell reactions
- (ii) Calculate the emf of the cell
- (iii) Is the cell reaction spontaneous or not?

Question 3: The following reaction takes place in the cell

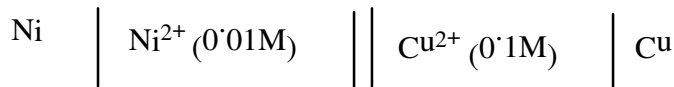


Write down the electrode reactions and calculate the standard emf of the cell.

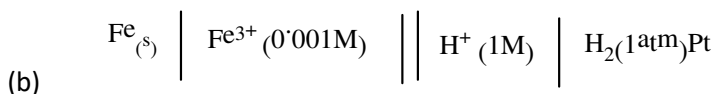
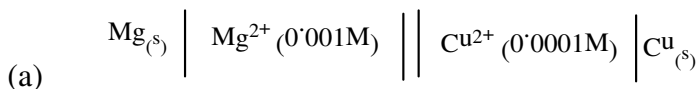
Given that

$$E^{\circ}_{\text{Zn}/\text{Zn}^{2+}} = 0.76\text{V}, E^{\circ}_{\text{Co}/\text{Co}^{2+}} = 0.28\text{V}$$

Question 4: Calculate the standard electrode potential of Ni^{2+}/Ni electrode, if the cell potential of the cell is 0.59 V.



Question 5: Calculate the emf of the following cells at 25 °C



$$\text{Given } E^{\circ}_{\text{Mg}^{2+}/\text{Mg}} = -2.37 \text{ V}, E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}, E^{\circ}_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$$

6.8 ANSWERS

1. 0.1184 V, No
2. 1.113, spontaneous
3. 0.48
4. – 0.2205 V
5. a) 2.6805 V (b) – 0.5286 V

SUGGESTED READINGS:

1. **Concise Inorganic Chemistry**, J.D. Lee, Oxford University Press
2. **Inorganic Chemistry**, Gary L. Miessler Donald A. Tarr, Pearson Publication
3. **Principles of Inorganic Chemistry**, Puri. Sharma. Kalia, Milestone Publishers & Distributors
4. **Inorganic Chemistry**, P.A.Cox, BIOS, Scientific Publisher, Taylor and Francis

Notes

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