# DMI - St. Eugene University

(Run by sisters of Daughters of Mary Immaculate and Collaborators)

DMI

ST. EUGENE

Fully Alive, Fully Human

Module Code : 760CH36 / 762CH36 / 763CH36

Module Name : Chemistry - IV

Programme : B.Sc. in Secondary Education

From the desk of
Dr. T. X. A. ANANTH, BBA, MSW, MBA, MPhil, PhD
President –University Council

Dear Student Teachers,

Greetings

On behalf of DMI – St. Eugene University, I welcome you to third semester of the fast track teacher training programme, 2015.

At this point, we at DMI – SEU need to thank the Lord Almighty for the strength we have gained to face the second year at IVDL with improved facilities and renewed energy. I am duty bound to express my gratitude for encouragement received from Rev. Fr. Dr. J. E. Arulraj, our Founder-Chancellor of DMI – St. Eugene University, for his moral support, the financial assistance and guidance.

These books form the learning materials for your course in the III Semester and supportive references which will help your teaching career. Each subject is mapped to the syllabus and discussed in detail for easy understanding of the texts. Our dedicated team works to create texts that will be an additional asset in your career as teaching faculty in your respective institutions.

I welcome each of you once again on behalf of our respected Chancellor, members of the faculty and on my own behalf to benefit from the programme and contribute effectively to serve Zambia to reach the level of development envisioned by the country's early freedom fighters and liberators during their years of struggle for independence. Your efforts will be appreciated in harnessing the natural resources to generate the financial wealth that will move Zambia forward in the eyes of the developed world.

It is our endeavour to help you all in building a modern Zambia, a country that is blessed with an abundance of human and natural resources. I wish you all the best there in your second year at IVDL.

Dr. T. X. A. ANANTH
President – University Council

CONTENTS

## Concepts in Inorganic Chemistry

### Unit – I Atomic Structure, the Elements and the Periodic Table

Electronic configuration: Bohr theory, dual nature of electrons, Heisenberg uncertainty principle, the Schrödinger equation, significance of wave functions, normalization of wave functions, radial and angular wave function, Pauli's exclusion principle, Hund's rule, sequence of energy levels (Aufbau principle) – Periodicity: periodic law and arrangement of elements in the periodic table, IUPAC nomenclature and group member, horizontal, vertical and diagonal relationships in the periodic table – General properties of atoms: size of atoms and atomic radii, ionic radii, covalent radii; trend in ionic radii, ionization potential, electron affinity; electronegativity – Pauling, Mulliken-Jaffe, Allred-Rochow definition; oxidation states and variable valency; isoelectronic relationship; inert-pair effect; standard reduction potentials, electrochemical series – The occurrence and isolation of elements: occurrence of elements; factors influencing the choice of extraction process; mineral benefication-pretreatment, dense medium separation, flotation process, solution methods, magnetic separation, electrostatic precipitation; thermal decomposition methods; displacement of one metal by another; high temperature chemical reduction methods-reduction by carbon, reduction by metal, self-reduction, reduction of oxides with hydrogen; electrolytic reduction-in aqueous solution, in non-aqueous solvents, in fused melts; thermodynamics of reduction processes – the Ellingham diagram.

### Unit II Ionic Bond

Properties of ionic compounds, factors favoring the formation of ionic compounds ionizationpotential, electron affinity, and electronegativity - Lattice energy: definition, Born-Landeequation (derivation not required), factors affecting lattice energy, Born-Haber cycle-enthalpy offormation of ionic compound and stability - Covalent character in ionic compounds-polarizationand Fajan's rules; effects of polarization-solubility, melting points, and thermal stability oftypical ionic compounds.

### Unit III: The Covalent Bond

Lewis theory-the octet rule and its exception, electron dot structural formula; Sidgwick-Powelltheory-prediction of molecular shapes; Valance Bond theory-arrangement of electrons inmolecules, hybridization of atomic orbitals and geometry of molecules - VSEPR model-effect ofbonding and nonbonding electrons on the structure of molecules, effect of electronegativity,isoelectronic principle, illustration of structures by VESPR model-$NH_3$, $SF_4$, $ICl_4$, $ICl_2$,$XeF_4$, $XeF_6$ - MO theory: LCAO method, criteria of orbital overlap, types of molecular orbitalss,p- and d-MOs; combination of atomic orbitals to give s- and p-MOs and their schematicillustration; qualitative MO energy level diagram of homoand heterodiatomic molecules- $H_2$ to$Ne_2$, CO, NO, HCl; bond order and stability of molecules.

### Unit IV Metallic and Weak Bonds

The Metallic bond: crystal structure of metals-ccp, hcp, metallic properties, band theory ofmetals - Alloys-mixture, interstitial- and substitutional solid solutions, Hume-Rothery rules,interstitial compounds - Weak bonds: hydrogen bonding-intra and intermolecular hydrogenbonding, influence on the physical properties of molecules, comparison of hydrogen bondstrength and properties of hydrogen bonded N, O and F compounds; associated moleculesethanoland acetic acid; crystalline hydrates and clathrates; van der waals forces, ion dipoledipoleinteractions.

## Unit V: Acids and Bases

Types of chemical reactions: acid-base, oxidation-reduction, electron transfer, and doubledecomposition reactions; balancing chemical reactions by oxidation number and ion electronmethod - Theories of acids and bases: Arrhenius theory, acids and bases in protic solvents,Bronsted-Lowry theory, Lewis theory, the solvent system, Lux-Flood definition, Usanovichdefinition; hard and soft acids and bases-HSAB principle - Nonaqueous solvents: classificationprotonicand aprotic solvents, liquid ammonia as solvent-solutions of alkali and alkaline earthmetals in ammonia.

## Unit – I Atomic Structure, the Elements and the Periodic Table

### Syllabus

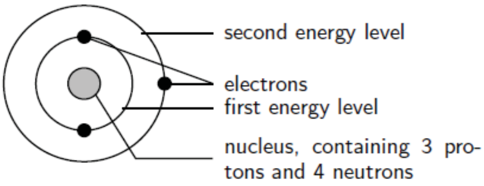
Electronic configuration: Bohr theory, dual nature of electrons, Heisenberg uncertainty principle, the Schrödinger equation, significance of wave functions, normalization of wave functions, radial and angular wave function, Pauli's exclusion principle, Hund's rule, sequence of energy levels (Aufbau principle) – Periodicity: periodic law and arrangement of elements in the periodic table, IUPAC nomenclature and group member, horizontal, vertical and diagonal relationships in the periodic table – General properties of atoms: size of atoms and atomic radii, ionic radii, covalent radii; trend in ionic radii, ionization potential, electron affinity; electronegativity – Pauling, Mulliken-Jaffe, Allred-Rochow definition; oxidation states and variable valency; isoelectronic relationship; inert-pair effect; standard reduction potentials, electrochemical series – The occurrence and isolation of elements: occurrence of elements; factors influencing the choice of extraction process; mineral benefication-pretreatment, dense medium separation, flotation process, solution methods, magnetic separation, electrostatic precipitation; thermal decomposition methods; displacement of one metal by another; high temperature chemical reduction methods-reduction by carbon, reduction by metal, self-reduction, reduction of oxides with hydrogen; electrolytic reduction-in aqueous solution, in non-aqueous solvents, in fused melts; thermodynamics of reduction processes – the Ellingham diagram.

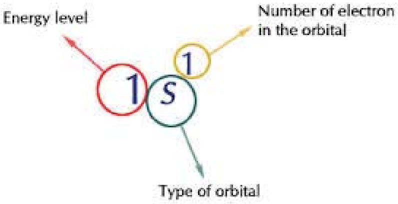
## 1.1 Electronic configuration of atoms

It is known that atoms consist of a positively charged nucleus withprotons and neutrons in it. Negatively charged particles calledelectrons constantly revolve around the nucleus in set of orbits. Theelectron orbits are numbered as 1, 2, 3, etc, starting from the orbitclosest to the nucleus. These orbits are also called **K, L, M, N** shells, asmentioned in the atom model proposed by Niel's Bohr.The maximum number of electrons in an orbit is given by $\mathbf{2n^2}$, where**n** is the orbit number.

For the first **orbit n = 1**, and the number of electrons it can hold is $\mathbf{2x1^2=2}$electrons.
For the second **orbit n = 2**, and it can hold a maximum of $\mathbf{2x2^2=8}$electrons.
For the third **orbit n = 3**, and it can hold a maximum of $\mathbf{2x3^2=18}$electrons.

It must be understood that the second orbit begins only after the firstorbit is filled.The third orbit begins to fill only after the second orbit is filled. But thefourth orbit commences even before the third orbit is completelyfilled. The reason for this lies in the concept of quantum numbers.Thus the term electronic configuration or electronic structure refers to the way the electrons are arranged around the nucleus. Most of theproperties of elements and their compounds depend on their electronicconfigurations.



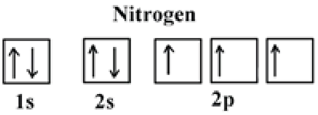


To write electronic configuration, the principal quantum number ofthe shells must be known. This number describes the number of orbitspresent in the atom.

The electronic configuration of atoms can be represented in two ways.

**With orbitals or** **s, p, d or f**

**With orbital picture**

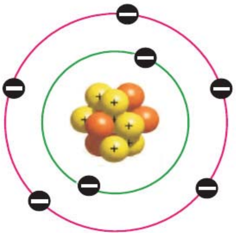


Let us consider sodium atom.Atomic number of **sodium is 11 i.e.** Total number of electrons in sodium =**11**

**Orbit wise distribution of electrons in a sodium atom**

**Orbit Number of electrons**

1. **(K-Shell)** $2n^2$ = $2x1^2$ =2 electrons

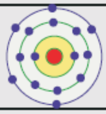
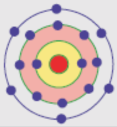
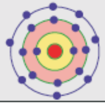


2. **(L-Shell)** $2n^2 =$ $2x2^2$ =8 electrons
3. **(M-Shell)** Remaining =1 electron

Thus the electronic distribution in sodium is **2, 8, 1**.Similarly the electronic configuration of nitrogen is **2, 5**. The electronic configurations of some of the elements with their distributions in orbitals are shown below:

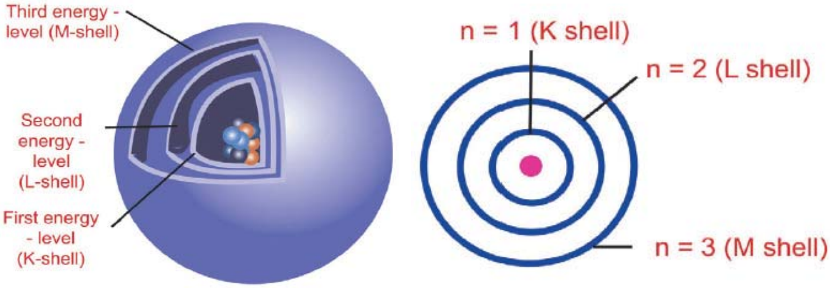
| Element | Atomic Number | Electronic dot structure | Electron distribution |
|---|---|---|---|
| Hydrogen<br>**(H)** | **1** |  | **1** |
| Helium<br>**(HO)** | **2** |  | **2** |
| Lithium<br>**(Li)** | **3** |  | **2.1** |
| Berylium<br>**(Bo)** | **4** |  | **2.2** |
| Boron<br>**(B)** | **5** |  | **2.3** |

| Element | Atomic Number | Electronic dot structure | Electron distribution |
|---|---|---|---|
| Carbon<br>( C ) | **6** |  | **2.2** |
| Nitrogen<br>**(N)** | **7** |  | **2,5** |
| Oxygen<br>**(O)** | **8** |  | **2,6** |
| Fluorine<br>**(F)** | **9** |  | **2,7** |
| Neon<br>**(Ne)** | **10** |  | **2,8** |

| Element | Atomic Number | Electronic dot structure | Electron distribution |
|---|---|---|---|
| Sodium<br>**(Na)** | **11** |  | **2,2,1** |
| Magnesium<br>**(Mg)** | **12** |  | **2,8,2** |
| Aluminium<br>**(Al)** | **13** |  | **2,8,3** |
| Silicon<br>**(Si)** | **14** |  | **2,8,4** |
| Phosphoru<br>**(P)** | **15** |  | **2,2,5** |
| Sulphur<br>**(S)** | **16** |  | **2,2,6** |
| Chlorine<br>**(Cl)** | **17** |  | **2,2,7** |
| Argon<br>**(Ar)** | **18** |  | **2,2,8** |

## 1.2 Bohr's Theory

The electron in an atom moves in a definite circular orbit with a fixed energy. These orbits are called stationary states because the energy of the electrons remains stationary as long as they keep on moving in the same orbit. Since each orbit is associated with a definite energy, they are also called energy levels. Starting from the nucleus these orbits are numbered as 1, 2, 3, 4, etc. or K, L, M, N, etc. The mathematical condition for stationary orbits is that the angular momentum of the moving electron is an integral multiple of $h/2\pi$, where h is the Planck's constant. Thus $mvr = n.h/2\pi$ .Where mvr denotes the angular momentum and n is called principal quantum number and is equal to 1, 2, 3.



## 1.3 Dual nature of electrons

(1) In 1924, the French physicist, Louis de Broglie suggested that if light has electron, behaves both as a material particle and as a wave.

(2) This presented a new wave mechanical theory of matter. According to this theory, small particles like electrons when in motion possess wave properties.

(3) According to de-broglie, the wavelength associated with a particle of mass m, moving with velocity v is given by the relation $\lambda = h/mv$ where h = Planck's constant.

(4) This can be derived as follows according to Planck's equation,

$$E = hv = hc/\lambda \therefore v = c/\lambda \text{(energy of photon}$$

(on the basis of Einstein's mass energy relationship) $E = mc^2$,

Equating both $hc/\lambda = mc^2$ or $\lambda = h/mc$ which is same as de-Broglie relation. ($\therefore mc = p$)

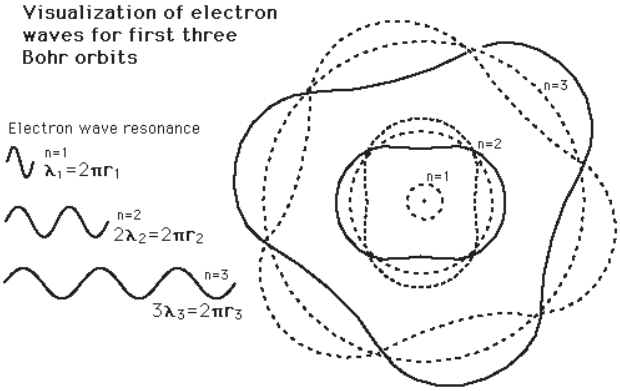
(5) This was experimentally verified by Davisson and Germer by observing diffraction effects with an electron beam. Let the electron is accelerated with a potential of V than the Kinetic energy is

$$\mathbf{(1/2)\ mv^2 = eV;\ m^2V^2 = 2eVm}$$
$$\mathbf{mv = \sqrt{}2eVm = P; \lambda = h/\sqrt{}2eVm}$$

(6) If Bohr's theory is associated with de-Broglie's equation then wave length of an electron can be determined in bohr's orbit and relate it with circumference and multiply with a whole number $2\pi r = n\lambda$ or $\lambda = (2\pi r/2\pi)$ From de-Broglie equation, $\lambda = (h/mv)$.

$$\mathbf{Thus\ h/mv = (2\pi r/n)\ or\ mvr = (nh/2\pi)}$$

(7) The de-Broglie equation is applicable to all material objects but it has significance only in case of microscopic particles. Since, we come across macroscopic objects in our everyday life, de-broglie relationship has no significance in everyday life.



## 1.4 Heisenberg's Uncertainity Principle

The consequences of de Brogle's concept are the Heisenberg uncertainty principle. According to him —*It is impossible to specify at any given moment both the position and momentum (velocity) of an electron."*

In view of Heisenberg uncertainty principle it is more correct to say that an electron is associated with a definite energy, i.e. it belongs to a definite energy levels and not that it belongs to a particular orbit. Mathematical representation of Heisenberg principle is,

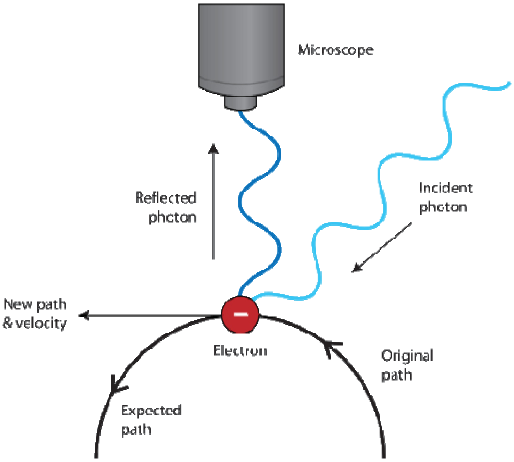
$$\Delta x.\Delta p = h/2\pi$$

Let $\Delta x$ is the uncertainty in position and $\Delta p$ is the uncertainty in momentum, then these two quantities can be related as follows.

**Explanation of Uncertainty Principle**

**Heisenberg uncertainty principle can be understood by following description.**

1. For measuring the position and momentum of electron, a light phenomenon is used.
2. To know the position of electron, a photon of light is become strike on the electron.
3. The microscope is used to see the reflected photon.
4. Due to hitting with photon, both the position and momentum of electron is disturbed.
5. The electron has wave particle duality. It shows an intrinsic uncertainty position and momentum.
6. Due to small and light weight of electron, the incident photon changes the motion of electron after interacting with the electron.



## 1.15 The Schrödinger wave equation

In 1926, Schrodinger proposed a wave equation to describe the motion of the subatomic particle in a similar manner to that used for the macroscopic particles. In three dimensions, the Schrödinger equation is,

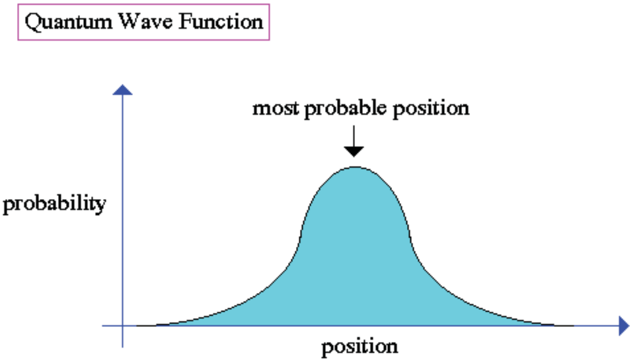
$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0.$$

Where m is the mass of the particle, $E$ and $V$ are the total energy and the potential energy of the particle, and $h$ is the Planck‘s constant. Hence, the Schrondinger‘s equation is valid for a particle executing simple harmonic motion. This however does not prove the equation, but merely shows that it is applicable to material system.

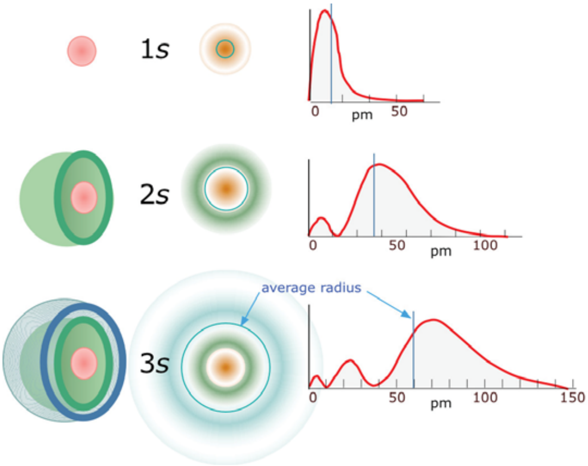
### Significance of wave functions

The wave function used in the Schrödinger equation play the role of Newton's laws and conservation of energy in classical mechanics – i.e., it predicts the future behavior of a dynamic system. It predicts analytically and precisely the probability of the events or outcome. The detailed outcome depends on chance, but given a large number of events, the Schrödinger equation will predict the distribution of results.

**Wave function,** in quantum mechanics, is a variable quantity that mathematically describes the wave characteristics of a particle. It is designated by the Greek letter psi, Ψ. Each "particle" is represented by a wave function Ψ (position, time) such that Ψ*Ψ is equal to the probability of finding the particle at that position at that time. Following are the significance of the wave function Ψ.



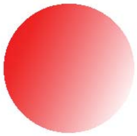
Wave functions of various *s* orbitals are provided below:



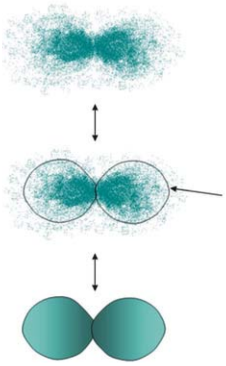
$\Psi$ – Does not have a physical meaning, but a simple mathematical function.
$\Psi$ – It is a function of r, the distance from the nucleus.
$\Psi$ – Allows energy calculations via the Schrödinger equation.
$\Psi$ – Permits calculation of the effective average value (expectation value) of a given variable.
$\Psi$ – For a free particle, it is a sine wave, implying a precisely determined momentum and a totally uncertain position.
$\Psi$ – Contains all the measurable information about the particle.
$\Psi$ – Established the probability distribution in three dimensions.
$\Psi$ – Continuous.
$\Psi$ – $\Psi^*\Psi$ summed over all space = 1 (if the particle exists, the probability of finding it somewhere must be one).

The value of the wave function of a particle at a given point of space and time is related to the likelihood of the particle's being there at the time. By analogy with waves such as those of sound, a wave function, may be thought of as an expression for the amplitude of the particle wave (or de Broglie wave), although for such waves amplitude has no physical significance. The square of the wave function, $\Psi^2$, however, does have physical significance: the probability of finding the particle described by a specific wave function $\Psi$ at a given point and time is proportional to the value of $\Psi^2$.

The shape of the wavefunction
when l = 1 (p orbital)



The shape of the wave function
when l = 0 (s orbital)



the electron density in an electron wave

90% of the electron density is inside the
two lobes drawn on the electron wave

these balloons represent the region of space
which contains 90% of the electron density
for this particular electron wave

## Normalization of wave functions

Let $|\Psi(x,t)|^2$ is the probability density for finding the particle at a point $x$, at time $t$. Because the particle must be found somewhere between $x = -\infty$ and $x = +\infty$ the wave function must obey the normalization condition,

$$\int_{-\infty}^{+\infty} |\Psi(x,t)|^2 \, dx = 1$$

Without this, the statistical interpretation would be meaningless. Thus, there is a multiplication factor. However, the wave function is a solution of the Schrödinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi.$$

Therefore, one cannot impose an arbitrary condition on $\Psi$ without checking that the two are consistent.

Interestingly, if $\Psi(x,t)$ is a solution, $A\Psi(x,t)$ is also a solution where $A$ is any (complex) constant.

Therefore, one must pick an undetermined multiplicative factor in such a way that the Schrödinger equation is satisfied. This process is called **normalizing** the wave function.

### Radial and angular wave functions

Each wave function has two parts, the radial part which changes with distance from the nucleus and an angular part whose changes correspond to different changes.

$$\Psi_{xyz} = \varphi_{radial}(r)\varphi_{angular}(\emptyset,\theta)$$

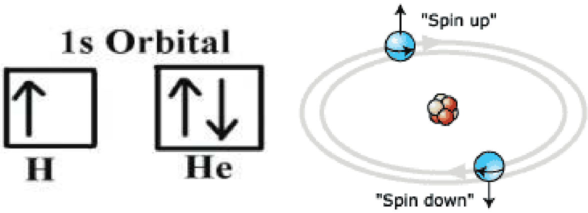
$\Psi_{xyz} = R_{nl}(r)Y_{lm}(\emptyset,\theta)$

The radial part of the wave function, $R_{nl}(r)$ determines the size of the orbital.

The angular part of the wave function, $Y_{lm}(\emptyset,\theta)$determines the shape of the orbital.

### 1.16 Pauli's exclusion principle

The Pauli Exclusion Principle states that, in an atom, no two electrons can have the **same** four electronic quantum numbers.

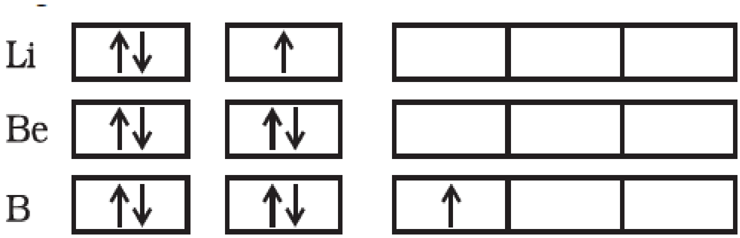


The two electrons in an orbital may have the same *n*, *l*, and *m* values, but atleast they differ in the value of spin quantum number.That means one of the electron in the orbital would spin up (+1/2) and the other would spin down (-1/2).

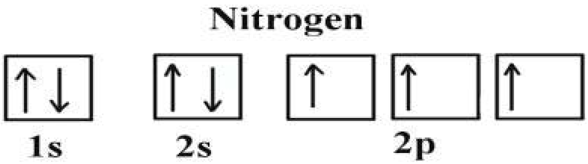
### 1.17 Hund's rule

Hund's Rule states that: „*Every orbital in a sublevel is singly occupied before any orbital is doubly occupied. All of the electrons in singly occupied orbitals have the same spin (to maximize total spin)*".

When assigning electrons in orbitals, each electron will first fill all the orbitals with similar energy (also referred to as degenerate) before pairing with another electron in a half-filled orbital. Atoms at ground states tend to have as many unpaired electrons as possible. When visualizing this processes, think about how electrons are exhibiting the same behavior as the same poles on a magnet would if they came into contact; as the negatively charged electrons fill orbitals they first try to get as far as possible from each other before having to pair up.



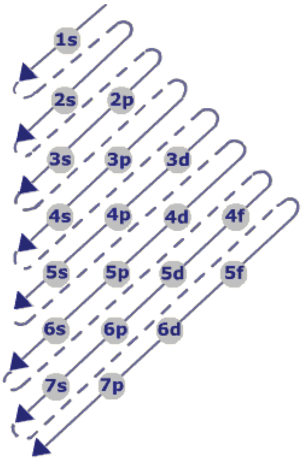
**Example: Nitrogen atom**

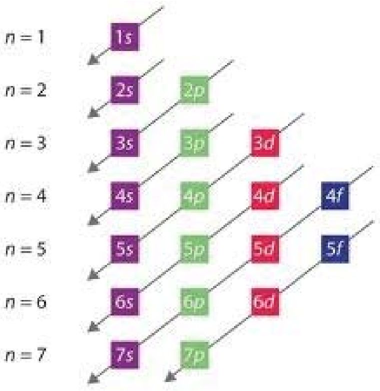


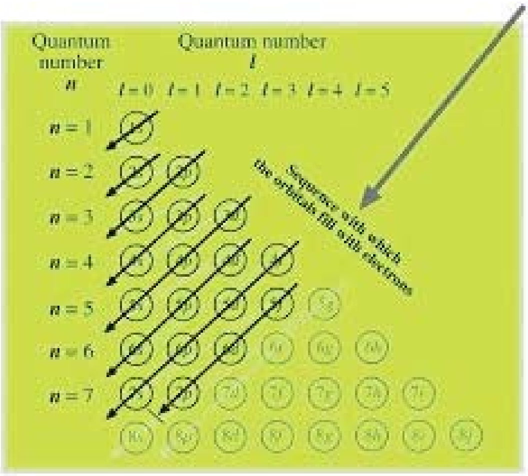
If we look at the correct electron configuration of the nitrogen (Z = 7) atom: $1s^2\ 2s^2\ 2p^3$. We can clearly see that *p* orbitals are half filled as there are three electrons and three *p* orbitals. This is because the three electrons in the 2*p* subshell will fill all the empty orbitals first before pairing with electrons in them. Keep in mind that elemental nitrogen is found in nature typically as di-nitrogen, $N_2$, which would require the filling in of molecular orbitals instead of atomic orbitals as demonstrated above.

## 1.18 Sequence of energy levels (Aufbau principle)

Aufbau comes from the German word "Aufbauen" which means "to build". In essence when writing electron configurations we are building up electron orbitals as we proceed from atom to atom. As we write the electron configuration for an atom, we will fill the orbitals in order of increasing atomic number.







*"The Aufbau principle originates from the Pauli"s exclusion principle which says that no two* fermions *(e.g., electrons) in an atom can have the same set of quantum numbers, hence they have to "pile up" or "build up" into higher energy levels"*.

How the electrons build up is a topic of electron configurations. If we follow the pattern across a period from B (Z=5) to Ne (Z=10) the number of electrons increase and the subshells are filled. Here we are focusing on the p subshell in which as we move towards Ne, the p subshell becomes filled.

## 1.19 Periodicity

Periodicity refers to the recurring trends that are seen in the elementproperties. These trends became apparent to Mendeleev when he arranged the elements in order of increasing mass.

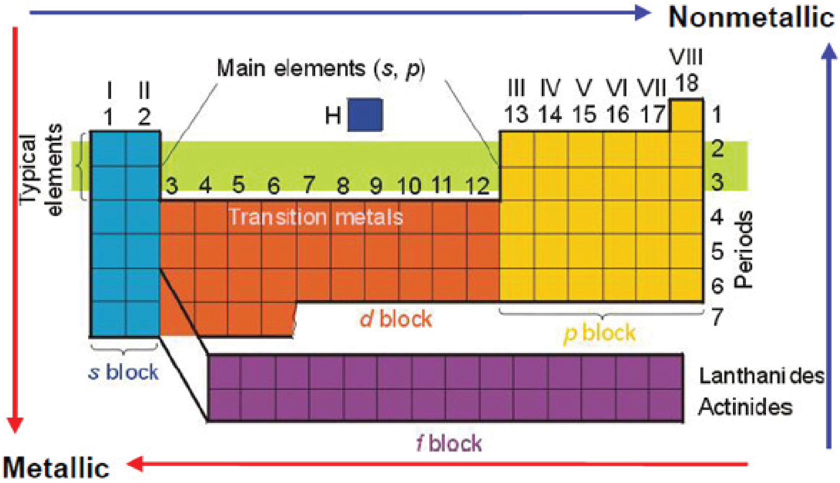
### Periodic law

The modern periodic table is very similar to Mendeleev's table, but today elements are ordered by increasing atomic number, which reflects the number of protons in an atom. There aren't any 'undiscovered' elements, although new elements can be created that have even higher numbers of protons.

**Modern Periodic Law** can be stated as: The physical and chemical properties of the elements are periodic functions of their atomic numbers.

### Arrangement of elements in the periodic table, IUPAC Nomenclature and Group Number

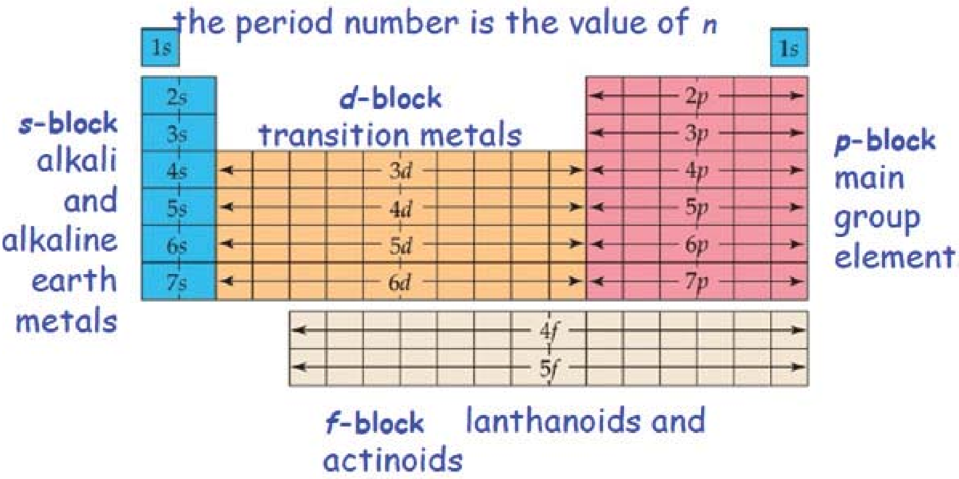
Numerous forms of Periodic Table have been devised from time to time. Some forms emphasis chemical reactions and valence, whereas others stress the electronic configuration of elements. A modern version, the so-called 'long form' of the Periodic Table of the elements is the most convenient and widely used. The horizontal rows are called **periods** and the vertical columns are called **groups**.

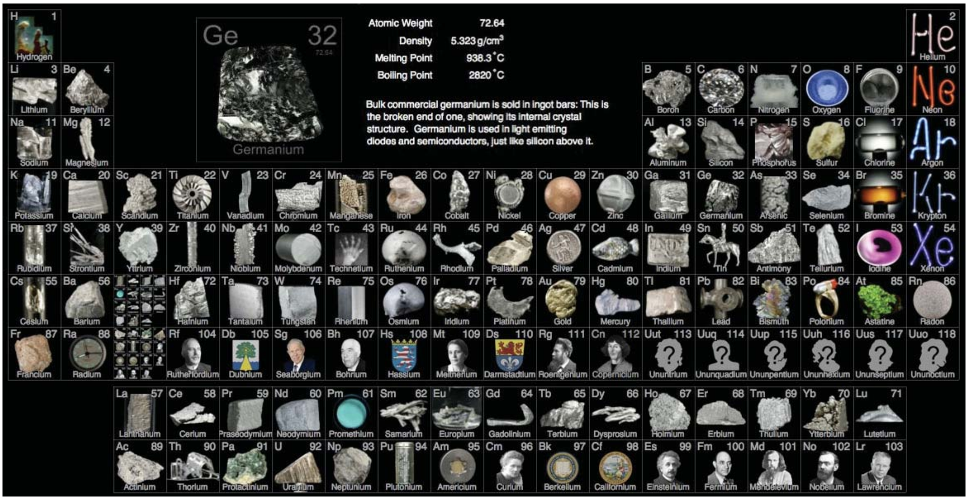


**A group** is a vertical column of the periodic table. Elements with similar physical and chemical properties belong in a group. The group number gives the number of valence electrons in an element.

**A period** is a horizontal row of the periodic table. Physical and chemical properties change gradually going across a period. The period number indicates the number of energy levels surrounding the nucleus. These periodic trends can clearly be seen in atomic radii, ionic radii, ionization energies and electronegativities. These specific trends will be investigated in this activity.

Elements having similar outer electronic configurations in their atoms are arranged in vertical columns, referred to as **groups** or **families**.





According to the recommendation of International Union of Pure and Applied Chemistry (IUPAC), the groups are numbered from 1 to 18 replacing the older notation IA … VIIA, VIII, IB … VIIB and 0.

There are altogether **7** periods. The period number corresponds to the highest principal quantum number (n) of the elements in the period. The first period contains **2** elements. The subsequent period consists of **8**, **8**, **18**, **18** and **32** elements, respectively. The seventh period is incomplete and the sixth period would have a theoretical maximum (on the basis of quantum numbers) of **32** elements. In this form of the Periodic Table, **14** elements of both sixth and seventh periods (lanthanoids and actinoids) are placed in separate panels at the bottom.

## The Anatomy of the Periodic Table

As you are probably well aware, in the periodic table, elements are arranged in order of increasing atomic number. The 18 vertical columns of the table are called groups or families, while the seven horizontal rows are called periods and correspond to the sevenprincipal quantum energy levels, $n = 1$ through $n = 7$. On the right side of the periodic table is a dividing line resembling a staircase. To the left of the staircase lie the metals, and to the right of the staircase lie the nonmetals. Many of the elements that touch the staircase are called metalloids, and these exhibit both metallic and nonmetallic properties. Study the diagram below and memorize the names of the different types of elements, because you will definitely see questions about these groupings on the test!

**Metals** are malleable, ductile, and have luster; most of the elements on the periodic table are metals. They oxidize (rust and tarnish) readily and form *POSITIVE* ions (cations). They are excellent conductors of both heat and electricity. The metals can be broken down into several groups.

**Transition metals** (also called the transition elements) are known for their ability to refract light as a result of their unpaired electrons. They also have several possible oxidation states. Ionic solutions of these metals are usually colored, so these metals are often used in pigments. The actinides and lanthanides are collectively called the**rare earth elements** and are filling the *f* orbitals. They are rarely found in nature. Uranium is the last naturally occurring element; the rest are man-made.

**Nonmetals** lie to the right of the staircase and do not conduct electricity well because they do not have free electrons. All the elemental gases are included in the nonmetals. Notice that hydrogen is placed with the metals because it has only one valence electron, but it is a nonmetal. Here are some specific families you should know about, within the three main groups (metals, nonmetals, and metalloids):

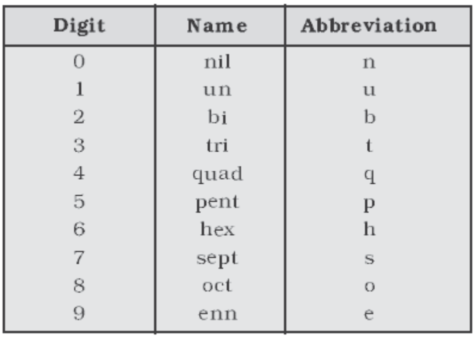
**Alkali metals (1A) –** The most reactive metal family, these must be stored under oil because they react violently with water! They dissolve and create an alkaline, or basic, solution, hence their name.

**Alkaline earth metals (2A)** – These also are reactive metals, but they don't explode in water; pastes of these are used in batteries. **Halogens (7A)** – Known as the "salt formers," they are used in modern lighting and always exist as diatomic molecules in their elemental form.

**Noble gases (8A)** – Known for their extremely slow reactivity, these were once thought never react; neon, one of the noble gases, is used to make bright signs.

### IUPAC Nomenclature

IUPAC has maderecommendation that until a new element'sdiscovery is proved, and its name is officially recognized, a systematic nomenclature bederived directly from the atomic number of theelement using the numerical roots for 0 andnumbers 1-9. These are shown in Table.  The roots are put together in order of digits which make up the atomic number and "ium"is added at the end. The IUPAC names forelements with *Z* above 100 are shown inTable.



| Digit | Name | Abbreviation |
|---|---|---|
| 0 | nil | n |
| 1 | un | u |
| 2 | bi | b |
| 3 | tri | t |
| 4 | quad | q |
| 5 | pent | p |
| 6 | hex | h |
| 7 | sept | s |
| 8 | oct | o |
| 9 | enn | e |

Nomenclature of the elements with atomic number above 100 are provided in the table above.

| Atomic Number | Name | Symbol | IUPAC Official Name | IUPAC Symbol |
|---|---|---|---|---|
| 101 | Unnilunium | Unu | Mendelevium | Md |
| 102 | Unnilbium | Unb | Nobelium | No |
| 103 | Unniltrium | Unt | Lawrencium | Lr |
| 104 | Unnilquadium | Unq | Rutherfordium | Rf |
| 105 | Unnilpentium | Unp | Dubnium | Db |
| 106 | Unnilhexium | Unh | Seaborgium | Sg |
| 107 | Unnilseptium | Uns | Bohrium | Bh |
| 108 | Unniloctium | Uno | Hassnium | Hs |
| 109 | Unnilennium | Une | Meitnerium | Mt |
| 110 | Unnnillium | Uun | Darmstadtium | Ds |
| 111 | Unununnium | Uuu | Rontgenium* | Rg* |
| 112 | Ununbium | Uub | * | * |
| 113 | Ununtrium | Uut | + | |
| 114 | Ununquadium | Uuq | * | * |
| 115 | Ununpentium | Uup | + | |
| 116 | Ununhexium | Uuh | * | * |
| 117 | Ununseptium | Uus | + | |
| 118 | Ununoctium | Uuo | + | |

Thus, the new element first gets atemporary name, with symbol consisting ofthree letters. Later permanent name andsymbol are given by a vote of IUPACrepresentatives from each country. Thepermanent name might reflect the country (orstate of the country) in which the element wasdiscovered, or pay tribute to a notable scientist.As of now, elements with atomic numbers upto 118 have been discovered. Official names ofelements with atomic numbers 113, 115, 117and 118 are yet to be announced by IUPAC.

## 1.20 Horizontal, vertical, and diagonal relationships in the periodic table and General properties of atoms

The periodicity of these properties follows trends as you move across a row or period of the periodic table or down a column or group:

Ionization Energy Increases,Electronegativity Increases, Atomic Radius Decreases.
Ionization Energy Decreases, Electronegativity Decreases, Atomic Radius Increases

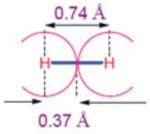
### Size of atoms and ions

The *size* of an isolated *atom* can't be measured because we can't determine the location of the electrons that surround the nucleus. We can estimate the *size* of an *atom*, however, by assuming that the radius of an *atom* is half the distance between adjacent *atoms* in a solid.

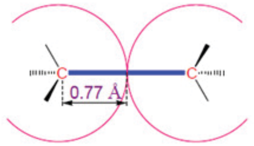
### Atomic radii

The *atomic* radius of a chemical element is a measure of the *size* of its *atoms*, usually the mean or typical distance from the center of the nucleus to the boundary of the surrounding cloud of electrons.

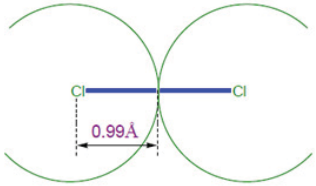
Example: Hydrogen (in $H_2$)



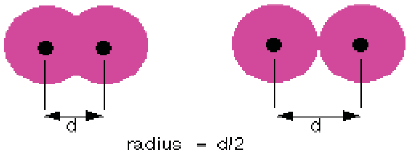
Example: Carbon (in diamond)



Example: Chlorine (in $Cl_2$)

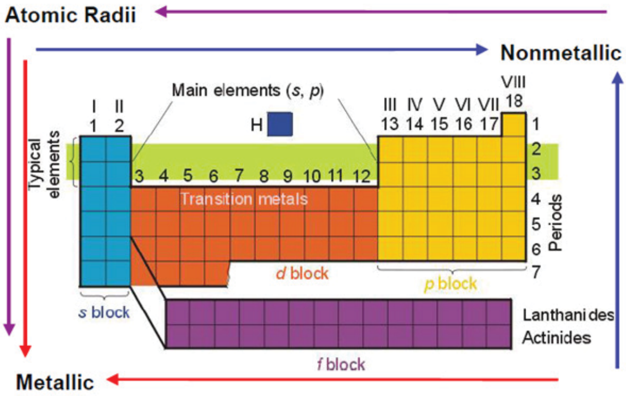


The atomic radius is simply the distance from the nucleus to the outermost electron. Since the position of the outermost electron can never be known precisely, the atomic radius is usually defined as half the distance between the nuclei of two bonded atoms of the same element:

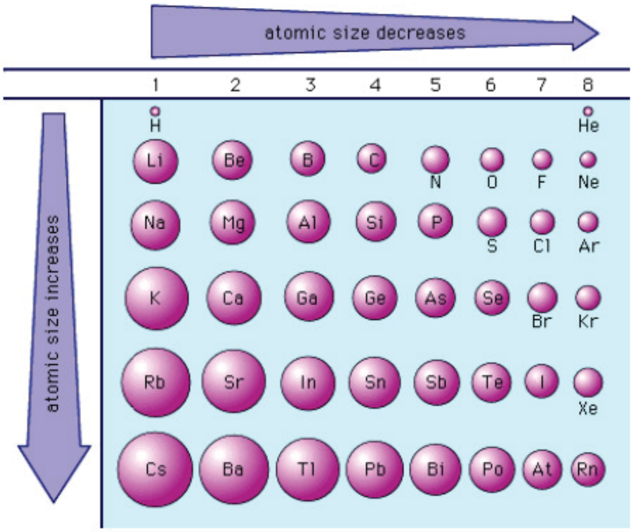


As a group is descended, the outermost electron is in a higher energy level which is further from the nucleus so the radius increases.

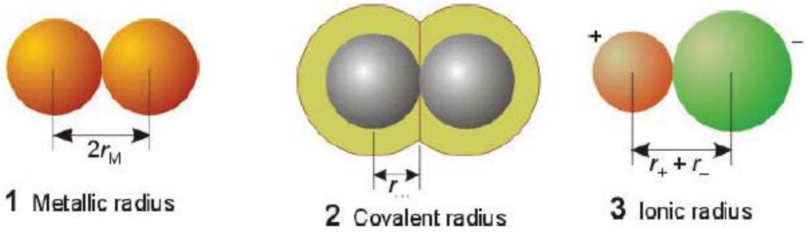
Across a period, electrons are being added to the same energy level, but the number of protons in the nucleus increases. This attracts the energy level closer to the nucleus and the atomic radius decreases across a period.



The following graph shows the trend in atomic radius:



Atomic Radius to refer to both covalent ormetallic radius depending on whether theelement is a non-metal or a metal.



## Ionic radii and Trend in ionic radii

Similar to atomic radius, the ionic radius of an element increases in size down a group as the number of electron shells increase.

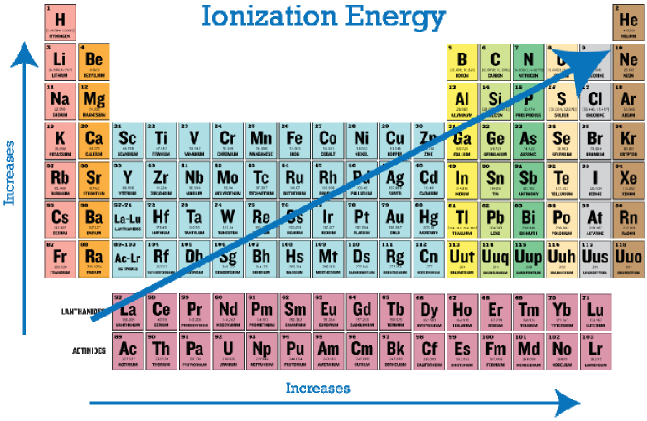
However, going across a period, the ionic radius decreases from Group 1 to Group 3 as with atomic radius, but then increases and decreases again as the large negative ions are formed from Groups 5 to 7. (Recall that Group 4 elements do not typically form ions). An example showing the relative ion sizes from Period 3 are shown above.

The cations ($Na^+$, $Mg^{2+}$ and $Al^{3+}$) contain fewer electrons than protons so the electrostatic attraction between the nucleus and the outermost electron is greater and the ion is smaller than the parent atom. It is also smaller because the number of electron shells has decreased by one. Across the period the ions contain the same number of electrons but an increasing number of protons so the ionic radius decreases in size.The anions ($P^{3-}$ and $S^{2-}$) contain more electrons than protons and therefore are larger that the parent atom. Across a period, the ionic size decreases because the number of electrons remains the same but the numbers of protons increase, pulling the outer shell closer to the nucleus.

***Note:** The size of an atom always decreases when being converted to a positive ion because it loses an electron and therefore there is less electron repulsion. The size of an atom always increases when being converted to a negative ion because since there is an increase in repulsion between electrons.

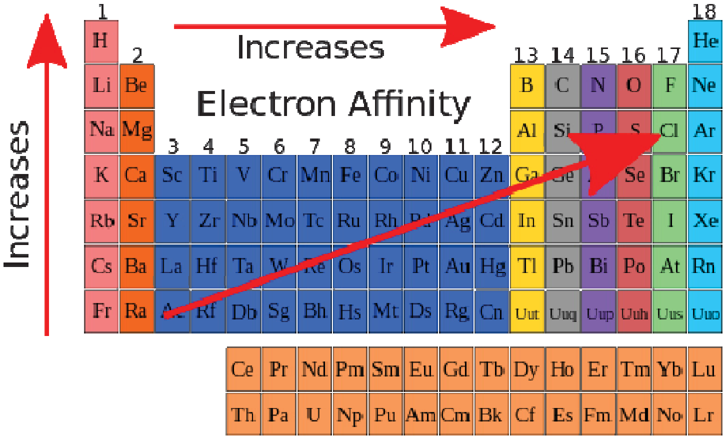
### Ionization potential

A quantitative measure of the tendency of anelement to lose electron is given by itsIonization Enthalpy. It represents the energyrequired to remove an electron from an isolated gaseous atom (X) in its ground state.



### Electron affinity

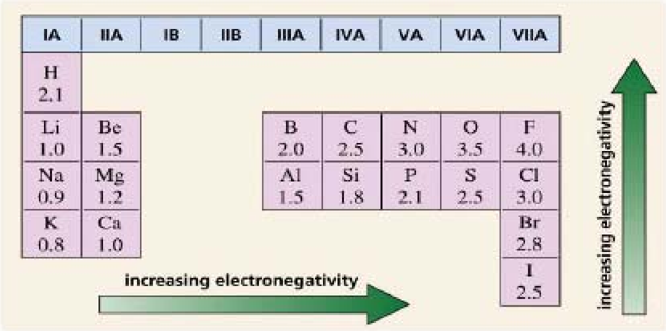
An atom‘s **electron affinity** is the amount of energy released when an electron is added to the atom in its gaseous state—when an electron is added to an atom, the atom forms a negative ion. Most often, energy is *released* as an electron is added to an atom, and the greater the attraction between the atom and the electron added, the more negative the atom‘s electron affinity.



## Electronegativity

Electronegativity is a relative measure of the attraction that an atom has for a shared pair of electrons when it is covalently bonded to another atom.

The electronegativity decreases as you go down a group. This is due to the shielding effect where electrons in lower energy levels shield the positive charge of the nucleus from outer electrons resulting in those outer electrons not being as tightly bound to the atom. Electronegativity increases as you go from left to right across a period. This is because there is more electron-attracting power of the nucleus with the increasing nuclear charge as the number of protons increase form left to right across the periodic table.



| IA | IIA | IB | IIB | IIIA | IVA | VA | VIA | VIIA |
|---|---|---|---|---|---|---|---|---|
| H<br>2.1 | | | | | | | | |
| Li<br>1.0 | Be<br>1.5 | | | B<br>2.0 | C<br>2.5 | N<br>3.0 | O<br>3.5 | F<br>4.0 |
| Na<br>0.9 | Mg<br>1.2 | | | Al<br>1.5 | Si<br>1.8 | P<br>2.1 | S<br>2.5 | Cl<br>3.0 |
| K<br>0.8 | Ca<br>1.0 | | | | | | | Br<br>2.8 |
| | | | | | | | | I<br>2.5 |

### a) Pauling

The most common and widely used scale for electronegativities is the **Pauling scale**, devised by Linus Pauling in 1932. This is the scale commonly presented in general chemistry textbooks. Pauling based his scale on thermochemical data, particularly bond energies, which allowed him to calculate differences in electronegativity between atoms in a covalent bond. He assigned a value of 4.0 to fluorine, the most electronegative element, and calculated other values with respect to that. Thus the Pauling scale runs from 0 to 4, with 4 being the most electronegative. The least electronegative element is francium. Recently, the scale was revised a little—fluorine was assigned an electronegativity value of 3.98, and some minor changes were made to other reported values.

### b) Mulliken-Jaffe

In 1934, shortly after Pauling proposed his approach for measuring electronegativity, Robert S. Mulliken proposed a different approach. Mulliken suggested that an atom's electronegativity should be the average value of the atom's electron affinity (EAv) and ionization energy (IEv). Mulliken electronegativities, $C_M$, may be estimated by the following equation.

$$C_M = 0.168\ (IE_v + EA_v - 1.23)$$

In this equation, the values for electron affinity and ionization energy (reported in electron volts) must be calculated for the atom as it exists within the molecule—they are not the experimentally determined values for the neutral atom.

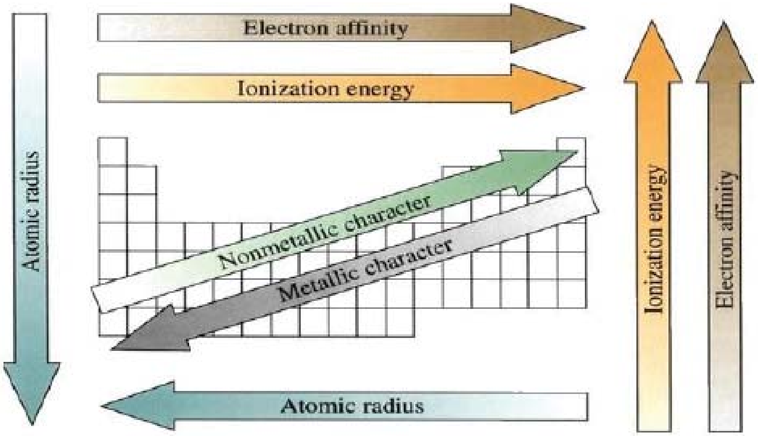
### c) Allred-Rochow definitions

In 1958, A. L. Allred and E. G. Rochow proposed a separate method, based on atomic size and charge, to calculate electronegativities. They defined electronegativity as the electrostatic force exerted by theatomic nucleus on the valence electrons (outermost electrons involved in chemical bonding). When calculated using the following equation, the electronegativity values ($C_{AR}$) on this scale agree well with those on the Pauling scale.

$$C_{AR} = 0.744 + 0.359Z_{eff}/r^2$$

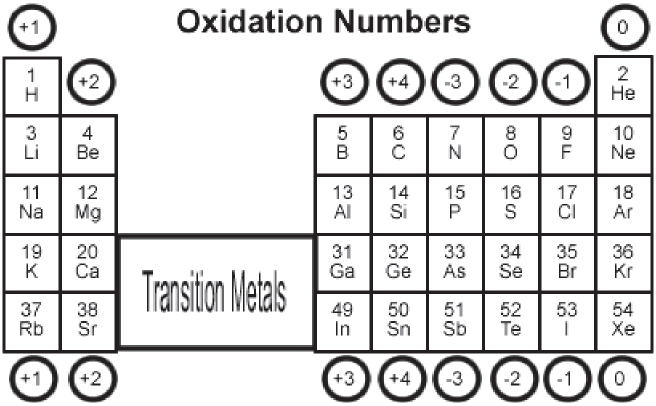
Where $Z_{eff}$ is the effective nuclear charge experienced by a valence electron, and r is the distance between the electron and the atomic nucleus (covalent radius).

### Summary of periodic trends

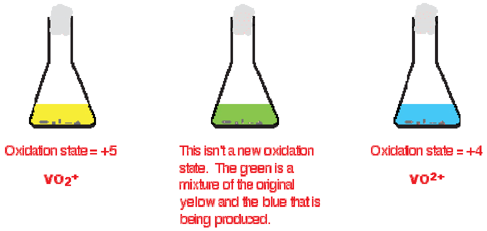


### 1.20 Oxidation states (Oxidation Number) and variable valency

Oxidation and reduction reactions take place through the transfer of electrons involved in chemical bonds. If, during the course of a reaction, an element loses electrons, it is said to have been oxidized. Conversely, if an element gains electrons, it is said to have been reduced. This loss or gain may be actual or theoretical.



*To follow the (actual or theoretical) loss and gain of electrons by the atoms involved in a reaction, chemists assign an* ***oxidation number*** *(or* ***oxidation state****) to each atom in the reactants and products.*



The oxidation number signifies the number of charges an atom (within a molecule or ionic compound) would have if electrons were transferred completely. Essentially, this means that the electrons in a chemical bond are considered as belonging to the more electronegative atom. Thus the rules for assigning oxidation numbers are based on this concept of electronegativity.

**Variable valencies**

Electrons exist in orbits around an atomic nucleus. The higher the orbit number, the greater the distance of the electrons from the nucleus. Atoms try to achieve a stable state similar to that of the noble gases or the inert elements in their outermost orbit by accepting or donating electrons. This property is called the atom's valency. Some elements differ in their capacity to combine with other elements depending on the nature of the reaction; this property is called variable valency.

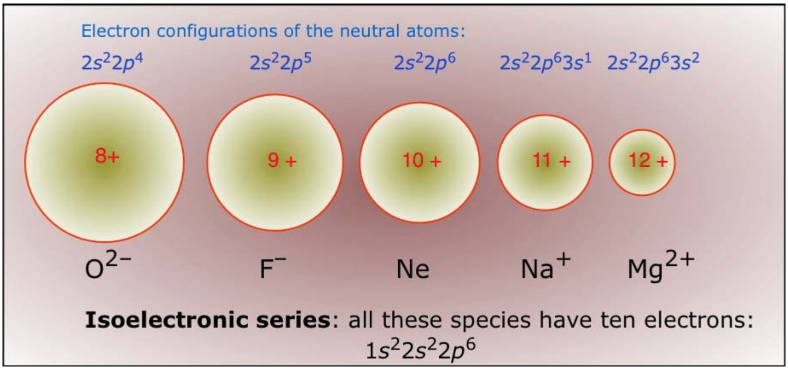
Iron has atomic number 26 and the electronic configuration is [Ar] 3d6 4s2.Iron has 4 unpaired electrons in 3d orbital and 2 paired electrons in 4s. So the possible oxidation states are + 2, + 3, + 4, + 6 but generally it shows +2 and +3 oxidation state.

Variable valencies of some of the elements are shown below:

| | "ous" | "ic" |
|---|---|---|
| Iron | $Fe^{2+}$ — Ferrous | $Fe^{3+}$ — Ferric |
| Copper | $Cu^{1+}$ — Cuprous | $Cu^{2+}$ — Cupric |
| Mercury | $Hg^{1+}$ — Mercurous | $Hg^{2+}$ — Mercuric |
| Gold | $Au^{1+}$ — Aurous | $Au^{3+}$ — Auric |
| Tin | $Sn^{2+}$ — Stannous | $Sn^{4+}$ — Stannic |
| Lead | $Pb^{2+}$ — Plumbous | $Pb^{4+}$ — Plumbic |

## 1.21 Isoelectronic relationship

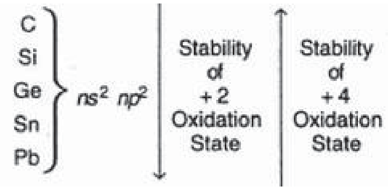
When we find some atoms and ions whichcontain the same number of electrons, we callthem isoelectronic species. For example, $O^{2-}$, $F^{-}$, $Na^{+}$ and $Mg^{2+}$ have the same number of electrons (10).



Their radii would be differentbecause of their different nuclear charges. Thecation with the greater positive charge will havea smaller radius because of the greater attraction of the electrons to the nucleus. Anionwith the greater negative charge will have thelarger radius. In this case, the net repulsion ofthe electrons will outweigh the nuclear chargeand the ion will expand in size.

## 1.22 Inert-pair effect

The reluctance of s electrons towards the bond formation is called inert pair effect or it can be said as the reluctance of electrons present in outermost shell (i.e $ns^2$) to get unpaired and involve in bond formation is called inert pair effect.
*Inert pair effect* is mostly shown by the 15 – 17th group elements. That is, the oxidation state reduces by 2 for elements below, which is more stable than the other oxidation states. The reason for this is the inertness of the inner electrons due to poor shielding.



**For example:**

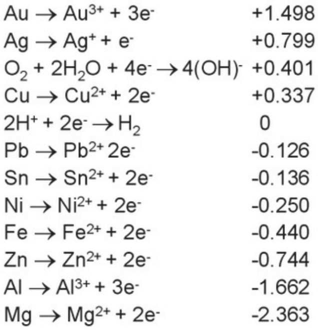
1) In 3rd, thallium can exhibit +1 and +3 oxidation states but it is stable in +1 oxidation state only due to inert pair effect

2) In 4th, lead shows both +2 and +4 oxidation states but it is stable in +2 oxidation state due to inert pair effect.

### 1.23 Standard reduction potentials (E°)

The standard reduction potential (E°)is the tendency for a chemical species to be reduced, and is measured in volts at standard conditions. The more positive the potential is the more likely it will be reduced.

### 1.24 Electrochemical series



| | |
|---|---|
| $Au \rightarrow Au^{3+} + 3e^-$ | +1.498 |
| $Ag \rightarrow Ag^+ + e^-$ | +0.799 |
| $O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^-$ | +0.401 |
| $Cu \rightarrow Cu^{2+} + 2e^-$ | +0.337 |
| $2H^+ + 2e^- \rightarrow H_2$ | 0 |
| $Pb \rightarrow Pb^{2+} 2e^-$ | -0.126 |
| $Sn \rightarrow Sn^{2+} + 2e^-$ | -0.136 |
| $Ni \rightarrow Ni^{2+} + 2e^-$ | -0.250 |
| $Fe \rightarrow Fe^{2+} + 2e^-$ | -0.440 |
| $Zn \rightarrow Zn^{2+} + 2e^-$ | -0.744 |
| $Al \rightarrow Al^{3+} + 3e^-$ | -1.662 |
| $Mg \rightarrow Mg^{2+} + 2e^-$ | -2.363 |

A serial arrangement of metallic elements or ions according to their electrode potentials determined under specified conditions; the order shows the tendency of one metal to reduce the ions of any other metal below it in the series. The electrochemical series is built up by arranging various redox equilibrium in order of their standard electrode potentials (or redox potentials). The most negative E° values are placed at the top of the electrochemical series, and the most positive at the bottom.

### 1.25 The occurrence and isolation of elements

#### Occurrence of elements

Nearly 80 metallic elements are obtained from mineral deposits on or beneath the surface of the earth. Metals which have low chemical reactivity are found in **free state** or **in native state**.

Gold, silver and platinum are examples of metals that are partly found in a free state. Most of the other metals are found in a combined state in the form of their oxide ores, halide ores, carbonate ores, halide ores, sulphide ores, sulphate ores and so on.

| Oxide Ores | Carbonate Ores | Halide Ores | Sulphide Ores |
|---|---|---|---|
| Bauxite ($Al_2O_3.2H_2O$) | Marble ($CaCO_3$) | Cryolite ($Na_3AlF_6$) | Galena ($PbS$) |
| Cuprite ($Cu_2O$) | Magnesite ($MgCO_3$) | Fluorspar ($CaF_2$) | Iron pyrite ($FeS_2$) |
| Haematite ($Fe_2O_3$) | Siderite ($FeCO_3$) | Rock salt ($NaCl$) | Zinc blende ($ZnS$) |

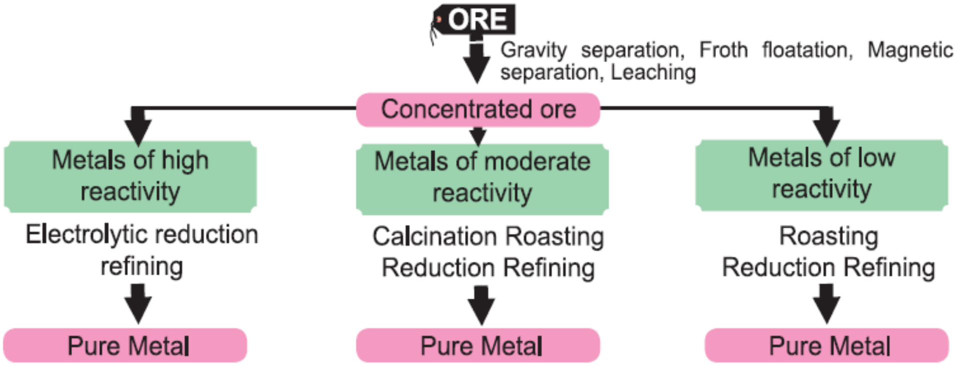
**Factors influencing the choice of extraction process**

Four major factors influence the choice of an extraction process:

1. The cost of production of the metal from the available feedstock (ore, concentrate, flue dust, etc.) by each of the possible extraction methods.
2. The feasibility of producing a metal with a composition suitable for the next stage of processing. This involves the consideration of the extent to which the possible reaction can proceed and is determined by thermodynamic constraints.
3. The rate at which the composition changes can be achieved, which controlled by the kinetics of the reactions.
4. Environmental and safety legislation, which is progressively becoming more restrictive and limiting the freedom of choice.

The illustration provided below provides a rough outline.

**Flow Chart (Extraction of Metal from its ore)**



**Mineral benefication-pretreatment**

Mineral processing begins with beneficiation, consisting of initially breaking down the ore to required sizes depending on the concentration process to be followed, by crushing, grinding, sieving, etc. Thereafter, the ore is physically separated from any unwanted impurity, depending on the form of occurrence and/or further process involved. Separation processes take advantage of physical properties of the materials. These physical properties can include density, particle size and shape, electrical and magnetic properties, and surface properties. Major physical and chemical methods include magnetic separation, froth floatation, leaching etc., whereby the impurities and unwanted materials are removed from the ore and the base ore of the metal is concentrated, meaning the percentage of metal in the ore in increased. This concentrate is then either processed to remove moisture or else used as is for extraction of the metal or made into shapes and forms that can undergo further processing, with ease of handling.

Ore bodies often contain more than one valuable metal. Tailings of a previous process may be used as a feed in another process to extract a secondary product from the original ore. Additionally, a concentrate may contain more than one valuable metal. That concentrate would then be processed to separate the valuable metals into individual constituents.

### Dense medium separation

Once the ore has been separated, it is mixed with finely ground ferrosilicon of a particular density. This process is called dense medium separation. Dense medium separation (DMS) is one of the techniques thatcan be used to upgrade low grade ores, such that they may become economic to process. Density separation is widely used to pre-concentrate ore minerals and reject unwanted gangueprior to the main processing stage of an ore (e.g. flotation). For base metal sulfide ores, densemedium separation (DMS) is used to separate the sulfide minerals, which are relatively dense,from the less dense silicate gangue minerals.

### Flotation process

Froth flotation is considered to be the most widely used method for ore beneficiation. In ore beneficiation, flotation is a process in which valuable minerals are separated from worthless material or other valuable minerals by inducing them to gather in and on the surface of a froth layer. Sulfide and non-sulfide minerals as well as native metals are recovered by froth flotation. This process is based on the ability of certain chemicals to modify the surface properties of the mineral(s). Other chemicals are used to generate the froth and still others are used to adjust the pH. Certain chemicals are even capable of depressing the flotation of minerals that are either to be recovered at a later time or are not to be recovered.

The process of froth flotation entails crushing and grinding the ore to a fine size. This fine grinding separates the individual mineral particles from the waste rock and other mineral particles. The grinding is normally done in water with the resultant slurry called the pulp. The pulp is processed in the flotation cells, which agitate the mixture and introduce air as small bubbles.

### Solution methods (Solution concentration and purification)

After leaching, the leach liquor must normally undergo concentration of the metal ions that are to be recovered. Additionally, undesirable metal ions sometimes require removal.

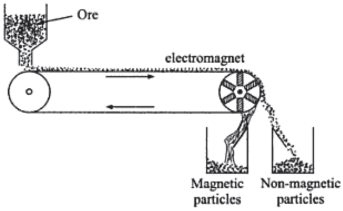
- Precipitation is the selective removal of a compound of the targeted metal or removal of a major impurity by precipitation of one of its compounds. Copper is precipitated as its sulfide as a means to purify nickel leachates.

- Cementation is the conversion of the metal ion to the metal by a redox reaction. A typical application involves addition of scrap iron to a solution of copper ions. Iron dissolves and copper metal is deposited.
- Solvent Extraction
- Ion Exchange
- Gas reduction. Treating a solution of nickel and ammonia with hydrogen affords nickel metal as its powder.

## Magnetic separation

**Magnetic separation** can be applied to minerals with weak magnetic properties to separate those with para and diamagnetic characteristics. Repeated passage through magnetic fields purifies the minerals. Depending on the application, drum, pulley, disc, ring and belt-type separators are available.

If the mineral or ore but not the gangue is attracted by a magnet, the two are separated easily by this method. The pulverized ore is spread thinly over a rubber belt carried over a pulley in a magnetic field. The gangue particles fall off as the belt becomes vertical but the ore particles are retained on the belt until they pass out of the influence of the magnet.



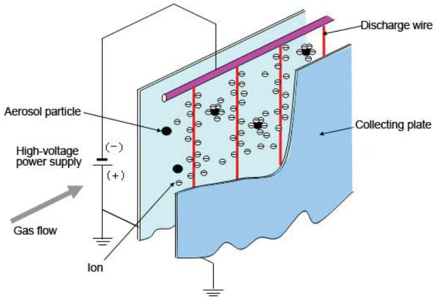
For example, chromite, $FeCr_2O_4$, an ore of chromium being magnetic, can be separated from silicon gangue by this method. Similarly, a mixture of wolframite, $FeWO_4$ (magnetic) is separated from cassiterite ($SnO_2$).

## Electrostatic precipitation

**Electrostatic separation** may be used to separate mineralparticles with different electrostatic affinities. Variations inthe electrostatic charge and densities of the particles are usedto differentiate the materials. The moisture content ofteninfluences the electrostatic characteristics.

## Principles of electrostatic separation

Electrostatic precipitation is a method of dust collection that uses electrostatic forces, and consists of discharge wires and collecting plates. A high voltage is applied to the discharge wires to form an electrical field between the wires and the collecting plates, and also ionizes the gas around the discharge wires to supply ions. When gas that contains an aerosol (dust, mist) flows between the collecting plates and the discharge wires, the aerosol particles in the gas are charged by the ions.



The Coulomb force caused by the electric field causes the charged particles to be collected on the collecting plates, and the gas is purified. This is the principle of electrostatic precipitation, and Electrostatic precipitator applies this principle on an industrial scale. The particles collected on the collecting plates are removed by methods such as (1) dislodging by rapping the collecting plates, (2) scraping off with a brush, or (3) washing off with water, and removing from a hopper.

**Thermal decomposition methods**

**Displacement of one metal by another**

In these methods a more noble metal is usually precipitated from a solution of its salt by the addition of an inexpensive metal. For example, copper sulphide ores, which are too lean to be worked up economically in the usual way, are oxidized by the exposure to air and rain to form a solution of $CuSO_4$. The $Cu^{2+}$ ions are displaced as Cu metal by adding scarp iron into the solution.

$$Cu^{2+} + Fe \longrightarrow Cu + Fe^{2+}$$

Similarly, silver and gold are obtained from their complex cyanides when more reactive Zn displaces them.

$$2M(CN)_2^- + Zn \longrightarrow Zn(CN)_4^{2-} + 2M \quad \text{(where, M = Ag or Au)}$$

**High temperature chemical reduction methods**

**Pyrometallurgy** is the processes of roasting an ore at a high temperature and then reducing its oxide product. Its characteristics include:

1. Large amount of waste as a product of concentration.
2. High energy consumption to maintain high temps.
3. Gaseous emissions that must be controlled (i.e. $CO_2$& $SO_2$)

**Reduction by carbon (Coke, Charcoal, Coal and CO)**

a) Zinc is obtained from its sulphide ore, ZnS – zinc blende. The ore is first roasted to oxide and the oxide is reduced to metal by heating with powdered coal in fire clay retorts.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$
$$ZnO + C \longrightarrow Zn + CO$$

b) Tin is obtained from cassiterite, $SnO_2$ by heating the concentrated ore with coke.

$$SnO_2 + 2C \longrightarrow Sn + 2CO$$

c) Haematite is reduced by carbon monoxide obtained from coke.

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

**Reduction by metal (Aluminium)**

The metals Mn and Cr are obtained from their oxides by reduction with aluminium powder. These oxides cannot be reduced by carbon or carbon monoxide. Al being more electropositive than Mn or Cr, it can reduce the oxides of these metals. The process is called **Godschmidt alumino thermic process.**

$$3MnO + 2Al \longrightarrow Al_2O_3 + 3Mn + heat$$
$$3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3 + heat$$
$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3 + heat$$

**Self-reduction or auto-reduction**

The sulphide ores of less electropositive metals like Hg, Pb, Cu, etc., are roasted as to convert part of the ore into oxide which then reacts with remaining sulphide ore to produce metal. No external reducing agent is used. For example, (i) the extraction of lead, its sulphide ore (galena) is partly roasted into oxide and then heated to a high temperature by adding necessary amount of fresh ore.

$$2PbS + 3O_2 \longrightarrow 2PbO + 3SO_2$$
$$PbS + 2PbO \longrightarrow 3Pb + SO_2$$

Similarly, in the manufacture of copper, the sulphide and oxide interact at an elevated temperature to give blister copper.

$$Cu_2S + 2Cu_2O \longrightarrow SO_2 + 6Cu$$

**Reduction of oxides with hydrogen**

Though hydrogen is a good reducing agent, however, reduction with hydrogen is costlier and therefore employed only in specific cases. For example,

$$\underset{\text{tungsten oxide}}{WO_3} + 3H_2 \xrightarrow{\text{high temp}} W + 3H_2O$$

### Electrolytic reduction in

This is a common extraction process for the more reactive metals - for example, for aluminium and metals above it in the electrochemical series. You may also come across it in other cases such as one method of extracting copper and in the purification of copper.

During electrolysis, electrons are being added directly to the metal ions at the cathode (the negative electrode).

The downside (particularly in the aluminium case) is the cost of the electricity. An advantage is that it can produce very pure metals.

#### a) Aqueous solution – Example: Electrolytic reduction of Alumina

Alumina — or aluminium oxide ($Al_2O_3$), is produced from extracted ore. Despite its name, it has nothing to do with clay or black soil but resembles a flour or very white sand. Alumina is then transformed into aluminium through electrolytic reduction. One tonne of aluminium is produced from every two tonnes of alumina.

Bauxite consist of 40-60% alumina, as well as earth silicon, ferrous oxide, and titanium dioxide. To separate pure alumina, the Bayer process is applied. First, the ore is heated in an autoclave with caustic soda. It is then cooled and a solid residue — «red mud» — is separated from the liquid. Aluminium hydroxide is then extracted from this solution and calcined to produce pure alumina.

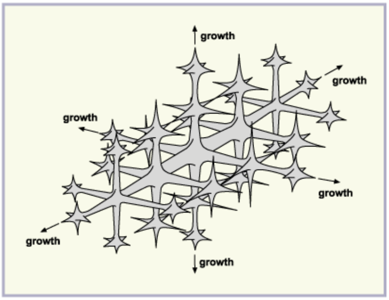
The final stage is the reduction of aluminium through the Hall-Heroult process. It is based on the following principle: when the alumina solution is electrolyzed in molten cryolite ($Na_3AlF_6$), pure aluminium is produced. The reduction cell bottom serves as a cathode, and coal bars immersed in cryolite serve as anodes. Molten aluminium is deposited under a cryolite solution with 3-5% alumina. During this process, temperatures reach 950°C, considerably higher than the melting point of the metal itself, which is 660°C.

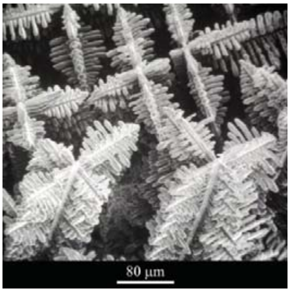
#### b) Non aqueous solvents

Some metals, which are difficult to deposit electrolytically from aqueous solutions, can be deposited from appropriate non-aqueous solutions. They are, for example, alkali metals, magnesium, and aluminum. They are usually deposited at more negative potentials than the reduction of water. The electrodeposition of lithium metal from electrolyte solutions in aprotic solvents is an important process in the lithium secondary batteries and the mechanistic study has been carried out extensively. The electrodepositions of magnesium and calcium metals have also been studied for developing secondary batteries. So far, however, the two metals cannot be deposited from common polar aprotic solvents containing normal salts (perchlorates, trifluoromethanesulfonates, etc.). The only solution for the deposition of magnesium is the ether (THF) solution of Grignard reagent [RMgCl(R=Me, Et, Bu), EtMgBr]. In the solution, magnesium can be deposited smoothly and uniformly at high plating efficiency. For calcium, the electrodeposition of this type is impossible because Grignard-type reagent cannot be obtained with calcium. The aluminum electrodeposition (mainly electroplating) has a great commercial significance. By use of appropriate electrolytic-bath compositions, highly pure aluminum can be deposited efficiently. Aluminum can be electroplated on a variety of metal surfaces, including steel, non-active metals, and active metals (e.g. Mg, Al). The electroplated aluminum can further be anodized in order to obtain hard, corrosion resistive, electrically insulating surfaces for various applications. Among the useful bath compositions are $AlCl_3$+$LiAlH_4$in ethers (diethyl ether,THF), $AlBr_3$+KBr in aromatic hydrocarbons (toluene, xylene), and $AlCl_3$+ LiCl indimethylsulfone [$(CH_3)_2SO_2$]. Room temperature molten salts, which are combinations of organic salts $R^+X^-$and aluminum halides $AlX_3$($R^+$: pyridinium, imidazolium, etc.), are also used.

**c) In fused melts**

Fused salt electrolysis is carried out at a temperature below the melting point of the metal. The deposition will occur in the form of small crystals with dendritic shape (fern like structure) as shown below. Powders of thorium, tantalum and vanadium have been prepared by fused salt electrolysis.





In this method of electrodeposition, depending upon the processing conditions, the final product may be obtained in three different forms. The deposit may be:

a) A hard brittle layer of pure metal which is subsequently milled to obtain powder (e.g. iron powder).
b) A soft, spongy substance which is loosely adherent and easily removed by scrubbing.
c) A direct powder deposit from the electrolyte which collects at the bottom of the cell. The last two methods are extensively used for the production of large quantities of powder.

**Thermodynamics of reduction processes (or Thermodynamic principles of metallurgy)**

Thermodynamics tells us that a spontaneous reaction is always accompanied by decrease in free energy ($\Delta G$), i.e. free change is negative. Therefore, in order that reduction of an oxide, sulphide or chloride of a metal takes place spontaneously at a given temperature and pressure, the free energy change of the reduction process must be negative.

In the reduction of an oxide, for example, there is competition between the metal and the other substance (used as reducing agent) for example oxygen. The reducing power of the substance is measured by the decrease in free energy during the formation of its oxide; the more negative $\Delta G$, greater is the reducing power of the substance.

Gibbs free energy change is related to enthalpy change ($\Delta H$) and entropy change ($\Delta S$) by the expression,

$$\Delta G = \Delta H - T\Delta G$$

When all the reacting species are at unit activity $\Delta G$ is equal to $\Delta_f G^o$, which is called standard free energy change for the reaction.

A non-spontaneous process i.e., with $\Delta G > 0$ or $\Delta G = +$ ve, can be made spontaneous by carrying out such reaction simultaneously with reaction having a very large negative free energy change of the reaction. This is known as **coupling** and such reactions are called **coupled reactions**.For example, decomposition of iron oxide ($Fe_2O_3$) to iron (Fe) is non-spontaneous as $\Delta G^o$ for the reaction is positive ($\Delta_f G^o = + 1487.0$ kJ/mol). This reaction is coupled with oxidation of carbon monoxide to carbondioxide to make the overall reaction spontaneous.

$$2Fe_2O_{3(s)} \rightarrow 4Fe_{(s)} + 3O_{2(g)} \Delta_f G^\circ = +1487.0\ kJ\ mol^{-1}$$

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)} \Delta_f G^\circ = -514.4\ kJ\ mol^{-1}$$

Overall reaction is:

$$2Fe_2O_{3(s)} + 6CO_{(g)} \rightarrow 6CO_{2(g)} + 4Fe_{(s)} \Delta_f G^\circ = -56.2\ kJ\ mol^{-1}$$

As $\Delta_f G^o$ for the overall reaction is negative, the overall reaction is spontaneous. This is, in fact, the reaction that takes place in the lower part of the blast furnace where oxide ore of iron is reduced into iron.

### The Ellingham diagrams

Ellingham diagrams are a particular graphical form of the principle that the thermodynamic feasibility of a reaction depends on the sign of $\Delta G$, the Gibbs free energy change, which is equal to $\Delta H - T\Delta S$, where $\Delta H$ is the enthalpy change and $\Delta S$ is the entropy change.

Generally, Ellingham diagrams are the plots of free energy change ($\Delta_f G^o$) of formation of metal oxide per mole of $O_2$ against temperature.

$$2xM_{(g)} + O_{2(g)} \rightarrow 2M_xO_{(s)}$$

These plots were first used by H.J.T. Ellingham. These plots provide a basis for considering the choice of a suitable reducing agent in the reduction of an oxide. These diagrams help us in predicting the feasibility of thermal reduction (pyrometallurgy) of an oxide ore.

a) Although, $\Delta H$ and $\Delta S$ vary with temperature, the variations are too small that the relationship between $\Delta G$ and $\Delta G^o$ with temperature (*T*) becomes linerar.

$$\text{The slope of the lines} = \frac{d(\Delta_f G^\circ)}{dT} = -\Delta S^\circ$$

Most of the lines have positive slope and the line slope upwards showing decrease in free energy of the reaction at high temperature.

For example, consider the oxide of copper

$$2Cu_{(s)} + O_{2(g)} \rightarrow 2CuO_{(s)}$$

In this case,$\Delta S < 0$ i.e., negative because gaseous reactant $O_2$ combines to form solid CuO. Hence, the factor $T\Delta S$ is positive and as T increases $\Delta G^o$ becomes more positive.

However, note the slope for the following reaction is negative:

$$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)}$$

Here, $\Delta S$ is positive and hence $\Delta G^o$ becomes increasing negative as T increases.

**(b) A typical Ellingham diagram** follows a straight line unless there is large entropy change due to melting or vaporization. The entropy change (or change in slope) at the melting point is generally of a smaller order but there is marked increase in the slope because of large entropy changes due to disappearance of both gaseous $O_2$ and metal vapor. For example, in Zn, ZnO plot, melting is indicated by an abrupt change in the slope of the curve.

**(c) From Elligham diagram** one can predict which metal will reduce a certain metal oxide. Any metal can reduce the oxides of the other metals which lie above it in the diagram. For example, aluminium should be able to reduce chromium (III) oxide to chromium because $\Delta_f G^o$ of the formation of $Al_2O_3$ is more negative than that of $Cr_2O_3$ at all temperatures. Similarly, Al will reduce oxides of iron and nickel but not that of magnesium until temperature rises beyond 1770 ºC.

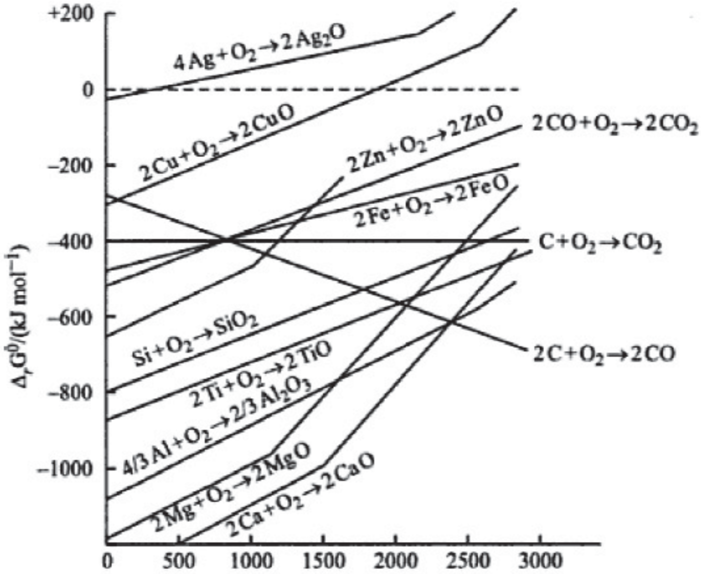
**(d) Reducing action of carbon:** Reducing capabilities of elements generally decrease with increase in temperature but that of carbon ($C \rightarrow CO$) increases until at 2000 ºC. It is the third most powerful reducing agent after calcium and aluminium. This is due to increase in entropy which accompanies the reaction.

$$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)}$$

But when carbon is oxidized to carbon dioxide,

$$C_{(s)} + 2O_{2(g)} \rightarrow 2CO_{2(g)}$$

The entropy change accompanying this reaction remains almost constant. $\Delta_f G^o$ v/s T curve for the formation of $CO_2$ is therefore, parallel, to temperature (T) axis and slope of the curve is zero.



Carbon oxidation curves have a common intersection at 710 ºC. Above 710 ºC, carbon is the best and cheapest reducing agent and below 710 ºC, carbon monoxide is the best reducing agent. The oxidation curve of carbon into CO cuts across the diagram indicating that carbon will reduce any oxide provided the temperature is high enough.

# Unit II Ionic Bond

## Syllabus

Properties of ionic compounds, factors favoring the formation of ionic compounds ionizationpotential, electron affinity, and electronegativity - Lattice energy: definition, Born-Landeequation (derivation not required), factors affecting lattice energy, Born-Haber cycle-enthalpy offormation of ionic compound and stability - Covalent character in ionic compounds-polarizationand Fajan's rules; effects of polarization-solubility, melting points, and thermal stability oftypical ionic compounds.

## Introduction

### Elementary theories on Chemical Bonding

The study on the "nature of forces that hold or bind atoms together to form a molecule" is required to gain knowledge of the following

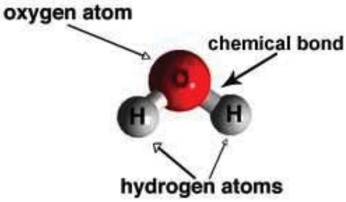
- To know about how atoms of same element form different compounds combining with different elements.
- To know why particular shapes are adopted by molecules.
- To understand the specific properties of molecules or ions and the relation between the specific type of bonding in the molecules.

### What is a Chemical bond?

Matter is made up of one or different type of elements.Under normal conditions no other element exists as anindependent atom in nature, except noble gases. However,a group of atoms is found to exist together as one specieshaving characteristic properties. Such a group of atoms iscalled a molecule. Obviously there must be some forcewhich holds these constituent atoms together in themolecules.

**The attractive force which holds variousconstituents (atoms, ions, etc.) together in differentchemical species is called a chemical bond.**

**Chemical Bond** is the existence of a strong force of binding between two or many atoms results in the formation of a stable compound with properties of its own. The bonding is permanent until it is acted upon by external factors like chemicals, temperature, energy etc. It isknown that, a molecule is made up of two or many atoms having its own characteristic properties which depend on the types of bonding present.



### Types of Bond

There is more than one type of chemical bonding possible betweenatoms which make the molecules to show different characteristicproperties. The different types of chemical bonding that are considered to exist in molecules are:

(i) **Ionic or electrovalent bond** which is formed as a result of complete electron transfer from one atom to the other that constitutes the bond.

(ii) **Covalent bond** which is formed as a result of mutual electron pair sharing with an electron being contributed by each atom of the bond and

(iii) **Coordinate - covalent bond** which is formed as a result of electron pair sharing with the pair of electrons being donated by only one atom of the bond.

### Classification of molecules

Molecules having two identical atoms like $H_2$, $O_2$, $Cl_2$, $N_2$ etc. are called as **homonuclear diatomic molecules**.

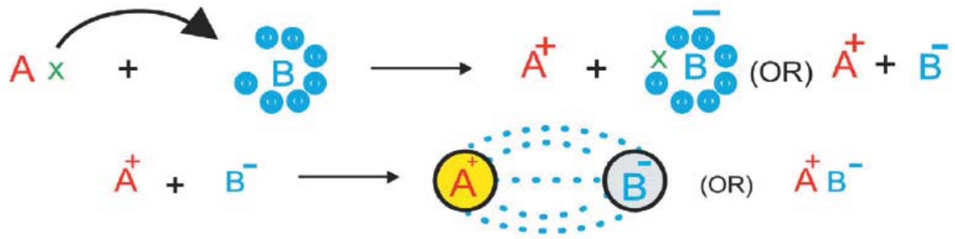
Molecules containing two different atoms like CO, HCl, NO, HBr etc., are called as **heteronuclear diatomic molecules.**

Molecules containing identical but many atoms bonded together such as $P_4$, $S_8$ etc., are called as **homonuclear polyatomics.**

In most of the molecules, more than two atoms of different kinds are bonded such as in molecules like $NH_3$, $CH_3COOH$, $SO_2$, HCHO and they are called as **heteronuclear polyatomics.**

### Formation of ionic or electrovalent Bond

Let us consider two atoms A and B. The atom A has 1 electron in its valence (outermost) shell. B has 7 electrons in its valence shell. A has 1 electron excess and B has 1 electron lesser than the stable octet configuration. Therefore, A transfers an electron to B. In this transaction both the atoms A and B acquire a stable electron-octet configuration. A becomes a positive ion (cation) and B becomes a negative ion (anion). Both the ions are held together by electrostatic force of attraction. Formation of ionic bond between A and B can be shown as,



The electrostatic attraction between cation (+) and anion (-) produced by electron transfer constitutes an ionic or electrovalent bond. The compounds containing such a bond are referred to as “ionic or electrovalent compound”.

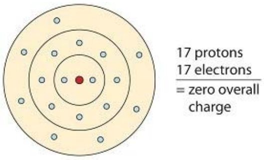
### Formation of ionic bond in various compounds

$$\text{i) } \underset{2s^22p^63s^1}{\text{Na(g)}} \xrightarrow{\text{ionisation}} \underset{\substack{2s^2sp^6\\ \text{sodium cation}}}{\text{Na}^+_{(g)} + e^-}$$

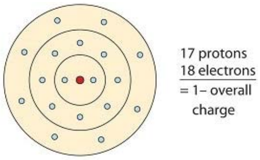
$$\text{ii) } \underset{3s^23p^5}{\text{Cl(g)} + e^-} \xrightarrow{\text{affinity}} \underset{\substack{3s^2,\ 3p^6\\ \text{chloride anion}}}{\text{Cl}^-}$$

$$\text{iii) } \underset{\substack{\text{Sodium}\\ \text{ion}}}{\text{Na}^+} + \underset{\substack{\text{Chloride}\\ \text{ion}}}{\text{Cl}^-} \xrightarrow[\text{attraction}]{\text{electrostatic}} \underset{\substack{\text{ionic/crystalline}\\ \text{compound is formed}}}{\text{NaCl}}$$

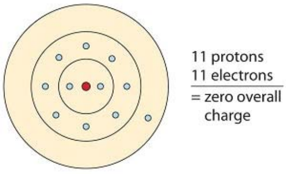
**NaCl** is formed by the electron ionisation of sodium atom to Na+ ion due to its low ionisation potential value and chlorine atom to chloride ion by capturing the odd electron due to high electron affinity. Thus, NaCl (ionic compound) is formed. In NaCl, both the atoms possessunit charges.



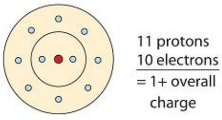
Cl



Cl⁻



Na



Na⁺

In **CaO**, which is an ionic compound, the formation of the ionic bond involves two electron transfers from Ca to O atoms. Thus, doubly charged positive and negative ions are formed.

$$\underset{3p^6\,4s^2}{\text{Ca}} \xrightarrow{\text{ionisation}} \text{Ca}^{2+} + 2e^- \quad \text{(Calcium Cation)}$$

$$\underset{2s^22p^4}{\text{O} + 2\bar{e}} \xrightarrow[\text{aaffinity}]{\text{electron}} \underset{2s^22p^6}{\text{O}^{2-}} \quad \text{(Oxide anion)}$$

Ionic bond may be also formed between a doubly charged positive ion with single negatively charged ion and vice versa. The molecule as a whole remains electrically neutral. For example in **$MgF_2$**, Mg has two positive charges and each fluorine atom has a single negative charge. Hence, $Mg^{2+}$ binds with two fluoride ($F^-$) ions to form $MgF_2$ which is electrically neutral.

$$\mathrm{Mg} \rightarrow \mathrm{Mg}^{2+} + 2e^-$$
$(2s^2\ 2p^6\ 3s^2$ $(2s^2\ 2p^6)$

$$2e + 2F \rightarrow 2F^-$$
$(2s^2\ 2p^5)$ $(2s^2\ 2p^6)$

i.e.:- $\mathrm{Mg}^{2+} + 2F^- \rightarrow \mathrm{MgF_2}$

Magnesium - fluoride
(an ionic compound).

$$\mathrm{Al} \rightarrow \mathrm{Al}^{3+} + 3e^-$$
$2p^6\ 3s^2\ 3p^1$ $(2s^2, 2p^6)$

$$3\ \mathrm{Br} + 3e^- \rightarrow 3\ \mathrm{Br}^-$$
$(4s^2\ 4p^5)$ $(4s^2\ 4p^6)$

$\mathrm{Al}^{3+} + 3\mathrm{Br}^- \rightarrow \mathrm{AlBr_3}$ (ionic bond)

Similarly in Aluminium bromide (**$AlBr_3$**), Aluminium ion has three positive charges and therefore it bonds with three Bromide ions to form $AlBr_3$ which is a neutral ionic molecule.

**Formation of KCl**

The electronic configuration of K and Cl and their ions ($K^+$ and $Cl^-$) are given below:

K : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$
Cl : $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$
$K^+$ : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$
$Cl^-$ : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$

$$K^+ + Cl^- \rightarrow KCl$$

Formation of ions is major criteria for the ionic bonding. The different types of the outer electronic configurations for the cations and the anions are discussed briefly.

**1. No outer electrons**

The hydrogen ion $H^+$ formed by the loss of the only electron present in the atom is the only ion of this type. The proton, a nucleus having a positive charge, is stabilized in solutions by solvation and has unique properties.

**2. Ions with inert gas configuration**

These ions have the inert gas configuration of $ns^2np^6$ in their outermost shell, except for $n = 1$, for which no $p$ orbitals exist and the inert shell configuration is $1s^2$. These configurations are achieved by the representative elements of group I, II and III by the complete loss of their valence shell electrons and by the elements of group VII, VI and V by acquiring 1, 2 and 3 electrons respectively in their outermost shells. Some of the examples are mentioned below.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | $H^-$ | He ($1s^2$) | $Li^+$ | | | |
| $N^{3-}$, | $O^{2-}$, | $F^-$ | Ne ($2s^2\ 2p^6$) | $Na^+$, | $Mg^{2+}$, | $Al^{3+}$ | |
| $P^{3-}$, | $S^{2-}$, | $Cl^-$ | Ar ($3s^2\ 3p^6$) | $K^+$, | $Ca^{2+}$, | $Sc^{3+}$, | $Ti^{4+}$ |
| $As^{3-}$, | $Se^{2-}$, | $Br^-$ | Kr ($4s^2\ 4p^6$) | $Rb^+$, | $Sr^{2+}$, | $Y^{3+}$, | $Zr^{4+}$ |
| | $Te^{2-}$, | $I^-$ | Xe ($5s^2\ 5p^6$) | $Cs^+$, | $Ba^{2+}$, | $La^{3+}$, | $Ce^{4+}$ |
| | | $At^-$ | Rn ($6s^2\ 6p^6$) | $Fr^+$ | $Ra^{2+}$, | $Ac^{3+}$, | $Th^{4+}$ |

Due to inefficient shielding of the nucleus by the $1s^2$ electrons, the $1s^2$ions have properties different from those of the rest of the members of the same group and tend to form more covalent compounds.

### 3. The Eighteen-Electron Shell Ions

The post-transition elements having the configuration of the last and penultimate shell as $(n-1)s^2\ (n-1)p^6\ (n-1)d^{10}ns^{1,2}np^{0,1,2}$, can lose their outer shell electrons giving the ions having their outer shell configuration $ns^2np^6nd^{10}$. Examples are $Cu^+$, $Zn^{2+}$, $Ga^{2+}$ and $Ge^{2+}$ with configuration $3s^23p^63d^{10}$; $Ag^+$, $Cd^{2+}$, $In^{3+}$ and $Sn^{4+}$ with the $4s^24p^64d^{10}$ configuration and $Au^+$, $Hg^{2+}$, $Tl^{3+}$ and $Pb^{4+}$ for the $5s^25p^65d^{10}$configuration.

### 4. The Inert Pair

When the elements having valence shell configuration $ns^2np^x$ ($x$ = 1, 2, 3) lose their *p* electrons only, cations with an $ns^2$ configuration are formed. This is possible only when the energies of the *ns* and *np* electrons differ sufficiently so as to result in the stepwise ionization during the chemical bond formation. Therefore, only the post-transition elements ions like $Ga^{2+}$, $Ge^{2+}$ and $As^{3+}$ for $4s^2$; $In^+$, $Sn^{2+}$ and $Sb^{3+}$ for $5s^2$ and $Tl^+$, $Pb^{2+}$and $Bi^{3+}$for $6s^2$ ions.

As these configurations are attained by only the loss of electrons, anions having this configuration are not possible. The only exception is $Au^-$, with $5s^25p^65d^{10}6s^2$ configuration, found only in CsAu.

### 5. The *d* and *f* ions

The transition metal ions formed by the loss of the outer valence shell electrons without the ionization of the *d* electrons have the configuration of the outer shell $ns^2np^6nd^x$ ($x$ = 1 to 9) and are classified as the *d* ions because of the similarities amongst themselves. Examples of the ions are $Tl^{3+}$, $V^{2+}$, $Cr^{2+}$, $Cr^{3+}$, $Co^{2+}$, $Fe^{3+}$, $Cu^{2+}$, etc.

The *f* ions are derived from the inner transition elements by the loss of the outer *s* and *d* electrons and have the configuration $(n-1)s^2\ (n-1)p^6\ (n-1)d^{10}\ (n-1)f^{1-13}ns^2np^6$ where $n$ = 6 for the actinons and 5 for the lanthanons. These ions are very similar to one another because of similar sizes and similar electronic configurations in which the *f* electrons do not enter chemical combinations.

### 6. Polyatomic ions

An element on combination with an electronegative element like O, F or Cl through covalent bonds can reduce their own electronegativity and the formal charge. The formation of a large number of the oxoanions, thio-anions, oxocations, halocomplexes, etc., is too complicated to be listed together under a single heading. These and other ions like $[Cu(NH_3)_4]^{2+}$ are properly considered as the coordination compounds and treated as such.

### 7. Ions with irregular configurations

These are certain ions that cannot be classified into any particular class, e.g. $Hg_2^{2+}, Ge_2^{2+}, Pb_9^{4-}$, etc.

From the above, it can be seen that the ion formation is easy if:

a) The charge on the ion, especially the cation is small, generally one or two units only.
b) Anions are small sized and the cations are large sized, and
c) The ion formed has a stable structure, i.e. the 8-electron inert gas shell, the 18-electron pseudo-inert gas shell, the inert $6s^2$ pair, *d* or *f* ion (in the order of decreasing stability).

The comparative instability of the $3d^{10}$ and $5d^{10}$ ions in the case of copper and gold must be noted, stable ions for these are the $Cu^{2+}$ ($3d^9$) and $Au^{2+}$ ($5d^8$). A possible explanation may be that the nuclear charge of these elements is not high enough to hold the 18 electrons firmly, more so in the case of gold where the increased size leads to the 3+ state as the most stable state.

The stability of $Ag^+$ ($4d^{10}$) and the formation of auride ion ($Au^-$) are however, not in line with this explanation.

## 2.1 Properties of ionic compounds

Ionic compounds share many features in common:

- Ionic bonds form between metals and nonmetals.
- In naming simple ionic compounds, the metal is always first, the non-metal second (e.g., sodium chloride).
- Ionic compounds dissolve easily in water and other polar solvents.
- In solution, ionic compounds easily conduct electricity.
- Ionic compounds tend to form crystalline solids with high melting temperatures.

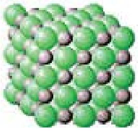
### 1. Ionic compounds form crystals.

Ionic compounds form crystal lattices rather than amorphous solids. Although molecular compounds form crystals, they frequently take other forms plus molecular crystals typically are softer than ionic crystals.

### 2. Ionic compounds have high melting points and high boiling points.

High temperatures are required to overcome the attraction between the positive and negative ions in ionic compounds. Therefore, a lot of energy is required to melt ionic compounds or cause them to boil.

Ionic compounds are solids, results from the intermolecular forces (forces between molecules) in ionic solids. If we consider a solid crystal of sodium chloride, the solid is made up of many positively charged sodium ions (pictured below as small gray spheres) and an equal number of negatively charged chlorine ions (green spheres). Due to the interaction of the charged ions, the sodium and chlorine ions are arranged in an alternating fashion as demonstrated in the figure shown below. Each sodium ion is attracted equally to all of its neighboring chlorine ions, and likewise for the chlorine to sodium attraction. The concept of a single molecule becomes blurred in ionic crystals because the solid exists as one continuous system. Forces between molecules are comparable to the forces within the molecule, and ionic compounds tend to form crystal solids with high melting points as a result.

| | |
|---|---|
|  | $Cl^{-1}$ $Na^{+1}$ $Cl^{-1}$ $Na^{+1}$ $Cl^{-1}$<br>$Na^{+1}$ $Cl^{-1}$ $Na^{+1}$ $Cl^{-1}$ $Na^{+1}$<br>$Cl^{-1}$ $Na^{+1}$ $Cl^{-1}$ $Na^{+1}$ $Cl^{-1}$<br>$Na^{+1}$ $Cl^{-1}$ $Na^{+1}$ $Cl^{-1}$ $Na^{+1}$ |
| **Sodium Chloride** | **NaCl Crystal Schematic** |

The factors which affect the melting point of an ionic compound are:

- The charge on the ions.

  In general the greater is the charge, the greater the electrostatic attraction, the stronger the ionic bond and the higher the melting point.
  The table below compares the melting point and ion charges for sodium chloride and magnesium oxide.

| Ionic Compound | Melting Point (°C) | Cation Charge | Anion Charge |
|---|---|---|---|
| NaCl | 801 | +1 | -1 |
| MgO | 2800 | +2 | -2 |

MgO has a higher melting point than NaCl because 2 electrons are transferred from magnesium to oxygen to form MgO while only 1 electron is transferred from sodium to chlorine to form NaCl.

- The size of the ions

  Smaller ions can pack closer together than larger ions so the electrostatic attraction is greater, the ionic bond is stronger, the melting point is higher.

  The melting point of Group IA (alkali) metal fluorides is compared to the ionic radius of the cation in the table below.

| Ionic Compound | Melting Point (°C) | Cation Radius (pm) |
|---|---|---|
| NaF | 992 | 99 |
| KF | 857 | 136 |
| RbF | 775 | 148 |
| CsF | 683 | 169 |

As the radius of the cations increases down Group I from $Na^+$ to $Cs^+$, the melting points of the fluorides decrease.

### 3. Ionic compounds have higher enthalpies of fusion and vaporizationthan molecular compounds.

Just as ionic compounds have high melting and boiling points, they usually have enthalpies of fusion and vaporization that may be 10 to 100 times higher than those of most molecular compounds. The enthalpy of fusion is the heat required melt a single mole of a solid under constant pressure. The enthalpy of vaporization is the heat required for vaporize one mole of a liquid compound under constant pressure.

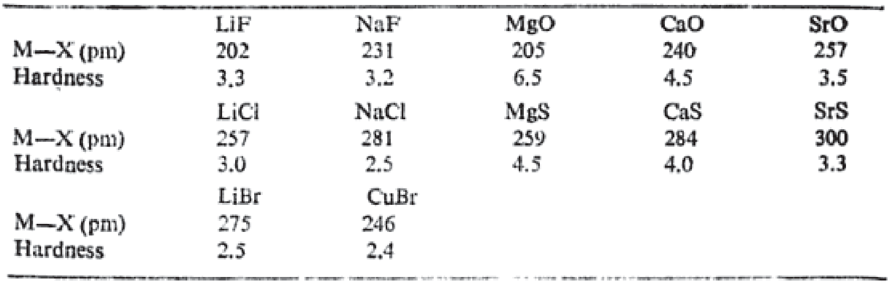
### 4. Stereochemistry

Ionic bonds are quite strong and are omnidirectional. Ionic force extend throughout the space and are equally strong in all directions.

### 5. Ionic compounds are hard and brittle.

#### Hardness

The multivalent electrostatic attraction forces within the ionic crystal make the crystal hard. Hardness increase with the decrease in interionic distances and increase in the ionic charge. Further, the ions with an inert gas shell configuration (the 8-electron ions) give harder crystals than ions with pseudo inert gas configuration (18-electrons).



| | | | | | |
|---|---|---|---|---|---|
| | LiF | NaF | MgO | CaO | SrO |
| M—X (pm) | 202 | 231 | 205 | 240 | 257 |
| Hardness | 3.3 | 3.2 | 6.5 | 4.5 | 3.5 |
| | LiCl | NaCl | MgS | CaS | SrS |
| M—X (pm) | 257 | 281 | 259 | 284 | 300 |
| Hardness | 3.0 | 2.5 | 4.5 | 4.0 | 3.3 |
| | LiBr | CuBr | | | |
| M—X (pm) | 275 | 246 | | | |
| Hardness | 2.5 | 2.4 | | | |

#### Brittleness

If sufficient energy is supplied to the crystal layer of a unit cell, the attractive forces becomes repulsive due to the anion-anion and cation-cation repulsions and the crystal crumbles. Hence, ionic crystals though hard, are brittle and can be powdered easily by hammering.

### 6. Ionic compounds conduct electricity when they are dissolved in water.

When ionic compounds are dissolved in water the dissociated ions are free to conduct electric charge through the solution. Molten ionic compounds (molten salts) also conduct electricity.

In order for a substance to conduct electricity it must contain mobile particles capable of carrying charge.

| | **Ionic Solid** | **Ionic Liquid** | **Aqueous Solution** |
|---|---|---|---|

| | | | |
|---|---|---|---|
| **Mobility of Ions** | very poor | good | good |
| **Electrical Conductivity** | very poor | good | good |

Solid ionic compounds do not conduct electricity because the ions (charged particles) are locked into a rigid lattice or array. The ions cannot move out of the lattice, so the solid cannot conduct electricity.

When molten, the ions are free to move out of the lattice structure.

- Cations (positive ions) move towards the negative electrode (cathode)

$$M^+ + e \to M$$

- Anions (negative ions) move towards the positive electrode (anode)

$$X^- \to X + e$$

When an ionic solid is dissolved in water to form an aqueous solution, the ions are released from the lattice structure and are free to move so the solution conducts electricity just like the molten (liquid) ionic compound.

**6. Ionic solids are good insulators.**

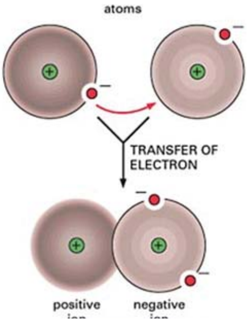
Although they conduct in molten form or in aqueous solution, ionic solids do not conduct electricity very well because the ions are bound so tightly to each other.

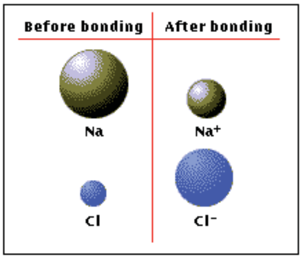
**7. Solubility**

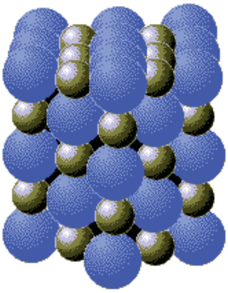
Ionic compounds dissolve in polar solvents having high dielectric constants due to (i) decrease in the attraction forces amongst the ions in a dielectric medium and (ii) ion-solvent dipole interactions, which provide considerable energy for breaking up the ionic lattice.

Many ionic compounds, however, dissolve in solvents having low dielectric constants (dioxane, nitrobenzene, ethers, alcohols, etc.), but the solubility here is due to (i) the partial covalent character of the compound and (ii) co-ordination of the solvent molecules through O atoms.

### 2.2 Factors favoring the formation of ionic compounds







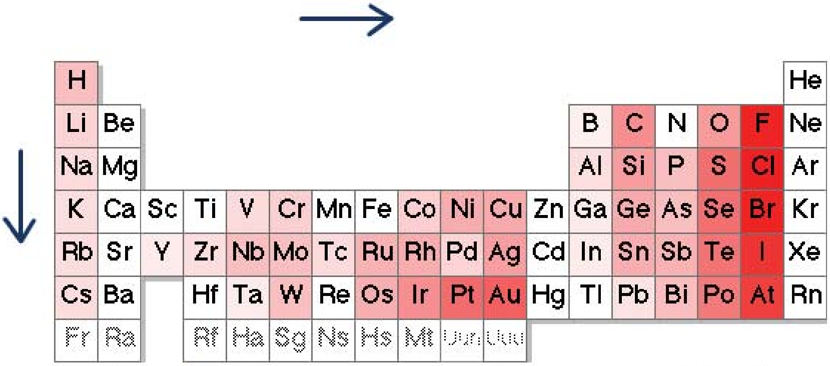
One of the species must have electrons in excess of octet while the other should be deficit of octet. Does this mean that all substance having surplus electron and species having deficient electron would form ionic bond? The answer is obviously no. Now you should ask why? The reasoning is that in an ionic bond one of the species is cation and the other is anion. To form a cation from a neutral atom energy must be supplied to remove the electron and that energy is called ionization energy. Now it is obvious that lower the ionization energy of the element the easier it is to remove the electron. To form the anion, an electron adds up to a neutral atom and in this process energy is released. This process is called electron affinity. So for an ionic bond one of the species must have low ionization energy and the other should have high electron affinity. Low ionization energy is mainly exhibited by the alkali and alkaline earth metals and high electron affinity by the halogen and chalcogens. Therefore these group of elements are predominant in the field of ionic bonding.

## Ionization energy

**i) Low ionization energy:** Ionization energy is the amount of energy, which is required to remove the most loosely bound electron(s) from an isolated gaseous atom to form a positive ion. In forming an ionic bond, one atom must form a cation by losing one or more electrons. In general, elements having low ionization energies have a more favorable chance to form a cation, thereby having a greater tendency to form ionic bonds. Thus, lower ionization energy of metallic elements favours the formation of an ionic bond. It is because of low ionization energy that the alkali and alkaline earth metals, form ionic compounds. For example, ionization energy of sodium is 495 kJ/mol while that of Magnesium is 743 kJ/mol.

$$Na_{(g)} \xrightarrow{495\ kJ\ mol^{-1}} Na^{+}_{(g)} + e\ ;\quad Mg_{(g)} \xrightarrow{743\ kJ\ mol^{-1}} Mg^{+}_{(g)} + e$$

The energy required to remove second electron is very high and thus, the formation of Mg2+ ion is very difficult. In case of Aluminium, the formation of Al3+ ion requires 3158 kJ/mol. This much of energy is generally not available and hence Aluminium does not form ionic bond. For ionic bond formation, the ionization energy of the metal should be low.



General trends in ionization energy with reference to the periodic table

## Electron affinity

**ii) High electron affinity:** Electron affinity is the amount of energy released, when an isolated gaseous atom accepts an electron to form a negative ion. The other atom participating in the formation of an ionic compound must form an anion by gaining an electron (s). Higher electron affinity favors the formation of an anion. Therefore, generally, the elements having higher electron affinity favor the formation of an ionic bond. Halogens have high electron affinities, and therefore halogens generally form ionic compounds.

The electron affinity of chlorine is the highest in the periodic table. It is 348 kJ/mol. Group 16 elements (oxygen, sulphur, etc.) do form divalent anions and in these cases, the formation of divalent anion from monovalent anion requires energy. Thus group 16 elements form ionic bonds with lesser ease compared to group 17 elements. For ionic bond formation, the electron affinity of an element should be high.

**iii) Electronegativity:**

Electronegativity is a relative measure of the attraction that an atom has for a shared pair of electrons when it is covalently bonded to another atom. The electronegative element will tend to form ionic bond quickly. So the difference in the more electronegativity is the possibilities of more ionic compound formation.

## Lattice Energy

### Introduction

Lattice energy is a type of potential energy. It is the amount of energy required to convert a mole of ionic solid to its constituent's ions in the gas phase. For example, the lattice energy of potassium Iodide is 632 KJ/mol. Thus, it takes 632 KJ of energy to convert 1 mole of $KI_{(s)}$ to 1 mole each of $K^+_{(g)}$and$I^-_{(g)}$.

$$KI_{(s)} \rightarrow K^+_{(g)} + I^-_{(g)}$$

***For example:*** LiI, NaI and KI all have the same anion (I-) and all have cations with the same charge (+1). The trend in their lattice energies (LiI > NaI > KI) can be explained on the basis of ionic radius. The radii of the alkali metal ions increase as we move down a group in the periodic table:

$$rLi^+ < rNa^+ < rK^+$$

The **lattice energy** of a crystalline solid is usually defined as the energy of formation of the crystal from infinitely-separated ions, molecules, or atoms, and as such is invariably negative. The concept of lattice energy was originally developed for rocksalt-structured and sphalerite-structured compounds like NaCl and ZnS, where the ions occupy high-symmetry crystal lattice sites. In the case of NaCl, the lattice energy is the energy released by the reaction:

$$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$$

Which would amount to +786 kJ/mol.

### Explanation

Lattice energy *U* of an ionic compound is defined as the energy released when one mole of the compound is formed in the regular lattice structure from the requisite number of ions in the gaseous state. Thus it is the energy change for the reactions:

$$M^{+}_{(g)} + X^{-}_{(g)} \rightarrow M^{+}X^{-}_{(s)}$$

$$M^{n+}_{(g)} + nX^{-}_{(g)} \rightarrow M^{n+}X^{-}_{n(s)}$$

$$mM^{n+}_{(g)} + nX^{m-}_{(g)} \rightarrow M^{n+}_{m}X^{m-}_{n(s)}$$

Or,

The significance of the lattice energy can be seen by considering the formation of ionic compound say $A^+B^-$ from A and B. The process can be considered to involve three independent steps.

a) Removal of an electron from A by the input of ionization energy of A:

$$A_{(g)} \rightarrow A^{+}_{(g)} + e^{-};\ \Delta H = IE_{A}$$

b) Addition of the electron to B forming $B^-$ with the release of the electron affinity (EA) of B:

$$B_{(g)} + e^{-} \rightarrow B^{-}_{(g)};\ \Delta H = -EA_{B}$$

c) Arrangement of the gaseous ions in a regular geometric pattern releasing the lattice energy of the compound $A^+B^-$:

$$A_{(g)} + B_{(g)} \rightarrow A^{+}B^{-}_{(s)}\ ;\ \Delta H = U$$

The formation of gaseous ions $A^+B^-$ where the ions are at infinite distances requires the input of energy (= $IE_A - EA_B$). As the minimum IE is equal to 375.7 kJ/mol for cesium and the maximum EA is 348.7 kJ/mol for chlorine, the formation of ions even in the case of most favorable combination requires an input of about 27 kJ/mol of energy. The more stable state in gaseous form is, therefore, the atomic rather than the ionic in which the ions are infinite separation.

For the formation of the ionic solids, therefore, the coulombic attractions between the oppositely charged ions must be considered. The energy of the regular arrangement of the ions in a lattice can be easily calculated by simple electrostatic model. Considering the two ions $M^{2+}$ and $X^{2-}$ as point charges separated by a distance *r*, the electrostatic energy of attraction is given by:

$$E_{cou} = \frac{Z_{+}Z_{-}e^{2}}{4\pi\epsilon r}$$

Where *e* is the electronic charge (1.6 x $10^{-19}$ C) and $\epsilon_o$ is the permittivity of vacuum. As one of the charges is negative this energy is negative with respect to the energy at infinite separation of ions and becomes infinite as *r* approaches zero.

But the ions are not point charges and have electrons in the outer shells. As the ions comes closer, short range inter-electronic repulsion forces are set in which do not permit the ions to fuse together.Born-Landé equation involves the calculation of the inter-electronic repulsions and helps to calculate the lattice energy theoretically.

## Born-Landé equation

The Born-Landé equation is a concept originally formulated in 1918 by the scientists Born and Lande and is used to calculate the lattice energy (measure of the strength of bonds) of a compound. This expression takes into account both the Born interactions as well as the Coulomb attractions.Due to its high simplicity and ease, the Born-Landé equation is commonly used by chemists when solving for lattice energy.

## Assumptions

1. Ions are point charges.
2. The crystals are infinitely large.
3. The distribution of ions is even and symmetric.
4. The environment around every ion in the crystal is the same.

Born-Landé equation is given below:

$$E = \frac{-N_A M\, Z^+ Z^-\, e^2}{4\pi\varepsilon_0 r_0}\left[1 - \frac{1}{n}\right]$$

Where,

$N_A$ - Avogadro constant

$M$ - Madelung constant, relating to the geometry of the crystal

$Z^+$ - Charge number of cation

$Z$ - Charge number of anion

$e$ - Elementary charge, equal to $1.6022\times10^{-19}$ C

$\varepsilon_0$ - Permittivity of free space, equal to $8.854\times10^{-12}$ $C^2$ $J^{-1}$ $m^{-1}$

$r_0$ - Distance to closest ion; and

$n$ -Born exponent, a number between 5 and 12, determined experimentally by measuring the compressibility of the solid, or derived theoretically.

The Born–Landé equation gives a reasonable fit to the lattice energy.

From the Born–Landé equation it can be seen that the lattice energy of a compound is dependent on a number of factors:

- as the charges on the ions increase the lattice energy increases (becomes more negative),
- when ions are closer together the lattice energy increases (becomes more negative)

Barium oxide (BaO), for instance, which has the NaCl structure and therefore the same Madelung constant, has a bond radius of 275 picometers and a lattice energy of -3054 kJ/mol, while sodium chloride (NaCl) has a bond radius of 283 picometers and a lattice energy of -786 kJ/mol.

**Factors affecting lattice energy**

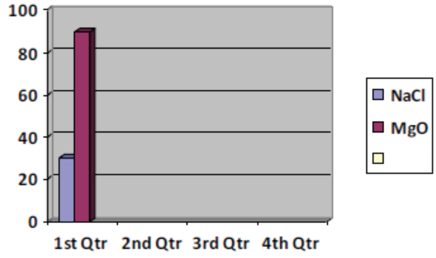
The lattice enthalpy of an ionic compound is affected by the size and charge on the ions which make it up.

1. A decrease in the size of any ion increases the lattice enthalpy (more negative/exothermic). This is because small ions can be close together and the smaller distance of separation the larger the attractive force between the ions.
2. An increase in charge also increases lattice enthalpy. (makes it more negative/exothermic). This is because the force of attraction between ions increases as the charge on the ion increases.
3. The lattice energies of ionic compounds are relatively large. The lattice energy of NaCl, for example, is 787.3 kJ/mol, which is only slightly less than the energy given off when natural gas burns.
4. The bond between ions of opposite charge is strongest when the ions are small.

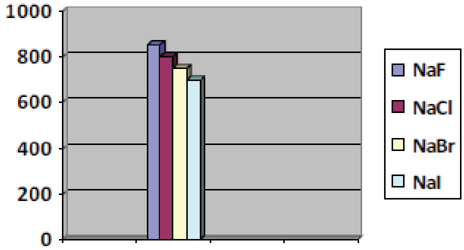
**a) The charges on the ion:**

Sodium chloride and magnesium oxide have exactly the same arrangements of ions in the crystal lattice, but the lattice enthalpies are very different. It can be seen that lattice energy of magnesium oxide is much greater than that of sodium chloride. That is because in magnesium oxide, $2^+$ ions are attracting $2^-$ ions; in sodium chloride, the attraction is only between $1^+$ and $1^-$ ions.

Lattice Enthalpy of Sodium Chloride



Lattice energy of Halides



**b) The radius of the ions:**

The lattice enthalpy of magnesium oxide is also increased relative to sodium chloride because magnesium ions are smaller than sodium ions, and oxide ions are smaller than chloride ions. That means that the ions are closer together in the lattice and that increase the strength of attraction. We can also see this effect of ion size on lattice enthalpy as you go down a group in the periodic table.

**For example:**

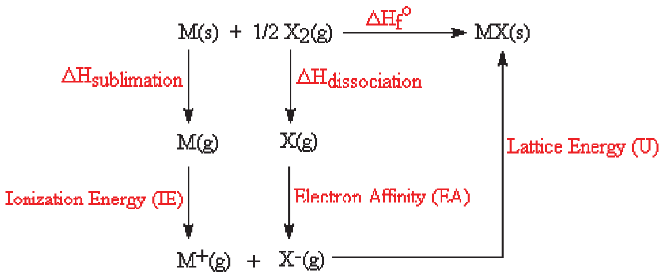
As we go down group 7 of the periodic table from fluorine to iodine, you would expect the lattice enthalpies of their sodium salts to fall as the negative ions get bigger-and that is the case. Attractions are governed by the distance between the centers of the oppositely charged ions, and that distance is obviously greater as the negative ion gets bigger.

**Born-Haber cycle – enthalpy of formation of ionic compound and stability**

The direct calculation of lattice enthalpy is quite difficult because the required data is often not available. Therefore lattice enthalpy is determined indirectly by the use of the **Born – Haber cycle**.

The cycle uses ionization enthalpies, electron gain enthalpies and other data for the calculation of lattice enthalpies. The procedure is based on the Hess's law, which states that the enthalpy of a reaction is the same, whether it takes place in a single step or in more than one step. In order to understand it let us consider the energy changes during the formation of sodium chloride from metallic sodium and chlorine gas. The net energy change during the process is represented by $\Delta H_f$.

Born - Haber Cycle



$$\Delta H_f^\circ = \Delta H_{sub} + IE + \Delta H_{diss} + EA + U$$

Experimental values of lattice are obtained from a cycle of thermochemical data. This is as Born-Haber cycle. It relates lattice energy of an ionic crystal to other thermochemical data viz. sublimation energy, dissociation energy, ionization energy etc. for example; NaCl is formed according to the equation.

$$Na_{(s)} + \frac{1}{2} Cl_{2\,(g)} \rightarrow NaCl \qquad \Delta H = -E \text{ (Heat of formation)}$$

The above reaction involves the following steps.

1.Conversion of metallic sodium into gaseous sodium atoms.

$Na_{(s)} \rightarrow Na_{(g)}$ $\Delta H = S$ (sublimation energy)

2. Dissociation of chlorine molecules into chlorine atoms

$\frac{1}{2} Cl_{2\,(g)} \rightarrow Cl_{(g)}$ $\Delta H = \frac{1}{2} D$ (Dissociation energy)

3. Conversion of gaseous sodium atom into gaseous sodium ion.

$Na_{(g)} \rightarrow Na^+_{(g)} + e^-$ ΔH = I (Ionization energy)

1. Conversion of gaseous chlorine atom into gaseous chloride ion.

$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}$ ΔH = -A (Electron affinity)

2. Formation of sodium chloride crystal from gaseous sodium ion and chlorine ion

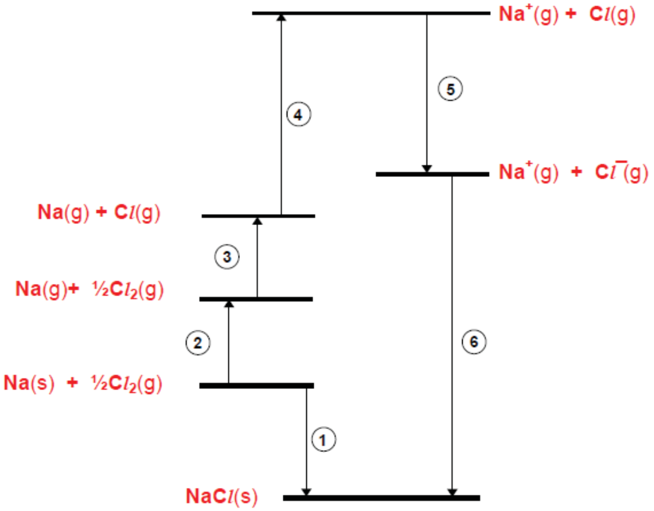
$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$ ΔH = -U (Lattice energy)

Applying Hess's law of constant heat summation

$-E = S + \frac{1}{2} D + I - A - U_\circ$

$U_\circ = E + S + \frac{1}{2} D + I - A$

### BORN-HABER CYCLE FOR SODIUM CHLORIDE



*STEPS (values are in kJ mol⁻¹)*

| | | | |
|---|---|---|---|
| ① Enthalpy change of formation of NaCl | $Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$ | **– 411** |
| ② Enthalpy change of sublimation of sodium | $Na(s) \longrightarrow Na(g)$ | **+ 108** |
| ③ Enthalpy change of atomisation of chlorine | $\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$ | **+ 121** |
| ④ Ist Ionisation Energy of sodium | $Na(g) \longrightarrow Na^+(g) + e^-$ | **+ 500** |
| ⑤ Electron Affinity of chlorine | $Cl(g) + e^- \longrightarrow Cl^-(g)$ | **– 364** |
| ⑥ Lattice Enthalpy of NaCl | $Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$ | |

According to **Hess's Law**, the enthalpy change is independent of the path taken. Therefore,

STEP 6 = - (STEP 5) - (STEP 4) - (STEP 3) - (STEP 2) + (STEP 1)

**- (-364) - (+500) - (+121) - (+108) + (-411) = - 776 kJ mol⁻¹**

**Theoretical values for the lattice enthalpy may be calculated using the Born-Lande equation and compared to the value obtained from the Born-Haber cycle. Good**

**agreement suggests that the ionic model of bonding is a good one for the compound being considered, whilst poor agreement suggests that there are other important contributions which are not incorporated into the ionic model.**

**Uses of Born-Haber cycle**

The Born-Haber type of calculations is useful, some important uses are provided below:

The enthalpy of formation of ionic compounds $\Delta H_f$ can be calculated within a few percent using the Born-Landé equation and the Born-Haber cycle. Thus, as the inter-nuclear distance in NaCl crystal is 281.4 pm, Madelung's constant for NaCl lattice is 1.747456 and the Born exponent, taking the average of the values for $Na^+$ (7) and $Cl^-$(9), is 8; the Born-Landé equation gives the lattice energy for the crystal as –757.2 kJ/mol while the Born-Haber equation gives the same as -381.1 kJ/mol. This value of -381.1 kJ/mol compares well with the observed enthalpy of formation of NaCl which is -410.9 kJ/mol. This could be analyzed with the following factors.

**1. Atomization of elements**

The *S* and *D* values are generally low as compared with the other terms involved and do not change much from compound to compound. Though *D* values for N2 and O2 are 941 kJ/mol and 507 kJ/mol respectively, they are still too small to be of any consequence. If *S* for the metal is high, it contributes towards the nobility of the metals. Thus higher *S* (285.6 kJ/mol) of silver in comparison with that of sodium (108.4 kJ/mol) makes silver nobler, though the lattice energy for AgCl is – 899 kJ/mol which is -214 kJ/mol higher than that of NaCl (-757 kJ/mol).

**2. Ionization Energies**

The ionization energies are always endothermic and increase with successive ionization, limiting the charge on the cations to one or two units, with +3 charge rather uncommon and +4 charge found only on $Th^{4+}$. For the main group of elements, though the successive ionization energies increase, the increase is only moderate, except when the noble gas octet is broken. The most stable oxidation states for the representative elements are therefore, for groups I, II and III, the ones that maximize the charge without breaking the *noble* gas octet (because of the more than the compensatory nature of the lattice energy term). Thus it requires 5.1339 MJ per mole energy for the formation form Al, it is stable in the ionic lattices. As the energy differences between the outer *ns* electrons and the $(n-1)d$ electrons is not much in the case of the transition elements, there is no sudden change in the ionization energy values and the stability of the ionic lattices becomes comparable for the element in the different valence states.

**3. Electron affinities**

The electron affinity for halogens is exothermic; that for all other elements it is highly endothermic. As stated earlier, the sum of ionization energy and electron affinity is always endothermic even for the most favorable pair of ions. Obviously, atoms with endothermic electron affinity will tend to give covalent compounds, but the lattice energies of solids containing oxide ions are so high that it compensates for the ionization energy and electron affinity difference, even for the tetra-valent metal ions like $Ti^{4+}$ and $Zr^{4+}$, because of the small size and comparatively higher ionic charge on the oxide ion.

### 4. Lattice energy

As the summation of above terms (1), (2) and (3) will always be endothermic, the large number of the ionic compounds owes their stability to the large lattice energy due to the electrostatic energies involved. As the electrostatic term will always be released during the ion formation even in the gas phase as

$$energy\ of\ the\ ion\ pair = \frac{Z^+ Z^- e^2}{4\pi\varepsilon_0 r_0}\left[1 - \frac{1}{n}\right]$$

Thus a large number of the ionic oxides and the sulphides are known despite the highly endothermic electron affinity of both oxygen as well as sulphur simply because of the high lattice energy released during the crystal formation.

## 2.4 Covalent character in ionic compounds – *polarization*

Pure ionic bonding is not known to exist. All ionic compounds have a degree of covalent bonding. The larger the difference in electronegativity between two atoms, the more ionic the bond. Ionic compounds conduct electricity when molten or in solution. They generally have a high melting point and tend to be soluble in water.

In reality, purely ionic bonds do not (and cannot) exist, as this would require an infinitely large electronegativity difference, and complete charge transfer is unfavorable from the view point of raising the electronic kinetic energy. All ionic bonds have some covalent character. For example, Na-Cl and Mg-O bonds have percent covalency, while Si-O bonds are usually ~ 50 % covalent. Predominantly covalent bonds with partial ionic character are called *polar covalent*.

**Stability of ionic compound:** The energy required to produce any cation from an atom, the ionization energy of the atom, is always larger, and usually much larger than the energy which is released when an electron is added to an atom, the electron affinity. This is true even if an electron is relatively easily like sodium and is being added to an atom which readily acquires it such as chlorine. The enthalpy changes in the formation of an ionic lattice from the gaseous isolated sodium and chloride ion is -788KJ/mol. That enthalpy change which corresponds to the reaction

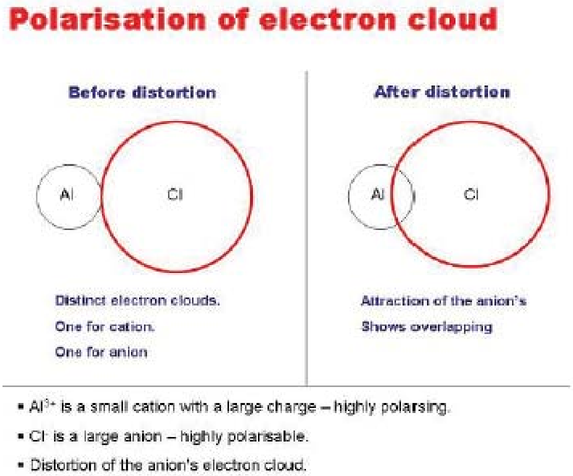
$$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$$

is called the lattice energy of the ionic crystal. Although the lattice energy is not directly measurable, there are various ways to estimate it from theoretical considerations and some experimental values. For all known ionic crystals, the lattice energy has a large negative value. It is ultimately the lattice energy of ionic crystals which is responsible for the formation and stability of ionic crystal structure.

### Covalent character in ionic bonding

Ionic and Covalent bonds are the two extremes of bonding. Polar covalent is the intermediate type of bonding between the two extremes. Some ionic bonds contain covalent characteristics and some covalent bonds are partially ionic. For example, most Carbon-based compounds are covalently bonded but can also be partially ionic. Polarity is a measure of the separation of charge in a compound.

A compound's polarity is dependent on the symmetry of the compound as well as differences in electronegativity between atoms. Polarity occurs when the electron pushing elements, left side of the periodic table, exchanges electrons with the electron pulling elements, right side of the period table. This creates a spectrum of polarity, with ionic(polar) at one extreme, covalent(nonpolar) at another, and polar covalent in the middle.



Polarisation of electron cloud

Distinct electron clouds.
One for cation.
One for anion

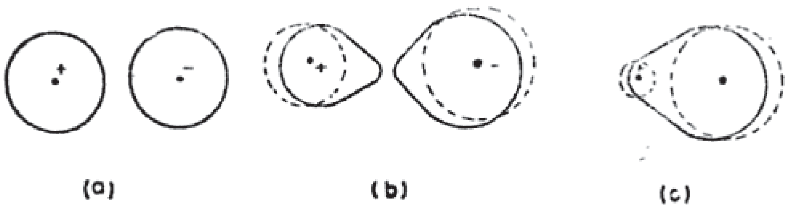
Attraction of the anion's
Shows overlapping

- $Al^{3+}$ is a small cation with a large charge – highly polarsing.
- $Cl^-$ is a large anion – highly polarisable.
- Distortion of the anion's electron cloud.

Both of these bonds are important in Organic Chemistry. Ionic bonds are important because they allow the synthesis of specific organic compounds. Scientists can manipulate ionic properties and these interactions in order to form products they desire. Covalent bonds are especially important since most carbon molecules interact primarily through covalent bonding. Covalent bonding allows molecules to share electrons with other molecules, creating long chains of compounds and allowing more complexity in life.

### 2.5 Fajan’s rules

**Fajan’s Rule:** The rules governing the transition from ionic to covalent bonding are called Fajan,s rules. They are based on the deformation of the interacting ions in the bond $A^+B^-$ (polarization of ions). When an anion approaches a cation,



Polarization effects. (a) Ideal ion pair without any polarization, (b) mutually polarized ion pair, (c) extreme polarization leading to covalent bond formation. Dashed circles represent 'ideal' ions.

Its electron cloud is not only attracted by the nucleus but also by the charge on the cation. This results in a net deformation of its electron cloud, called the polarization of the anion. Due to small cation size, the polarization of the cation is not significant. As a result of polarization, the bonded pair of the electrons is shared more by the bonded atoms than in the case of the ionic compounds, leading to a covalent bond.

**Effects of polarization:**

Effects of polarization depend upon the following factors.

1. **Higher charge:** The covalence of the bond increases with the increase in the cation charge. This can be seen from the melting points and the electrical conductivities of compounds with a common anion.

| *Ion* | *Ionic radius (pm)* | *Melting point (K)* |
|---|---|---|
| (a) *Increasing charge on the cation for the chlorides* | | |
| $Na^+$ | 97 | 1073 |
| $Mg^{2+}$ | 67 | 990 |
| $Al^{3+}$ | 50 | 453 |
| $Si^{4+}$ | 40 | 330 (b.p) |
| (b) *Increasing size of the cation for the fluorides* | | |
| $Na^+$ | 95 | 1268 |
| $K^+$ | 133 | 1130 |
| $Rb^+$ | 148 | 1048 |
| $Cs^+$ | 169 | 955 |
| (c) *Increasing size of the anions, sodium salts* | | |
| $F^-$ | 136 | 1268 |
| $Cl^-$ | 181 | 1073 |
| $Br^-$ | 195 | 1023 |
| $I^-$ | 216 | 924 |

2. **Small cationic radius:**The increasing charge density on smaller sized cations increases its polarizing power, and hence, its tendency to form covalence

3. **Large size of the anion:** The electron cloud on a bigger ion will be held less firmly by the nucleus and hence, the anion would be more easily polarizable. This may due to the shielding of the outer electrons by the inner shell electrons.

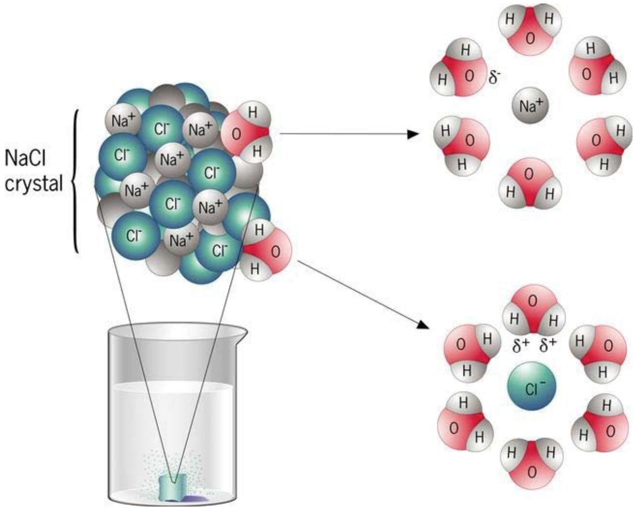
4. **Cations with 8-electron shells** have greater polarizing power than the 8- electrons shell ions with the same charge and size. This is due to the increased electronegativity of the 18-electron shell ions as the inner electrons have poor shielding effect of the nucleus (Na+ and Cu+ ions). Thus, many facts can be rationalized on the basis of the polarization of the anion by the cation.

   Some of these are:
   i) KI is soluble in alcohol (covalent) whereas KCl is insoluable.

**Solubility of the ionic Compounds:** Ionic or polar solutes dissolve more easily in polar solvents due to the predominant electrostatic attractions between the solute dipoles or ions and the solvent dipoles. Water is a good solvent due to its large dipole moment (1.84D), which in addition to the formation of diploe-dipole interactions, is able to dissociate polar covalent molecules like HCl, HBr, etc, into ions, by decreasing the coulombic attractions between the oppositely charged ions;

$$E_{cou} = \frac{Z_+ Z_- e^2}{4\pi\epsilon r}$$

Where ϵ is the dielectric constant of the medium and r is the inter ionic distance. For water it is 81.7



Many ionic compounds, however dissolve in solvents having low dielectric constants (dioxane, dinitrobenzene, ethers, alcohols, etc), but the solubility here is due to i) the partial covalent character of the compound and ii) Cordination of the solvent molecules through O atoms.

**Enthalpy Effect:** For a higher solubility, the enthalpy of solution per mole enthalpy change when one mole of the solute is dissolved in solvent to give a solution, which on dilution does not bring about any further enthalpy change) should be negative. From the process- -U + $\Delta Hsolv = \Delta Hsoln$ where , $\Delta Hsoln$ *is* the enthalpy of solution and $\Delta Hsolv$ is the enthalpy of salvation of the gaseous ions. It becomes more negative with increasing dielectric constant of the solvent. Hence, the solvents with higher dielectric constant are better media for dissolving ionic compounds.

**Size of the Ion:** *The solubility of the ionic compound increases with the size of the ion.* This is because of the greater decrease in the magnitude of the lattice energy than the decrease in the salvation energies of ions. Solubility increases in the following order. LiF < LiCl < LiBr < LiI LiF < NaF < KF < RbF < CsF. However, if one of the ions is very big, the solubility increases with decreasing size of the other ion. CsF > CsCl >CsBr > CsI (Very Big Cation) LiI > NaI > KI > CsI (Very Big Anion) $LiNO_3$> $NaNO_3$>$KNO_3$> $CsNO_3$(Very Big Anion).

**Charge on the Ion:** In general solubility increases with the increase in ionic charge. The order of the solubility is NaCl < $CaCl_2$< $YCl_3$< $ThCl_4$ $Na_2SO_4$< $MgSO_4$< $Al_2(SO_4)_3$.

$$\mathbf{NaCl < CaCl_2 < YCl_3 < ThCl_4}$$
$$\mathbf{Na_2SO_4 < MgSO_4 < Al_2(SO_4)_3}$$

**Effect of Temperature**

The van’t Hoff isochore

$$\frac{d\ln K}{dT} = \frac{\Delta H_{solv}}{RT^2}$$

Which indicates that the equilibrium constant K for the reaction,

$$M^+X^-_{(s)} \leftrightharpoons M^+_{(aq)} + X^-_{(aq)}$$

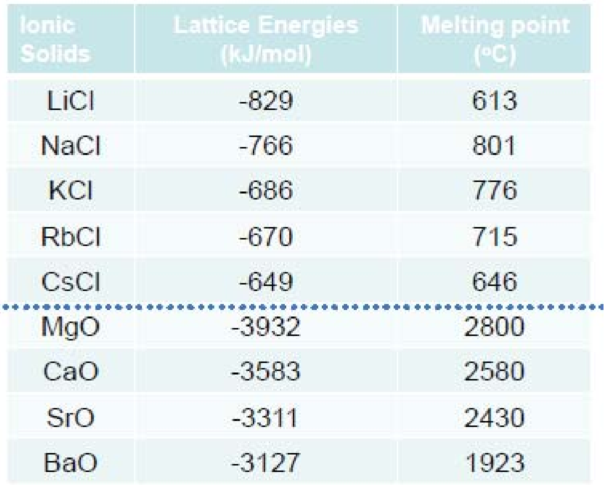
Will decrease with increase in temperature as $\Delta H_{soln}$ for most of the substances is negative. However, despite the fact that the heat is evolved when ionic solids generally dissolve, with a few exceptions, the solubility of solids increases with a rise in temperature. This is in contradiction to the above equation. The explanation for this is that heat of solution varies with temperature and the sign of,

$$(\Delta H_{soln})_{T_1} - (\Delta H_{soln})_{T_2}$$

becomes negative due to decreasing solvation of ions at higher temperature.

**Melting points**

Due to strong electronic cation-anion interactions, extending throughout the crystal lattice, ionic compounds have high melting and boiling points, high heat of fusion and vaporization. For example, in sodium chloride crystal, each sodium ion is surrounded by six sodium ions. This arrangement extends throughout the crystal lattice resulting in strong attraction forces throughout the crystal. The closer the ions are in a crystal, the stronger will be the attraction forces and the higher will be the melting points.



| Ionic Solids | Lattice Energies (kJ/mol) | Melting point (°C) |
|---|---|---|
| LiCl | -829 | 613 |
| NaCl | -766 | 801 |
| KCl | -686 | 776 |
| RbCl | -670 | 715 |
| CsCl | -649 | 646 |
| MgO | -3932 | 2800 |
| CaO | -3583 | 2580 |
| SrO | -3311 | 2430 |
| BaO | -3127 | 1923 |

Note that there is a ***positive correlation*** between the **melting point of an ionic compound**and the **strength of the ionic bonds** in the compound.
The stronger the ionic bond → the higher the melting point.

**Thermal stability of typical ionic compounds**

Due to most ionic compounds lattice energies being high, ions do not easily detach themselves from their crystal structure into a gaseous state. Ionic solids no not go from a solid state to as state at ordinary temperatures. They can although be melted by applying thermal energy enough to interrupt the crystalline lattice. Therefore, the higher the lattice energy is of an ionic compound, the higher the melting point is.

Energy that is needed to break apart an ionic crystal when it is dissolved comes from the interaction of ions in the crystal (solid) with the molecules of the solvent. The lattice energy of an ionic solid is what an ionic solid depends on to dissolve in a solvent. Therefore the lower the lattice energy, the higher the quantity an ionic solid that can be dissolved in any quantity of solvent.

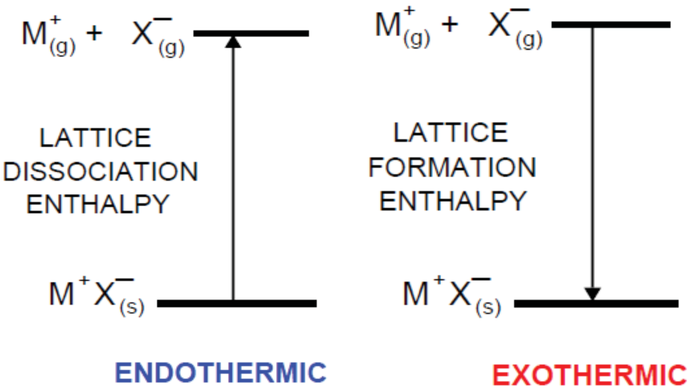
High temperatures are required to overcome the attraction between the positive and negative ions in ionic compounds. Therefore, a lot of energy is required to melt ionic compounds or cause them to boil. Just as ionic compounds have high melting and boiling points, they usually have enthalpies of fusion and vaporization that may be 10 to 100 times higher than those of most molecular compounds. The enthalpy of fusion is the heat required melt a single mole of a solid under constant pressure. The enthalpy of vaporization is the heat required for vaporize one mole of a liquid compound under constant pressure. Thus the thermal stability is depends upon the lattice energy in which the electrostatic force of attraction held the oppositely charged ions more strongly that it require higher temperature to break down the ionic bond which probably leads to higher melting and boiling point.

The thermal stability could be explained through lattice energy approach.

Lattice energy could be approached in two different ways, they are:

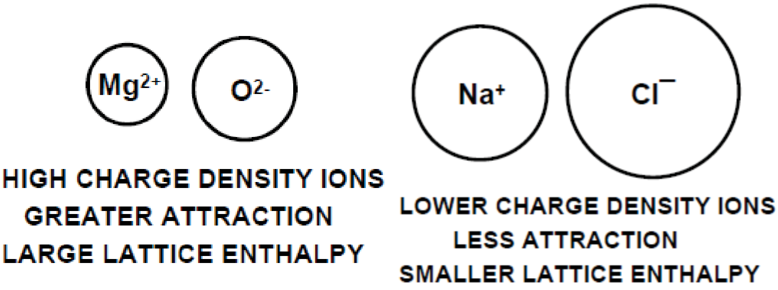
1. The enthalpy change when one mole of ion lattice dissociates into isolated gaseous atoms. In this case, there is strong electrostatic attraction between ions of opposite charge, so lot of energy is required to overcome the attraction.

$$Na^+Cl^-(g) \longrightarrow Na^+(g) + Cl^-(g)$$

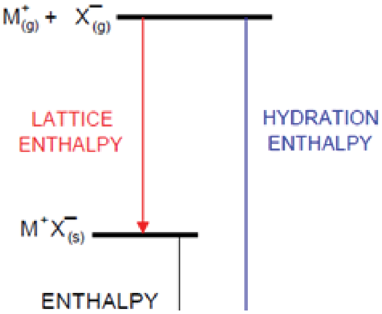


2. The enthalpy change when one mole of an ionic crystal lattice is formed from its isolated gaseous atoms. In this case, there is a strong electrostatic attraction between ions of opposite charge as lot of energy is released as the bond is formed.

$$Na^+(g) + Cl^-(g) \longrightarrow Na^+Cl^-(s)$$



## Thermal stability and solubility



If a pair of oppositely charged gaseous ions are placed together, they will attract each other. The energy change **lattice enthalpy** (LE) **is highly exothermic.**

If the ions were put in water, they would be attracted to polar water molecules. The resulting energy change **hydration enthalpy** (HE) **is highly exothermic.**

In both the above cases, the greater the charge density of the ions will lead to a more exothermic reaction.The missing stage of this cycle is known as **Enthalpy of Solution.**The size and the value of the enthalpy of solution depend on the relative values of the lattice enthalpy and the hydration enthalpy.

If **HE >> LE** then the salt will be probably soluble.

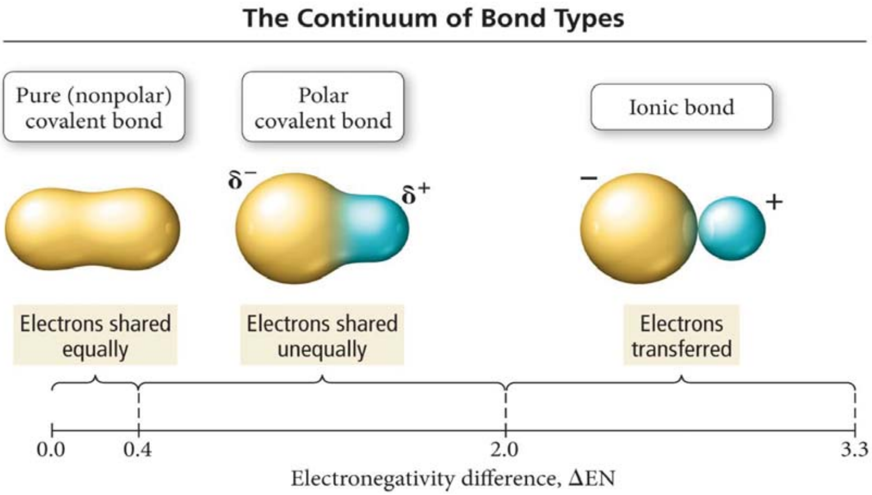
## Unit III: The Covalent Bond

### Syllabus

Lewis theory – the octet rule and its exception, electron dot structural formula; Sidgwick-Powelltheory-prediction of molecular shapes; Valance Bond theory-arrangement of electrons inmolecules, hybridization of atomic orbitals and geometry of molecules – VSEPR model-effect ofbonding and nonbonding electrons on the structure of molecules, effect of electronegativity,isoelectronic principle, illustration of structures by VESPR model–$NH_3$, $SF_4$, $ICl_4$, $ICl_2$,$XeF_4$, $XeF_6$– MO theory: LCAO method, criteria of orbital overlap, types of molecular orbitalss,p- and d – MOs; combination of atomic orbitals to give s- and p-MOs and their schematicillustration; qualitative MO energy level diagram of homoand heterodiatomic molecules – $H_2$ to$Ne_2$, CO, NO, HCl; bond order and stability of molecules.

## Introduction

As the details of the ionic bond have been discussed in the Unit II, the discussion of covalent bond could be started with a small comparison which is shown below.



## Defnition

It is the formation of a bond between two atoms of same or different element in which they share their electrons equally to make a covalent bond.

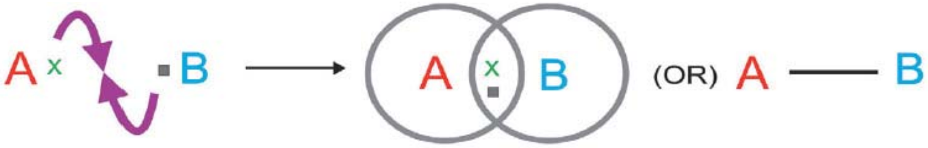
## 3.1 Lewis theory

When comparing with ionic compounds in which it tends to form between metals and non-metals when electrons are transferred from an element with low ionization energy (the metal) to one with a high electron affinity the (non-metal). When compounds form between elements with more similar properties, electrons are not transferred from one to another but instead are shared in order to give each atom a noble gas electron configuration.

It was Gilbert N. Lewis, an American chemist who first suggested that a chemical bond involves atoms sharing electrons, and this approach is known as the ***Lewis theory of bonding***.

### Formation of covalent bonds

According to G.N. Lewis, two atoms could achieve stable 2 or 8 electrons in the outer shell by sharing electrons between them. Atom A has 1 valence electron and atom B has 1 valence electron. As they approach each other, each atom contributes one electron and the resulting electron pair fills the outer shell of both the atoms.



Thus a shared pair of electrons contributes a covalent bond or electron pair bond. The compounds containing a covalent bond are covalent compounds.

**The octet rule and its exception**

Lewis pictured the atom in terms of a positively charged 'Kernel' (the nucleus plusthe innerelectrons) and the outer shell thatcould accommodate a maximum of eight electrons. He furtherassumed that theseeight electrons occupy the corners of a cube which surround the 'Kernel'. Thus the single outer shell electron of sodium would occupy one corner of the cube, while in the case of a noble gas all the eight corners would be occupied. This octet of electrons' represents a particularly stable electronic arrangement.

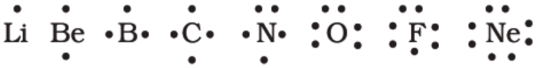
Kössel and Lewis in 1916 developed animportant theory of chemical combinationbetween atoms known as **electronic theory**of **chemical bonding**. According to this,atoms can combine either by transfer ofvalence electrons from one atom to another(gaining or losing) or by sharing of valenceelectrons in order to have an octet in theirvalence shells. This is known as **Octet Rule**.

**Lewis postulated that atoms achieve thestable octet when they are linked bychemical bonds.** In the case of sodium andchlorine, this can happen by the transfer ofan electron from sodium to chlorine therebygiving the Na+ and Cl. ions. In the case ofother molecules like $Cl_2$, $H_2$, $F_2$, etc., the bondis formed by the sharing of a pair of electronsbetween the atoms. In the process each atomattains a **stable outer octet of electrons**.

$$\begin{array}{lcl} \mathrm{Na} & \rightarrow & \mathrm{Na^+} + e^- \\ [\mathrm{Ne}]\,3s^1 & & [\mathrm{Ne}] \\ \mathrm{Cl} + e^- & \rightarrow & \mathrm{Cl^-} \\ [\mathrm{Ne}]\,3s^2\,3p^5 & & [\mathrm{Ne}]\,3s^2\,3p^6 \text{ or } [\mathrm{Ar}] \\ \mathrm{Na^+} + \mathrm{Cl^-} & \rightarrow & \mathrm{NaCl} \text{ or } \mathrm{Na^+Cl^-} \end{array}$$

**Lewis Symbols:**

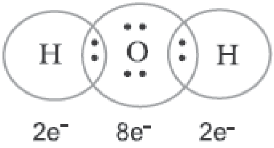
In the formation of amolecule, only the outer shell electrons takepart in chemical combination and they areknown as **valence electrons**. Lewis introducedsimple notations to represent valenceelectrons in an atom. These notations arecalled **Lewis symbols**. The inner shellelectrons are well protected and are generallynot involved in the combination process.For example, the Lewissymbols for the elements of second period areas under:



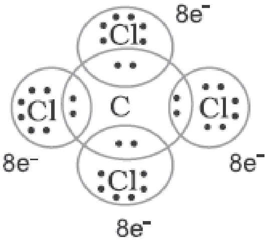
**Significance of Lewis Symbols:**Thenumber of dots around the symbol represents the number of valence electrons. This numberof valence electrons helps to calculate thecommon or **group valence** of the element. Thegroup valence of the elements is generallyeither equal to the number of dots in Lewissymbols or 8 minus the number of dots orvalence electrons.

The Lewis dot structures can be writtenfor other molecules also, in which thecombining atoms may be identical ordifferent. The important conditions being that:

- Each bond is formed as a result of sharing of an electron pair between the atoms.
- Each combining atom contributes at least one electron to the shared pair.
- The combining atoms attain the outershell noble gas configurations as a result of the sharing of electrons.
- Thus in water and carbon tetrachloride molecules, formation of covalent bonds can be represented as:



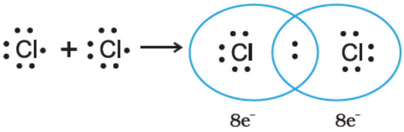
H atoms attain a duplet of electrons and O, the octet



Each of the four Cl atoms along with the C atom attains octet of electrons

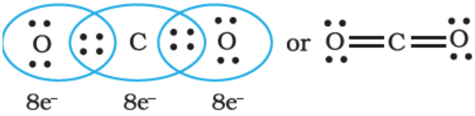
## Covalent bond

**Langmuir** (1919) refined the Lewispostulations by abandoning the idea of thestationary cubical arrangement of the octet,and by introducing the term **covalent bond**.The Lewis-Langmuir theory can beunderstood by considering the formation ofthe chlorine molecule,$Cl_2$. The Cl atom withelectronic configuration, [Ne]$3s^2$ $3p^5$, is oneelectron short of the argon configuration.The formation of the $Cl_2$ molecule can beunderstood in terms of the sharing of a pairof electrons between the two chlorine atoms,each chlorine atom contributing one electronto the shared pair. In the process both chlorine atoms attain the outer shell octet ofthe nearest noble gas (i.e., argon).

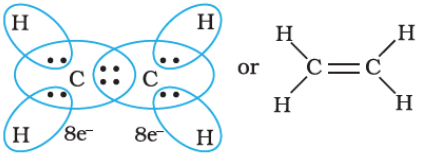


or Cl – Cl

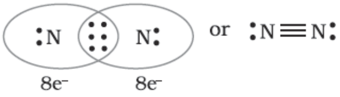
Covalent bond between two Cl atoms



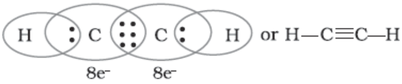
*Double bonds in $CO_2$ molecule*



*$C_2H_4$ molecule*



*$N_2$ molecule*



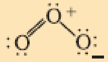
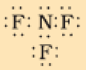
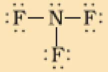
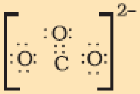
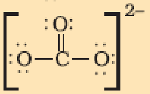
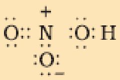
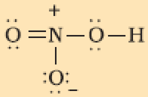
*$C_2H_2$ molecule*

Thus when two atoms share one electron pair they are said to be joined by a single covalent bond. In many compounds we have multiple bonds between atoms. The for mation of multiple bonds envisages sharing of more than one electr on pair between two atoms. If two atoms share two pairs of electrons, the covalent bond between them is called a double bond. For example, in the carbon dioxide molecule, we have two double bonds between the carbon and oxygen atoms. Similarly in ethane molecule the two carbon atoms are joined by a double bond.

### Lewis representation of simple molecules

The Lewis dot structures provide a pictureof bonding in molecules and ions in termsof the shared pairs of electrons and theoctet rule.

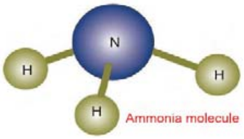
**Table 3.1 Picture of bonding in molecules**

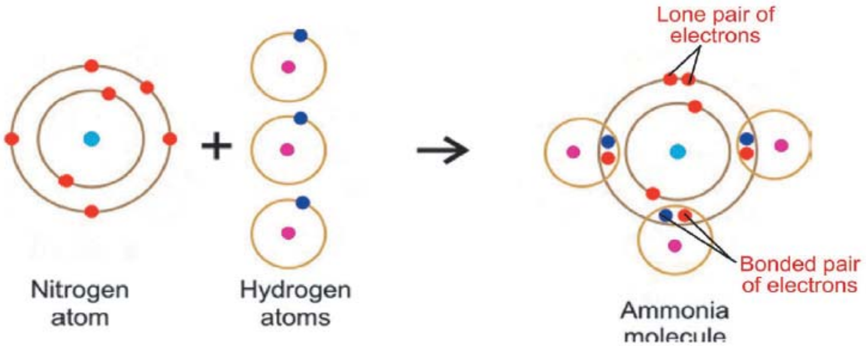
| Molecule/Ion | | Lewis Representation |
|---|---|---|
| $H_2$ | $H : H^*$ | $H - H$ |
| $O_2$ | $:\ddot{O}::\ddot{O}:$ | $:\ddot{O}=\ddot{O}:$ |
| $O_3$ |  |  |
| $NF_3$ |  |  |
| $CO_3^{2-}$ |  |  |
| $HNO_3$ |  |  |

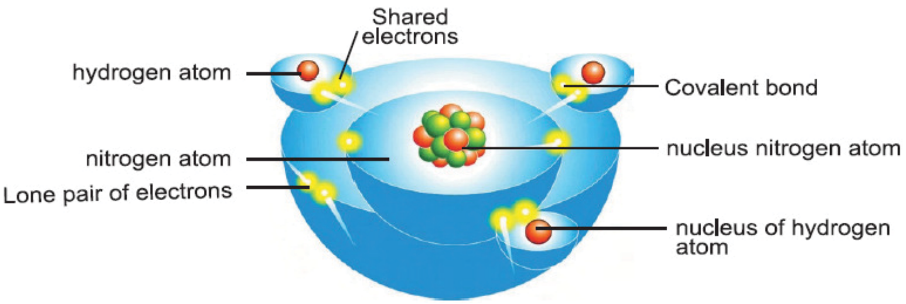
** Each H atom attains the configuration of helium (a duplet of electrons)*

### Formation of ammonia molecule

Nitrogen atom has five (2,5) valence electrons. Hydrogen atom has one valence electron. Nitrogen atom shares three electrons one each with the three hydrogen atoms.







**Exceptions to octet rule**

It is true that quite a few molecules had non-octet structure. Atoms in these molecules could have a number of electrons in the valence orbit in short of the octer or in excess of the octet.

a) Four electrons around central atom

Berylliumdichloride ($BeCl_2$)

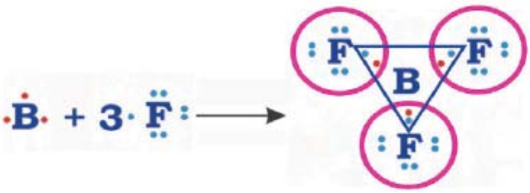
| | Beryllium | Chlorine |
|---|---|---|
| Atomic number | 4 | 17 |
| Electron distribution | 2,2 | 2,8,7 |
| Valence electrons | 2 | 7 |

Each chlorine atom is surrounded by **8** electrons, but beryllium is surrounded only by 4 electrons.

b) Six electrons around the central atom

Borontrifluoride ($BF_3$)

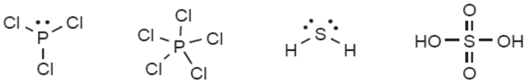
| | Boron | Fluorine |
|---|---|---|
| Atomic number | 5 | 9 |
| Electron distribution | 2,3 | 2,7 |
| Valence electrons | 3 | 7 |



Each fluorine atom is surrounded by **8** electrons but boron atom has only **6** electrons.

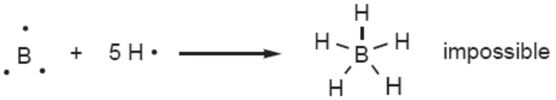
Few other examples are:

The maximum number of electrons possible in the valence shell of the second row elements is eight. However,the elements of the **third row**, such as **phosphorus** and **sulfur**, can form stable systems by sharing eight or more electrons. The presence of ***d*-orbitals**, which can accommodate up to ten electrons, makes this possible.

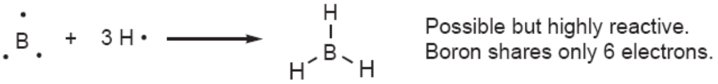


Some stable compounds of phosphorus and sulfur

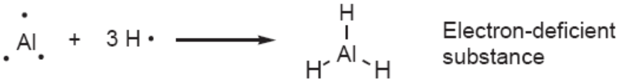
Now, back to the second row, what happens when the first nonmetal, boron (*Z*=3), combines with hydrogen?By repeating the process outlined before for carbon, nitrogen, oxygen, and fluorine, we conclude that boron.needs to bond to 5 hydrogen atoms to fulfill the octet rule. The problem is that with only three electrons inthe valence shell this is impossible:



The only possibility for boron is to bond to three hydrogen atoms, in which case it forms a compound(borane, BH3) that does not fulfill the octet rule. The compound actually exists, but it is highly reactive, thatis to say, unstable. Substances such as BH3 are referred to as electron-deficient molecules, and are veryreactive towards electron-rich substances.



Aluminum, which is also in group III, exhibits similar behaviour.



### 3.2 Sidgwick- Powell theory

**Sidgwick &Powell** in **1940** formulated a theory based on the repulsions between electron pairs, known as **Valence shell electron pair repulsion theory**. The various postulates of this theory are as follows;

- The unpaired electrons in the valence shell of central atom form bond pairs with surrounding atoms while paired electrons remain as lone pairs.
- The electron pairs surrounding the central atom repel each other. Consequently, they stay as far apart as possible in space to attain stability.
- The geometry and shape of the molecule depends upon the number of electron pairs (bond pair as well as lone pair) around the central atom. The geometrical arrangement of electron pairs with different number of electron pairs around central atom is shown in the table.
- The force of repulsion is minimum when the electron pairs are far away from one another.

- The force of repulsion among the bond pairs and the lone pairs is not same. The order of force of repulsion is as follows;

$$lp–lp > lp–bp > bp–bp$$

- A molecule has Regular geometry if it has no lone pair around it, but if it has lone pairs over it, the molecule has Irregular geometry.

Thus the shape of the molecule will tend to achieve maximum separation of bonds and lone pairs, taking into consideration the relative strengths of the repulsive forces. These are summarised as decreasing in the order:

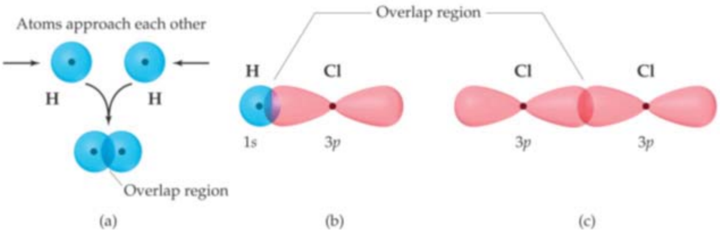
Lone pair > Multiple Bond > Single Bond

### 3.3 Valance Bond theory

Valence bond theory was introduced by Heitler and London (1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on the atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition. To start with, let us consider the formation of hydrogen molecule which is the simplest of all molecules.

Valence bond (VB) theory assumes that all bonds are localized bonds formed between two atoms by the donation of an electron from each atom. This is actually an invalid assumption because many atoms bond using delocalized electrons. Valence Bond theory describes covalent bond formation as well as the electronic structure of molecules. The theory assumes that electrons occupy atomic orbitals of individual atoms within a molecule, and that the electrons of one atom are attracted to the nucleus of another atom. This attraction increases as the atoms approach one another until the atoms reach a minimum distance where the electron density begins to cause repulsion between the two atoms. This electron density at the minimum distance between the two atoms is where the lowest potential energy is acquired, and it can be considered to be what holds the two atoms together in a chemical bond.

When a covalent bond is formed, there is shared electron density between the nuclei of thebonded atoms.The simultaneous attraction of the shared electron density for both nuclei holds the atoms together, forming a covalent bond.In valence bond theory, the shared electron density is described as occurring when a valence orbital from one atom overlaps with a valence orbital from another atom.Two electrons with opposite spin are shared in the overlap region, forming a covalent bond. **The greater the extent of orbital overlap, the stronger the bond.**



**Formation of sigma (σ) bonds in $H_2$, HCl and $Cl_2$**

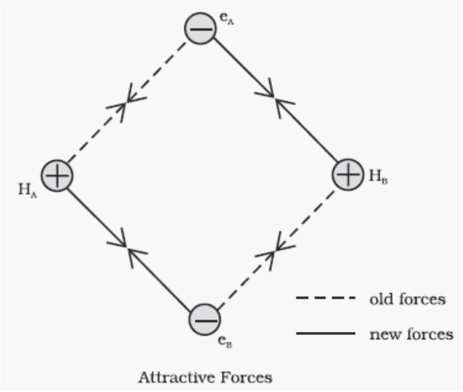
Consider two hydrogen atoms A and Bapproaching each other having nuclei NA andNB and electrons present in them arerepresented by eA and eB. When the two atomsare at large distance from each other, there isno interaction between them. As these twoatoms approach each other, new attractive andrepulsive forces begin to operate.Attractive forces arise between:

(i) nucleus of one atom and its own electronthat is $N_A - e_A$ and $N_B - e_B$.
(ii) nucleus of one atom and electron of otheratom i.e., $N_A - e_B$, $N_B - e_A$.

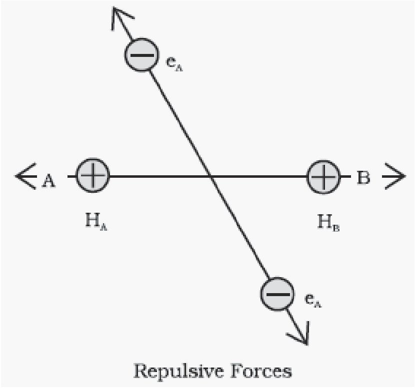
Similarly repulsive forces arise between

(i) electrons of two atoms like $e_A - e_B$,
(ii) nuclei of two atoms $N_A - N_B$.

Attractive forces tend to bring the twoatoms close to each other whereas repulsiveforces tend to push them apart.

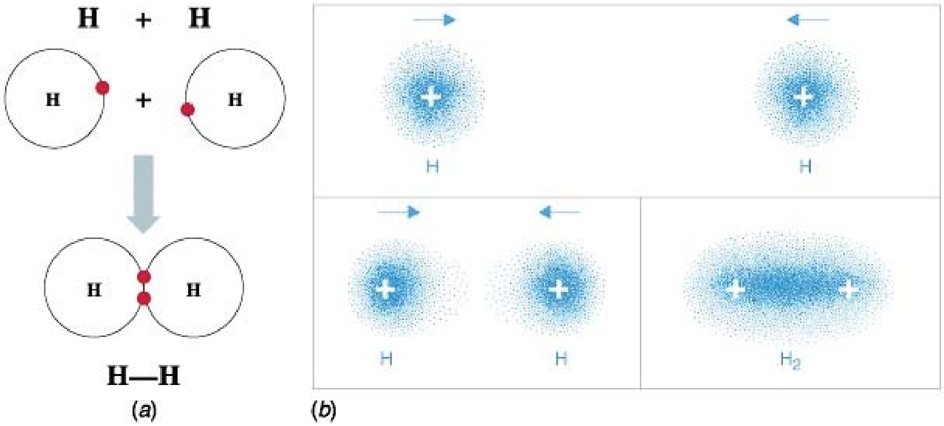


Attractive Forces



Repulsive Forces

**Orbital Overlap Concept**



(a) (b)

In the formation of hydrogen molecule, thereis a minimum energy state when two hydrogenatoms are so near that their atomic orbitalsundergo partial interpenetration. This partialmerging of atomic orbitals is called overlappingof atomic orbitals which results in the pairingof electrons. The extent of overlap decides thestrength of a covalent bond. In general, greaterthe overlap the stronger is the bond formedbetween two atoms. Therefore, according toorbital overlap concept, the formation of acovalent bond between two atoms results bypairing of electrons present in the valence shellhaving opposite spins.

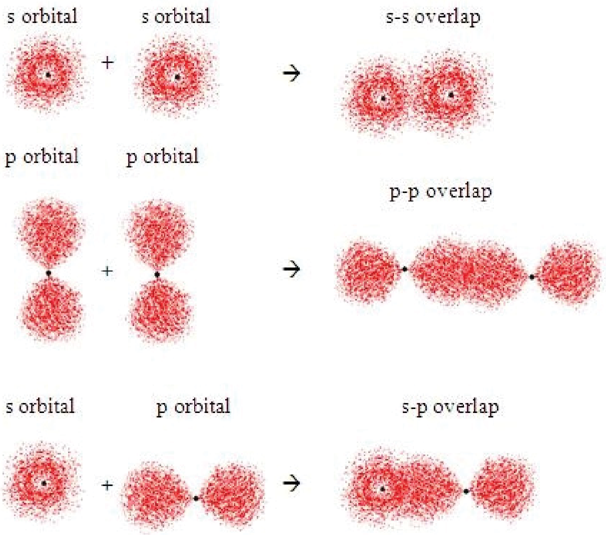
**Types of bonds**

**Sigma bond:**This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the inter-nuclear axis. This is called as head on overlap or axial overlap. This can be formed byany one of the following types of combinations of atomic orbitals.

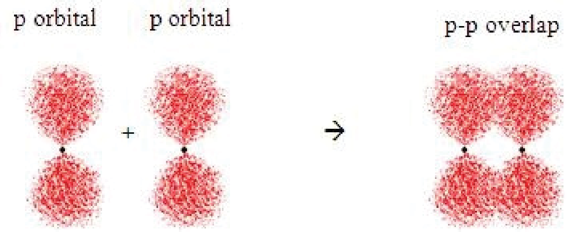
***s-s* overlapping**: In this case, there is overlap of two half-filled *s*-orbitals along the inter-nuclear axis

***s-p* overlapping**: This type of overlap occurs between half-filled *s*-orbitals of one atom and half-filled *p*-orbitals of another atom.

***p-p* overlapping**: This type of overlap takes place between the half-filled *p* orbitals of approaching atoms.



**Pi bond:** A covalent bond resulting from the formation of a molecular orbital by side-to-side overlap of atomic orbitals along a plane perpendicular to a line connecting the nuclei of the atoms, denoted by the symbol $\pi$. Sideways overlap of the formation of $\pi$ bond is shown below:



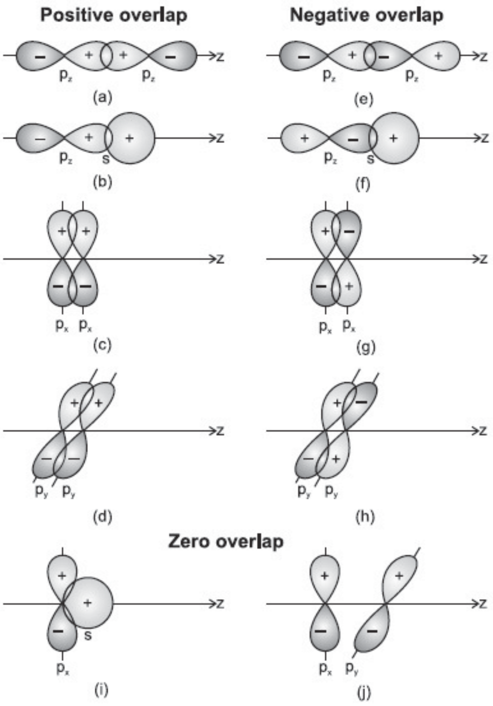
It is important to note that different sources use different terms to define what a sigma and pi bond is. However, once examined carefully, it will be evident that they all try to explain the same thing.

**Strength of Sigma and Pi bonds**

Basically the strength of a bond depends uponthe extent of overlapping. In case of sigma bond,the overlapping of orbitals takes place to alarger extent. Hence, it is stronger as comparedto the pi bond where the extent of overlappingoccurs to a smaller extent. Further, it isimportant to note that in the formation ofmultiple bonds between two atoms of amolecule, pi bond(s) is formed in addition to asigma bond.

**Overlapping of atomic orbitals**

When orbitals of two atoms come close to formbond, their overlap may be positive, negativeor zero depending upon the sign (phase) anddirection of orientation of amplitude of orbitalwave function in space (Figure). Positive andnegative sign on boundary surface diagramsin the figure show the sign (phase) of orbitalwave function and are not related to charge.Orbitals forming bond should have same sign(phase) and orientation in space. This is calledpositive overlap. Various overlaps of *s* and *p*orbitals are depicted in Fig. 4.9.The criterion of overlap, as the main factorfor the formation of covalent bonds appliesuniformly to the homonuclear/heteronucleardiatomic molecules and polyatomic molecules.



We know that the shapes of $CH_4$, $NH_3$, and $H_2O$molecules are tetrahedral, pyramidal and bentrespectively. It would be therefore interestingto use VB theory to find out if these geometricalshapes can be explained in terms of the orbitaloverlaps.

Let us first consider the $CH_4$ (methane)molecule. The electronic configuration ofcarbon in its ground state is $[He]2s^22p^2$ whichin the excited state becomes $[He]\ 2s^12p_x{}^12p_y{}^12p_z{}^1$. The energy required for this excitation iscompensated by the release of energy due tooverlap between the orbitals of carbon and thehydrogen.The four atomic orbitals of carbon,each with an unpaired electron can overlapwith the 1*s* orbitals of the four H atoms whichare also singly occupied. This will result in theformation of four C-H bonds. It will, however,be observed that while the three p orbitals ofcarbon are at 90° to one another, the HCHangle for these will also be 90°. That is threeC-H bonds will be oriented at 90° to oneanother. The 2*s* orbital of carbon and the 1*s*orbital of H are spherically symmetrical andthey can overlap in any direction. Thereforethe direction of the fourth C-H bond cannotbe ascertained. This description does not fitin with the tetrahedral HCH angles of 109.5°.Clearly, it follows that simple atomic orbitaloverlap does not account for the directionalcharacteristics of bonds in $CH_4$. Using similarprocedure and arguments, it can be seen that in the case of $NH_3$ and $H_2O$ molecules, the HNH andHOH angles should be 90°. This is indisagreement with the actual bond angles of107° and 104.5° in the $NH_3$ and $H_2O$ molecules respectively.

## Hybridization

In order to explain the characteristic geometrical shapes of polyatomic molecules like $CH_4$, $NH_3$ and $H_2O$ etc., Pauling introduced the concept of hybridisation. According to him the atomic orbitals combine to form new set of equivalent orbitals known as hybrid orbitals. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as hybridisation which can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. For example when one 2*s* and three 2*p*-orbitals of carbon hybridize, there is the formation of four new $sp^3$ hybrid orbitals.

Central atoms *do not use* atomic (s, p, d, f) orbitals to form sigma bonds.Central atoms mix or hybridize their valence atomic orbitals to form new bonding orbitals called hybrid orbitals.Orbital hybridization is simply the mathematical combination of two or more atomic orbitals(s, p, or d) to form new hybrid orbitals that are used for bonding.

## Salient features of hybridisation:

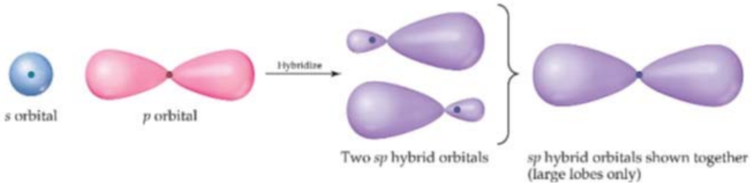
The mainfeatures of hybridisation are as under:

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridized.
2. The hybridized orbitals are always equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

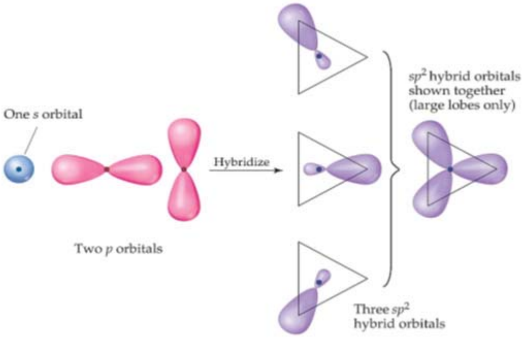
## Types of hybridization

How can we use valence bond theory to adequately describe the bonding for polyatomic molecules or ions having electron-domain geometries such as linear, trigonal planar, tetrahedral, trigonal bipyramid oroctahedral? Overlap of atomic s, p and d orbitals will not yield structures with these geometries (exceptlinear)! To explain bonding for these geometries, valence bond theory uses the concept of **orbitalhybridization**.

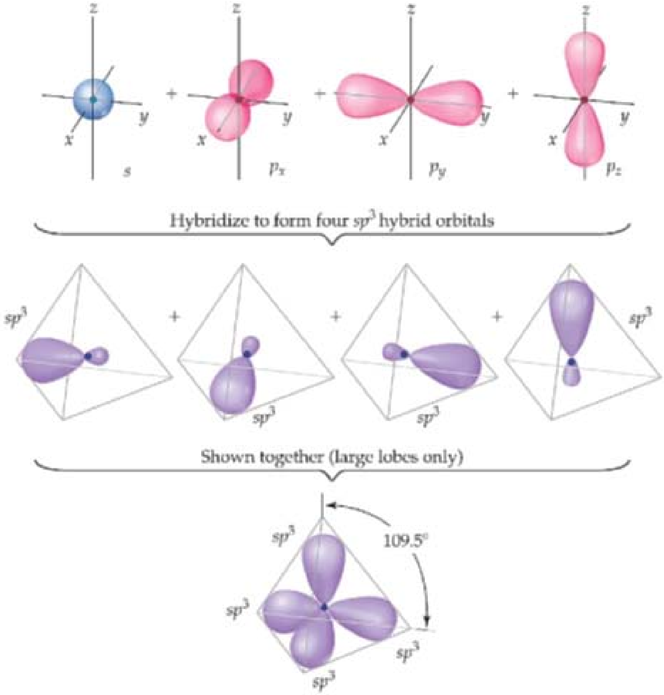
## SP hybridization



## SP$^2$ hybridization

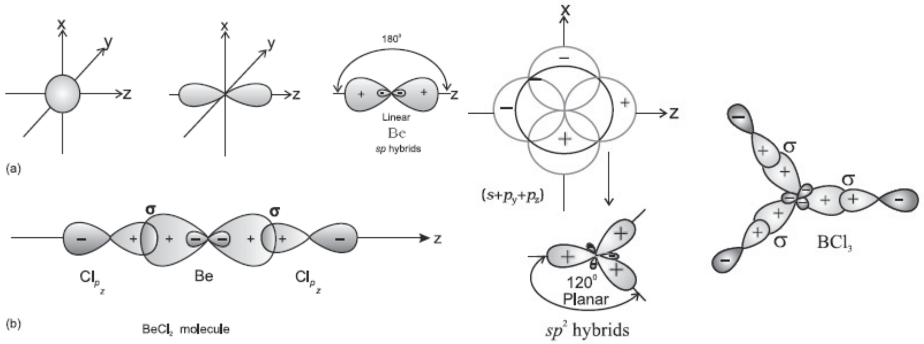


## SP$^3$ hybridization



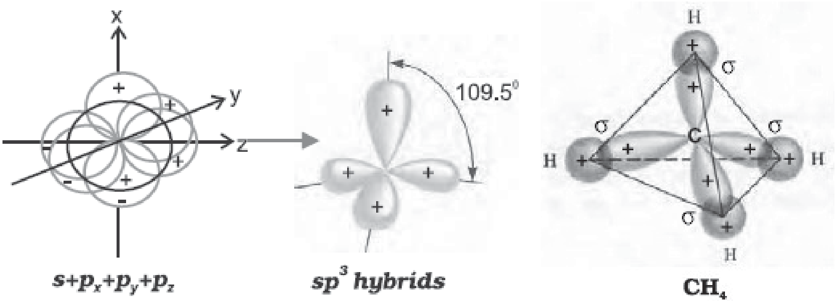
## Geometry of molecules

**$BeCl_2$**: The ground state electronicconfiguration of Be is $1s^2 2s^2$. In the exited stateone of the $2s$-electrons is promoted tovacant $2p$ orbital to account for its bivalency.One $2s$ and one $2p$-orbital gets hybridized toform two *sp* hybridized orbitals. These two*sp* hybrid orbitals are oriented in oppositedirection forming an angle of 180°. Each ofthe *sp* hybridized orbital overlaps with the$2p$-orbital of chlorine axially and form two Be-Cl sigma bonds. This is shown in the figure below.



In **$BCl_3$**molecule, the ground state electronicconfiguration of central boron atom is$1s^2 2s^2 2p^1$. In the excited state, one of the $2s$electrons is promoted to vacant $2p$ orbital as a result boron has three unpaired electrons.These three orbitals (one $2s$ and two $2p$)hybridize to form three *sp*2 hybrid orbitals. Thethree hybrid orbitals so formed are oriented ina trigonal planar arrangement and overlap with$2p$ orbitals of chlorine to form three B-Clbonds. Therefore, in $BCl_3$ (shown in the above figure), thegeometry is trigonal planar with ClBCl bondangle of 120°.

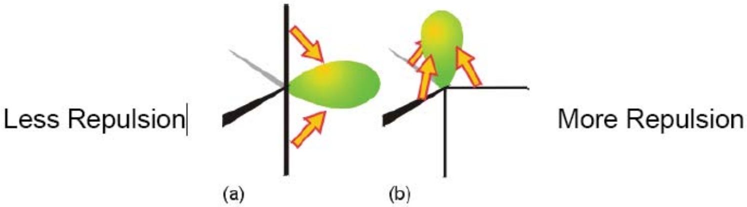
In **$CH_4$** molecule in which there ismixing of one *s*-orbital and three *p*-orbitals ofthe valence shell to form four $sp^3$ hybrid orbitalof equivalent energies and shape. There is 25%*s*-character and 75% *p*-character in each $sp^3$hybrid orbital. The four $sp^3$ hybrid orbitals soformed are directed towards the four cornersof the tetrahedron. The angle between $sp^3$hybrid orbitals is 109.5° as shown in figure.



**3.4 VSEPR** (Valence Shell Electron Pair Repulsion) **model**

VSEPR theory or model provides a simple procedure to predict the shapes of covalent molecules. Sidgwickand Powell in 1940, proposed a simple theorybased on the repulsive interactions of theelectron pairs in the valence shell of the atoms.It was further developed and redefined byNyholm and Gillespie (1957).

It is based on the number of regions of high electron density around a central atom. It can be used to predict structures of molecules or ions that contain only non-metals by minimizing the electrostatic repulsion between the regions of high electron density. It can also be used to predict structures of molecules or ions that contain multiple bonds or unpaired electrons.



The main postulates of VSEPR theory areas follows:

1. The shape of a molecule depends uponthe number of valence shell electron pairs(bonded or nonbonded) around the centralatom.
2. Pairs of electrons in the valence shell repelone another since their electron clouds arenegatively charged.
3. These pairs of electrons tend to occupysuch positions in space that minimize repulsion and thus maximize distancebetween them.
4. The valence shell is taken as a sphere withthe electron pairs localising on thespherical surface at maximum distancefrom one another.
5. A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
6. When two or more resonance structure applied to a molecule, the VSEPR model is applicable to any structure.

**The repulsive interaction of electron pairs decrease in the order:**

Lone pair (lp) – Lone pair (lp) >
Lone pair (lp) – Bond pair (bp) >
Bond pair (bp) – Bond pair (bp)

For the prediction of geometrical shapes of molecules with the help of VSEPR theory, it is convenient to divide molecules into two categories as **(i) molecules in which the central atom has no lone pair and (ii) molecules in which the central atom has one or more lone pairs.**

*The main postulate of this model is that the structure around a given atom is determined principally by minimizing electron-pair repulsions. The bonding the nonbonding pairs around a given atom should be positioned as far apart as possible.*

The following table **3.2** shows the arrangement of electron pairs about a centralatom A (without any lone pairs) andgeometries of some molecules/ions of the typeAB. Subsequent table shows shapes ofsome simple molecules and ions in which thecentral atom has one or more lone pairs. The third table4.8 explains the reasons for thedistortions in the geometry of the molecule.

**Table 3.2 Arrangement of electron pairs about a central atom**

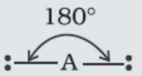
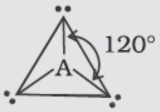
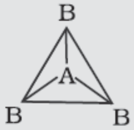
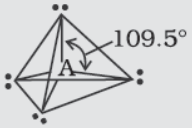
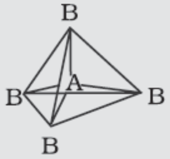
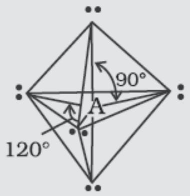
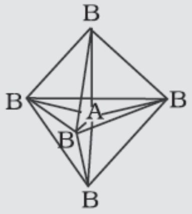
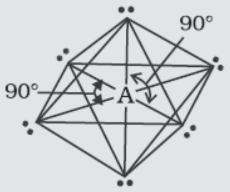
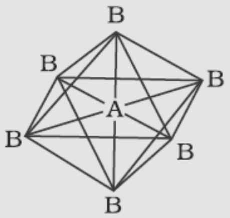
| Number of electron pairs | Arrangement of electron pairs | Molecular geometry | Examples |
|---|---|---|---|
| 2 |  Linear | B—A—B<br>Linear | $BeCl_2$, $HgCl_2$ |
| 3 |  Trigonal planar |  Trigonal planar | $BF_3$ |
| 4 |  Tetrahedral |  Tetrahedral | $CH_4, NH_4^+$ |
| 5 |  Trigonal bipyramidal |  Trigonal bipyramidal | $PCl_5$ |
| 6 |  Octahedral |  Octahedral | $SF_6$ |

**Table 3.3 Shapes of molecules having lone pair of electrons**

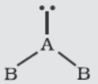
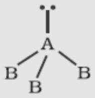
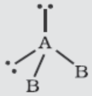
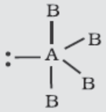
| Molecule type | No. of bonding pairs | No. of lone pairs | Arrangement of electron pairs | Shape | Examples |
|---|---|---|---|---|---|
| $AB_2E$ | 2 | 1 | <br>Trigonal planar | Bent | $SO_2$, $O_3$ |
| $AB_3E$ | 3 | 1 | <br>Tetrahedral | Trogonal pyramidal | $NH_3$ |
| $AB_2E_2$ | 2 | 2 | <br>Tetrahedral | Bent | $H_2O$ |
| $AB_4E$ | 4 | 1 | <br>Trigonal bi-pyramidal | See saw | $SF_4$ |
| $AB_3E_2$ | 3 | 2 | <br>Trigonal bi-pyramidal | T-shape | $ClF_3$ |
| $AB_5E$ | 5 | 1 | <br>Octahedral | Square pyramid | $BrF_5$ |
| $AB_4E_2$ | 4 | 2 | <br>Octahedral | Square planar | $XeF_4$ |

Table 3.4 Shapes of molecules containing bonding pairs and lone pairs with reason for Shapes acquired

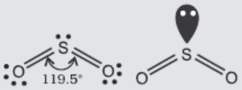
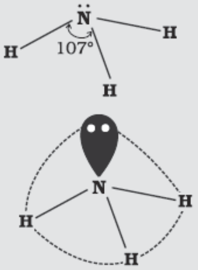
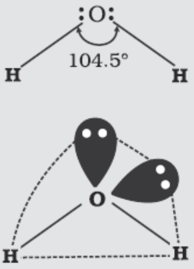
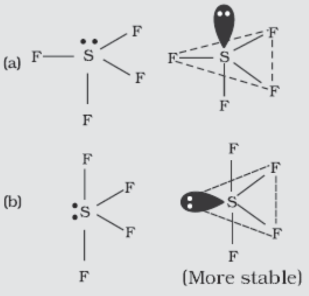
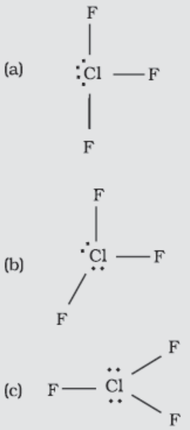
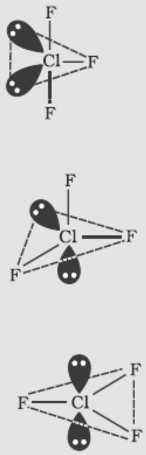
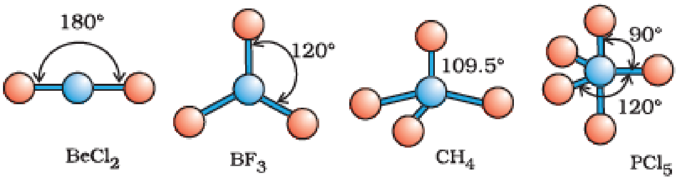
| Molecule type | No. of bonding pairs | No. of lone pairs | Arrangement of electrons | Shape | Reason for the shape acquired |
|---|---|---|---|---|---|
| $AB_2E$ | 4 | 1 |  | Bent | Theoretically the shape should have been triangular planar but actually it is found to be bent or v-shaped. The reason being the lone pair-bond pair repulsion is much more as compared to the bond pair-bond pair repulsion. So the angle is reduced to 119.5 from 120 . |
| $AB_3E$ | 3 | 1 |  | Trigonal pyramidal | Had there been a bp in place of lp the shape would have been tetrahedral but one lone pair is present and due to the repulsion between lp-bp (which is more than bp-bp repulsion) the angle between bond pairs is reduced to 107 from 109.5 . |
| $AB_2E_2$ | 2 | 2 |  | Bent | The shape should have been tetrahedral if there were all bp but two lp are present so the shape is distorted tetrahedral or angular. The reason is lp-lp repulsion is more than lp-bp repulsion which is more than bp-bp repulsion. Thus, the angle is reduced to 104.5 from 109.5 . |
| $AB_4E$ | 4 | 1 |  | See-saw | In (a) the lp is present at axial position so there are three lp—bp repulsions at 90 . In(b) the lp is in an equatorial position, and there are two lp—bp repulsions. Hence, arrangement (b) is more stable. The shape shown in (b) is described as a distorted tetrahedron, a folded square or a see-saw. |

**Table 3.4 Shapes of molecules containing bonding pairs and lone pairs with reason for Shapes acquired** (contd.)

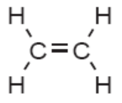
| Molecule type | No. of bonding pairs | No. of lone pairs | Arrangement of electrons | Shape | Reason for the shape acquired |
|---|---|---|---|---|---|
| $AB_3E_2$ | 3 | 2 |  | T-shape  | In (a) the lp are at equatorial position so there are less lp-bp repulsions as compared to others in which the lp are at axial positions. So structure (a) is most stable. (T-shaped). |

As depicted in the above tables, thecompounds of $AB_2$, $AB_3$, $AB_4$, $AB_5$ and $AB_6$,the arrangement of electron pairs and the Batoms around the central atom A are : linear,trigonal planar, tetrahedral, trigonalbipyramidaland octahedral, respectively.Such arrangement can be seen in themolecules like $BF_3$ ($AB_3$), $CH_4$ ($AB_4$) and $PCl_5$($AB_5$) as depicted below by their ball and stick models.



**Effect of bonding and nonbonding electrons on the structure of molecules**

In the ethane Lewis formula shown above all bonds are represented as single lines called **single bonds**. **Eachsingle bond is made up of two electrons, called bonding electrons**. It is also possible for two atoms bonded together to share 4 electrons. This bonding pattern is represented by two lines, each representing two electrons, and is called a **double bond**. The ethylene molecule shown below is an example. Finally, sharing of 6 electrons between two atoms is also possible. In such case, the representation uses three single lines, anarrangement called a **triple bond**. The acetylene molecule provides an example of a triple bond.



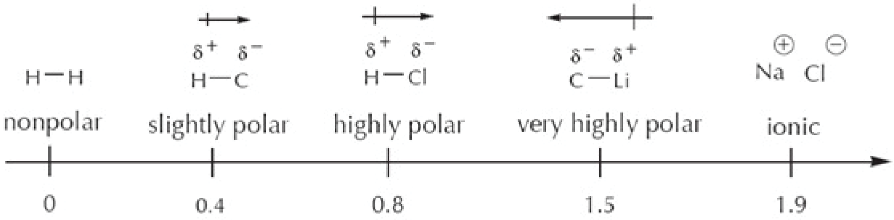
The double bond in ethylene

The triple bond in acetylene

This terminology (single, double, or triple bond) is very loose and informal. The formulas shown above donot do justice to the actual nature of the bonds. All they do is show how many electrons are being sharedbetween the two atoms (2, 4, or 6) but they say nothing about the electronic distribution, or the relativeenergies of the bonds, or the types of orbitals involved. They are, however, very useful in many situations.

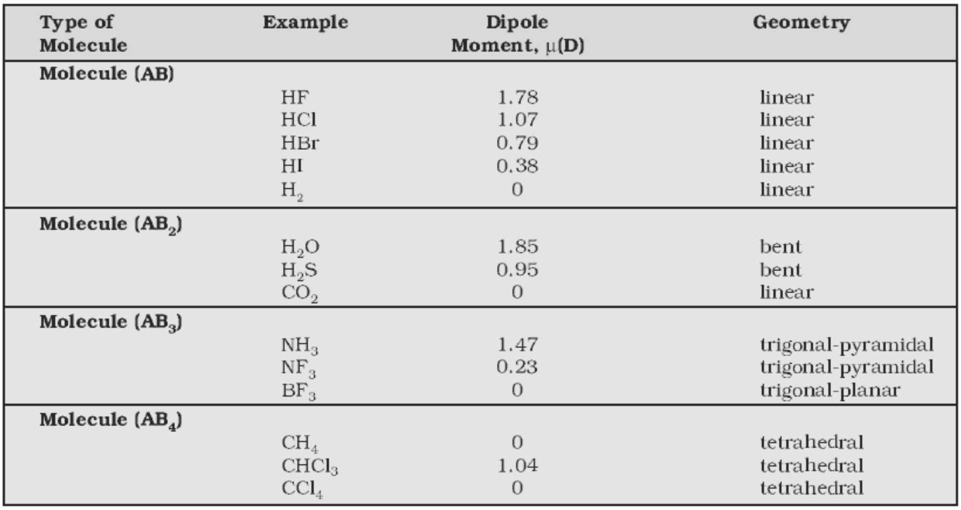
**Effect of electronegavity**

Since the difference in electronegativity between two bonding atoms can be zero or very large, there is a **polarity continuum**, ranging from nonpolar to highly polar bonds. In an extreme case where the difference in electronegativity is very large, the bond ceases to be covalent and becomes ionic.



Bond polarity is measured by the **dipole moment**. This parameter is reported in *Debye* units (D). For example,the dipole moment for the C-H bond is 0.3 D, whereas that for the H-Cl bond is 1.09 D. Dipole moment of selected molecules is provided in Table 3.5.

**Table 3.5 Dipole moment of selected molecules**

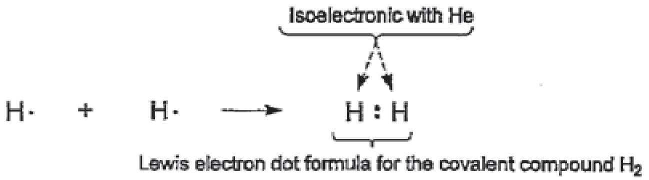


| Type of Molecule | Example | Dipole Moment, μ(D) | Geometry |
|---|---|---|---|
| **Molecule (AB)** | | | |
| | HF | 1.78 | linear |
| | HCl | 1.07 | linear |
| | HBr | 0.79 | linear |
| | HI | 0.38 | linear |
| | $H_2$ | 0 | linear |
| **Molecule ($AB_2$)** | | | |
| | $H_2O$ | 1.85 | bent |
| | $H_2S$ | 0.95 | bent |
| | $CO_2$ | 0 | linear |
| **Molecule ($AB_3$)** | | | |
| | $NH_3$ | 1.47 | trigonal-pyramidal |
| | $NF_3$ | 0.23 | trigonal-pyramidal |
| | $BF_3$ | 0 | trigonal-planar |
| **Molecule ($AB_4$)** | | | |
| | $CH_4$ | 0 | tetrahedral |
| | $CHCl_3$ | 1.04 | tetrahedral |
| | $CCl_4$ | 0 | tetrahedral |

**Isoelectronic Principle**

**Isoelectronic:** same number of electrons same electron configuration.

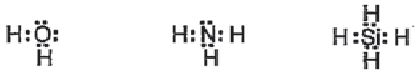
It is the tendency of an element to attain the nearest octet state of Noble gas configuration by gaining or losing of electrons.



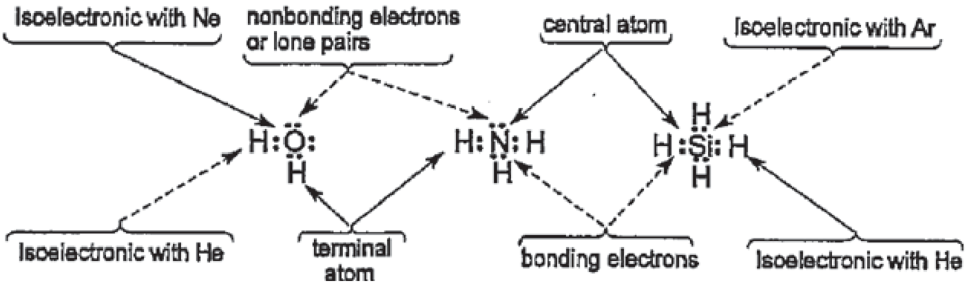
As shown above, hydrogen molecule is isoelectronic with He. Hydrogen molecule is formed by covalent bond. The covalency of an atom is the number of covalent bonds formed by the atom.

| Element | Common Covalency |
|---|---|
| H | 1 |
| F, Cl, Br, I | 1 |
| O, S, Se | 2 |
| N, P, As | 3 |
| C, Si, Ge | 4 |

Lewis dot structure of H2O, NH3 and SiH4 are shown below with their isoelectronic nature.



Each atom in the above formulas satisfies the octet rule. Shared electron pairs (bonding electrons) are considered to belong to both atoms and are counted in the determination of the number of valence electrons around each atom sharing the pair of electrons.



The sum of bonding and nonbonding electrons in a Lewis electron dot formula is equal to the sum of the valence electrons for each atom in the formula. The calculation of valence electron in $H_2O$ is shown below:

*Total number of bonding electrons*

+

$$\textit{Total number of nonbonding electrons}$$
$$= \textit{Total number of valence electrons}$$

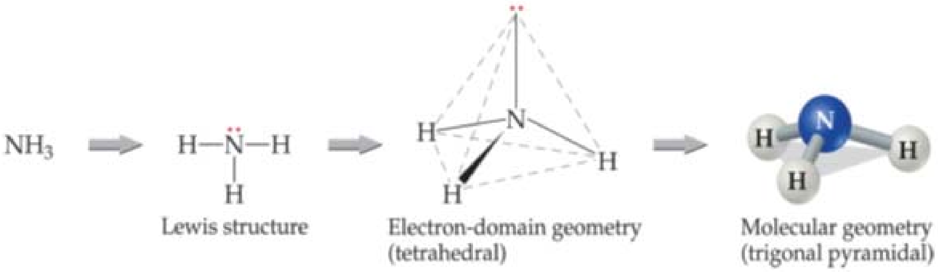
For $H_2O$,

$$4_{bonding\ electrons} + 4_{nonbonding\ electrons} = 6_O + 2(1_H) = 8$$

A central atom is any atom bonded to two or more other atoms. A terminal atom is any atom bonded to one and only other atom.

**Illustration of structures by VESPR model – $NH_3$, $SF_4$, $ICl_4$, $ICl_2$, $XeF_4$, $XeF_6$**

### VSEPR Model for $NH_3$

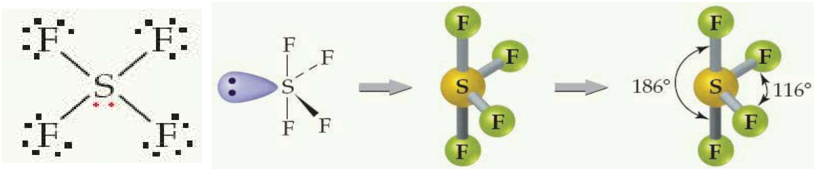


Above we have pictured only molecules whose central atoms have attained their maximum number of covalent bondswith other atoms. Remember that unbonded pairs of electrons also constitute regions of electrondensity and occupy a position in the predicted geometry. At right is $NH_3$. Having four pairsof valence electrons around its central atom, the form of $NH_3$ is based upon the tetrahedron.The geometry is called trigonal pyramidal.

Also note that lone pair - loan pair and loan pair -bonded pair repulsions are stronger than bonded pair - bonded pair repulsions. So the H--N—Hangle will be a little less than $109^o$ ($107^o$).

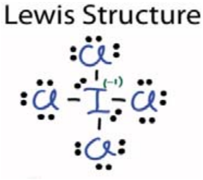
### VSEPR Model for $SF_4$

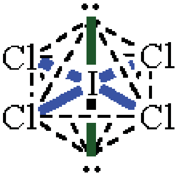
The Lewis structure for $SF_4$ shown below followed by the model based on VSEPR theory.



Sulphur has five electron domains round it: four from the S—F bonds and one from the nonbonding pair. Each domain points toward a vertex of a trigonal bipyramid. The domain from the nonbonding pair will point toward an equatorial position. The four bonds point toward the remaining four positions, resulting in a molecular geometry thatis described as see-saw-shaped.

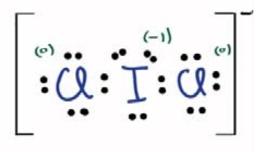
### VSPER Model for $ICl_4$

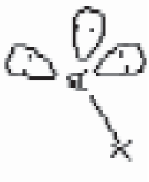




Iodine play its role of central atom once it shares the seven electrons, iodine gets four electrons to four chlorine atoms so it would displace three remaining ones onto two directed orbitals ; but this aggregate results a negative ion since it has one more electron so this aggregate (e.g. $ICl^{4-}$) binds four chlorine atoms by four bonds and place four other electron onto two other orbitals, e.g. those four electrons filled two remaining orbitals. five atoms depict a square planar figure.

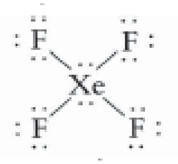
### VSEPR Model for $ICl_2$

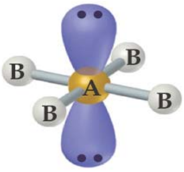




$ICl_2$ - is like $I_3$ - and has 22 available electrons. Oh, and a hint to learn 5 types of molecular geometries when there are no unbonded pairs. ABn = electronic geometry = molecular geometry. So the VSPER model is linear with two $Cl^-$ group lie 180$^\circ$C each other.

### VSEPR Model for $XeF_4$



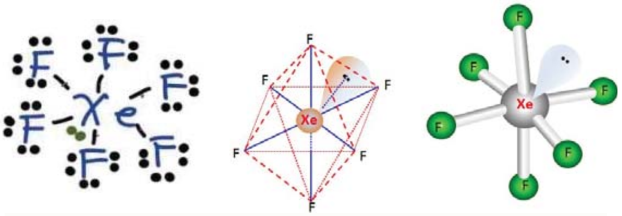


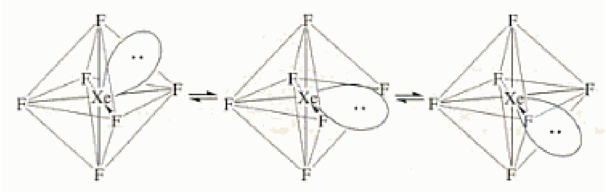
Square planar

The xenon atom surrounded by 6 pairs of electrons requires an octahedral arrangement. First structure shows the traditional structure but the other is the preferred structure since the lone pairs require more room than bonding pairs.There is an octahedral arrangement of electron pairs, but the atoms form a square planar structure. Although each Xe-F bond is polar (fluorine has a greater electronegativity that xenon), the square planar arrangement of these bonds causes the polarities to cancel.

### VSEPR Model for $XeF_6$

The movement of electrons in $XeF_6$ is highly unusual. They are consistent with a model in which there is a *distorted* octahedron with a nonbonding pair protruding from the center of one face. The distortion arises because the three fluorines at the corners of that face are pushed apart. The vibration of the molecule then continuously moves the nonbonding pair and accompanying distortion from face to face of the octahedron.





### 3.5Molecular Orbital (MO) theory

Molecular orbital (MO) theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features of this theory are:

1. The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.
2. The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.
3. While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.
4. The number of molecular orbital formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as **bonding molecular orbital** while the other is called **antibonding molecular orbital**.
5. The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
6. Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.
7. The molecular orbitals like atomic orbitals are filled in accordance with the *Aufbau* principle obeying the Pauli's exclusion principle and the Hund's rule.

### LCAO method

According to wave mechanics, the atomic orbitals can be expressed by wave functions (ψ) which represent the amplitude of the electron waves. These are obtained from the solution of Schrödinger wave equation.

However, since it cannot be solved for any system containing more than one electron, molecular orbitals which are one electron wave functions for molecules are difficult to obtain directly from the solution of Schrödinger wave equation. To overcome this problem, an approximate method known as **linear combination of atomic orbitals (LCAO)** has been adopted.

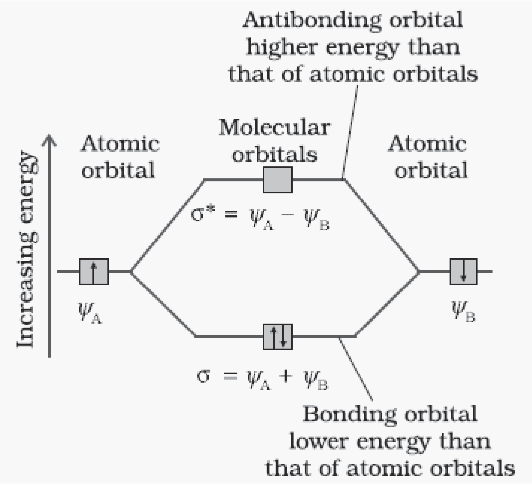
Let us apply this method to the homonuclear diatomic hydrogen molecule. Consider the hydrogen molecule consisting of two atoms A and B. Each hydrogen atom in the ground state has one electron in 1*s* orbital. The atomic orbitals of these atoms may be represented by the wave functions $\psi_A$ and $\psi_B$. Mathematically, the formation of molecular orbitals may be described by the linear combination of atomic orbitals that can take place by addition and by subtraction of wave functions of individual atomic orbitals as shown below:

$$\psi_{MO} = \psi_A \pm \psi_B$$

Therefore, the two molecular orbitals σ and σ* are formed.

$$\sigma = \psi_A + \psi_B$$
$$\sigma^* = \psi_A - \psi_B$$

The molecular orbital σ formed by the addition of atomic orbitals is called the **bonding molecular orbital** while the molecular orbital σ* formed by the subtraction of atomic orbital is called **antibonding molecular orbital** as depicted in the figure shown below.

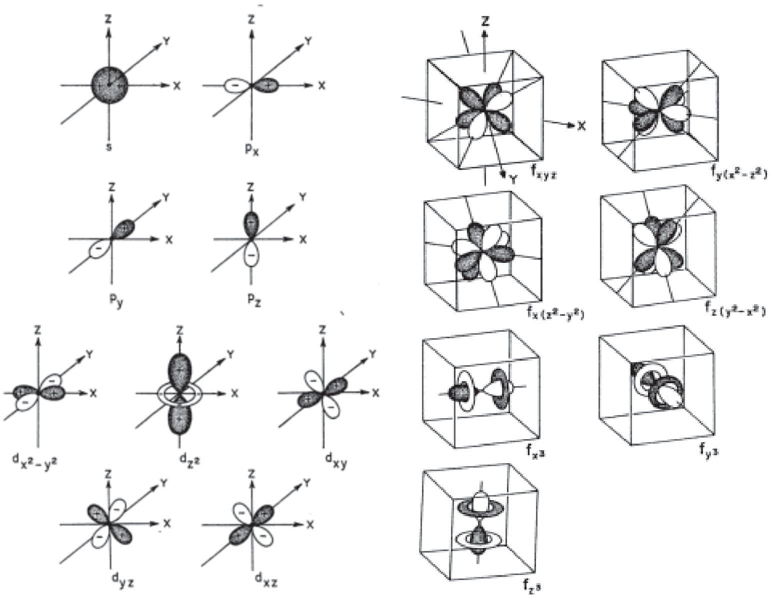


Qualitatively, the formation of molecularorbitals can be understood in terms of theconstructive or destructive interference of theelectron waves of the combining atoms. In theformation of bonding molecular orbital, the twoelectron waves of the bonding atoms reinforceeach other due to constructive interferencewhile in the formation of antibonding molecular orbital, the electron waves canceleach other due to destructive interference. Asa result, the electron density in a bondingmolecular orbital is located between the nucleiof the bonded atoms because of which therepulsion between the nuclei is very less whilein case of an antibonding molecular orbital,most of the electron density is located awayfrom the space between the nuclei. Infact, thereis a nodal plane (on which the electron densityis zero) between the nuclei and hence therepulsion between the nuclei is high. Electronsplaced in a bonding molecular orbital tend tohold the nuclei together and stabilize amolecule. Therefore, a bonding molecularorbital always possesses lower energy thaneither of the atomic orbitals that have combinedto form it. In contrast, the electrons placed inthe antibonding molecular orbital destabilizethe molecule. This is because the mutualrepulsion of the electrons in this orbital is morethan the attraction between the electrons andthe nuclei, which causes a net increase inenergy.

It may be noted that the energy of theantibonding orbital is raised above the energyof the parent atomic orbitals that havecombined and the energy of the bondingorbital has been lowered than the parentorbitals. The total energy of two molecularorbitals, however, remains the same as thatof two original atomic orbitals.

**Criteria for orbital overlap**

It is not possible for any particular atomic orbital to mix or overlap with just any other orbital. Therefore, certain criteria must be met when constructing a set of molecular orbitals by the use of LCAO method. Particularly the shape and disposition in space with different wave function signs for the atomic orbitals are very important. The shapes of s, p, d and f orbitals are shown for reference.



**The three important criteria to be observed are:**

1. The atomic orbitals under overlap must be approximately of the same energy, i.e. of comparable magnitude.
2. The atomic orbitals must overlap as extensively as possible, i.e. the overlap must be effective and appreciable.
3. Both the atomic orbitals must have the same symmetry relative to the inter-nuclear axis, i.e. the atomic orbitals must undergo similar changes in symmetry when rotated about the molecular axis.

The above features are explained in terms of symmetry and energy.

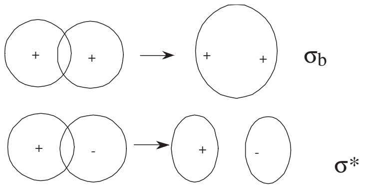
**Symmetry**

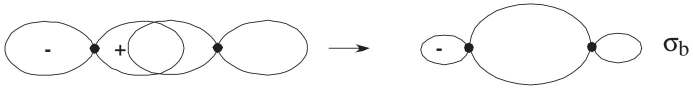
Symmetry either allows or forbids bond formation. If the symmetry is correct then the two orbitals and form bonding and antibonding MOs and if it is wrong the two orbitals will not mix and you get MOs that are only the atomic orbitals you start with. If the orbitals do not have the right symmetry they will have no net overlap. The symmetry is defined alone the line connection to two nuclei. If the two orbitals have the same symmetry relative to this line then the symmetry is correct.

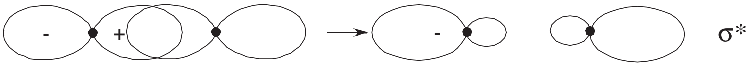
Examples:

Overlap of an s with an s orbital will give significant overlap and you get a bonding and antibonding pair as shown at right side, where the bonding orbital has lower energy then the antibonding orbital.

For two $p_z$ orbitals you will also get a σ bonding and σ* antibonding pairwith again the bonding orbital having lower energy then the antibonding orbital.

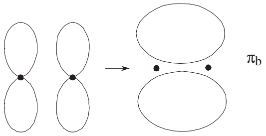


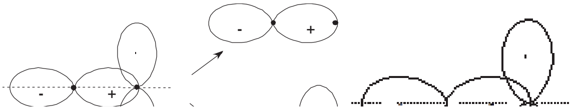




And for two $p_y$ or two $p_z$ orbitals you find similar symmetries and get bonding and antibonding molecular orbitals but they are now π in symmetry. Now what happens when the two orbitals have different symmetries? If we take a $p_z$ with a $p_x$ orbital that the net overlap for the two is zero since the symmetry of the two orbitals is such that any positive overlap the occurs below the dotted line is canceled by negative overlap that occurs above the dotted line.

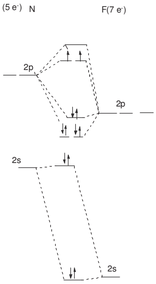
When the net overlap is zero we say the orbitals are **nonbonding**. This means that the two orbitals will **not** mix. The two atomic orbitals yield two molecular orbitals that look just like the original atomic orbitals thus we get two nonbonding orbitals. Both nonbonding orbitals are shown above and they have the **same** energies as the original orbitals.



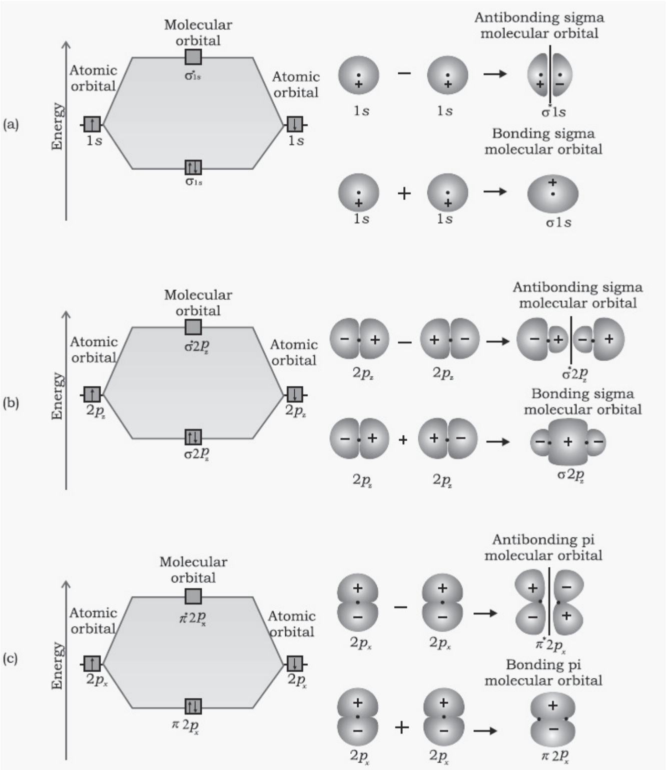


## Energy

If the energies of the two orbitals are similar you get better bonding and when they are a lot different they don’t interact very well and the orbitals look like they are center on only one of the atoms. Thus in NF we drew as shown or right.
The lowest $\sigma_s$ orbital is mainly a 2*s* orbital of fluorine and the antibonding $\sigma_s$* is mostly the 2s orbital of nitrogen.



## Combination of atomic orbitals and their schematic illustration



## Types of Molecular Orbitals

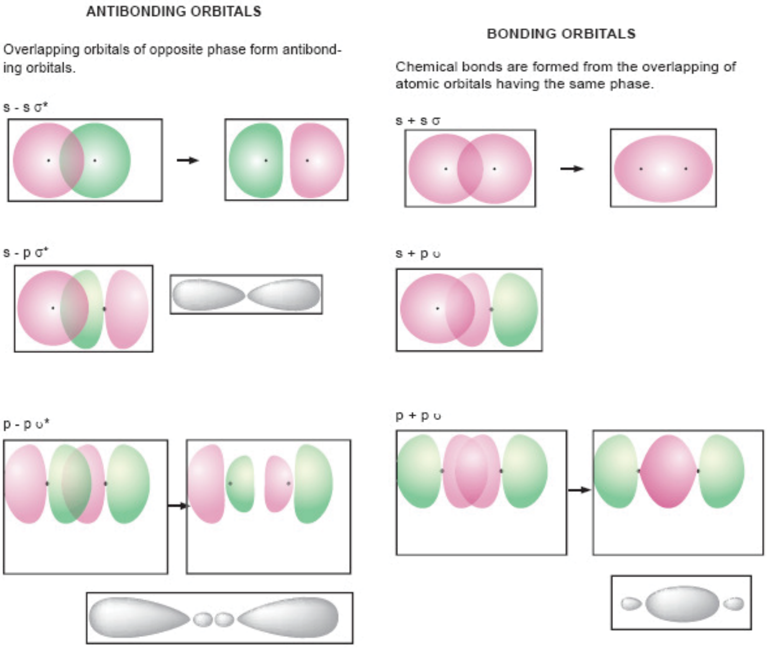
Molecular orbitals of diatomic molecules are designated as σ (sigma), π (pi), δ (delta), etc.In this nomenclature, the **sigma (σ) molecular orbitals are symmetrical around the bond-axis while pi (π) molecular orbitals are not symmetrical**.

For example, the linear combination of 1s orbitals centered on two nuclei produces two molecular orbitals which are symmetrical around the bond-axis. Such molecular orbitals are of the σ type and are designated as $\sigma 1s$ and $\sigma^* 1s$. **If inter nuclear axis is taken to be in the z-direction, it can be seen that a linear combination of *2pz* orbitals of two atoms also produces two sigma molecular orbitals designated as $\sigma 2p_z$ and $\sigma^* 2p_z$.**

Molecular orbitals obtained from $2p_x$ and $2p_y$ orbitals are not symmetrical around the bond axis because of the presence of positive lobes above and negative lobes below the molecular plane. Such molecular orbitals are labeled as π and π*. A π bonding MO has larger electron density above and below the inter-nuclear axis. The π* antibonding MO has a node between the nuclei.

**Conditions for the Combination of Atomic Orbitals**

The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied:



1. **The combining atomic orbitals must have the same or nearly the same energy**. This means that 1*s* orbital can combine with another 1*s* orbital but not with 2*s* orbital because the energy of 2*s* orbital is appreciably higher than that of 1*s* orbital. This is not true if the atoms are very different

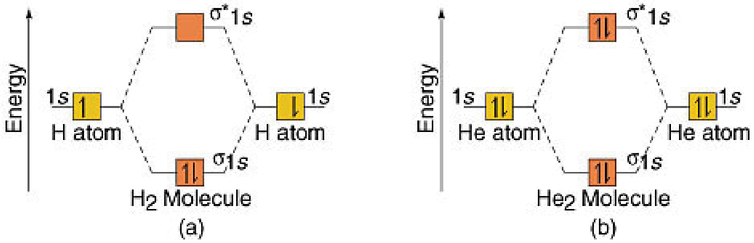
2. **The combining atomic orbitals must have the same symmetry about the molecular axis**. By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having same or nearly the same energy will not combine if they do not have

the same symmetry. For example, $2p_z$orbital of one atom can combine with $2p_z$orbital of the other atom but not with the $2px$ or $2p_y$orbitals because of their different symmetries.

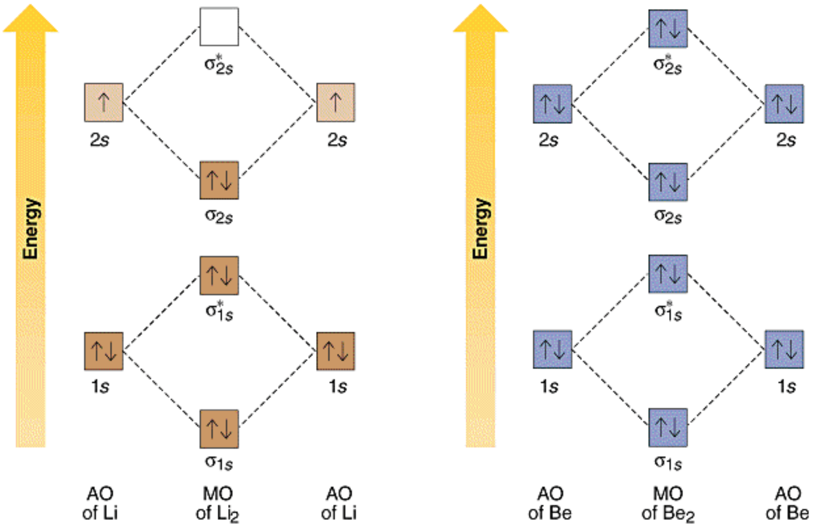
3. **The combining atomic orbitals must overlap to the maximum extent**. Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

### Qualitative MO energy level diagram of homo and hetero diatomic molecules – $H_2$ to $Ne_2$, CO, NO, HCl;

### Energy level diagram of hydrogen and helium

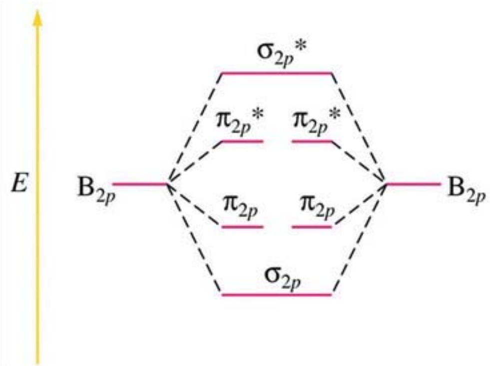


### Energy level diagram of lithium and beryllium

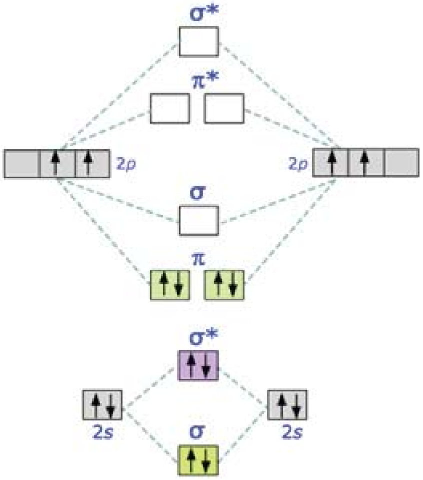


**A** $Li_2$ bond order = 1 **B** $Be_2$ bond order = 0

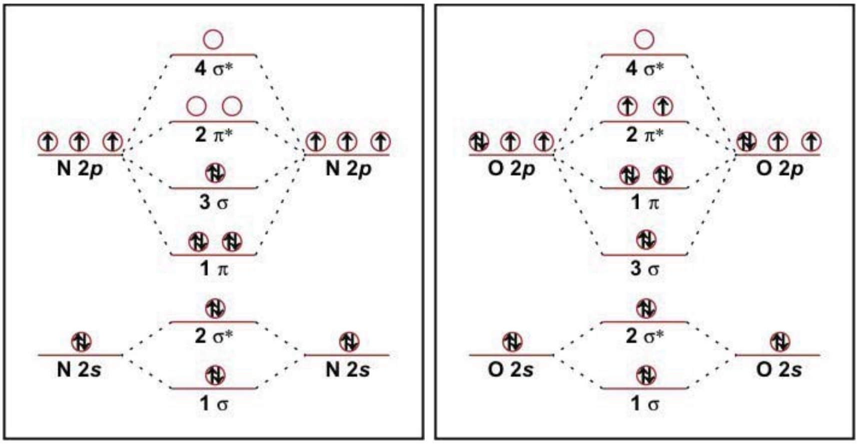
### Energy level diagram of boron



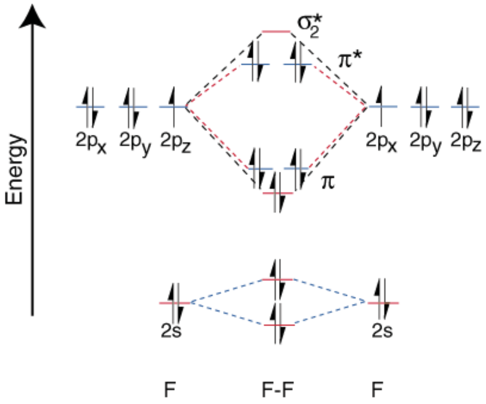
Energy level diagram of carbon



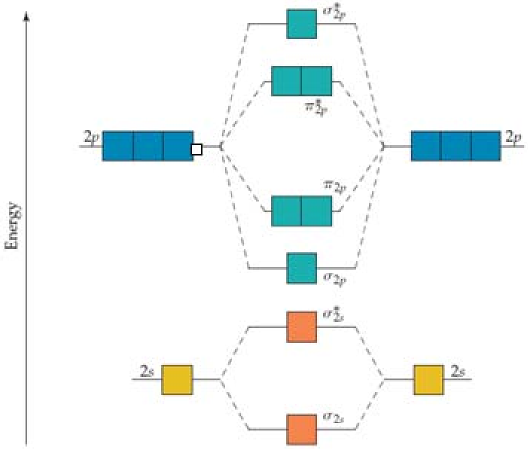
Energy level diagram of nitrogen and oxygen



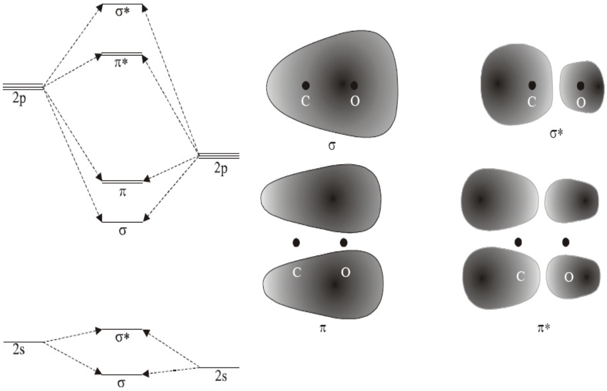
Energy level diagram of fluorine



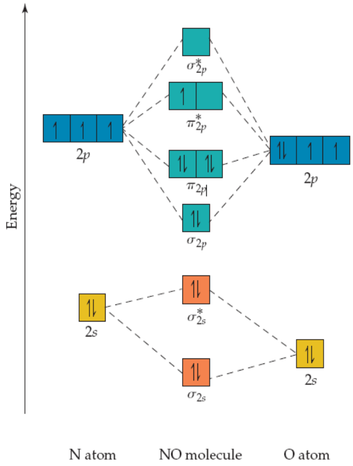
## Energy level diagram of neon



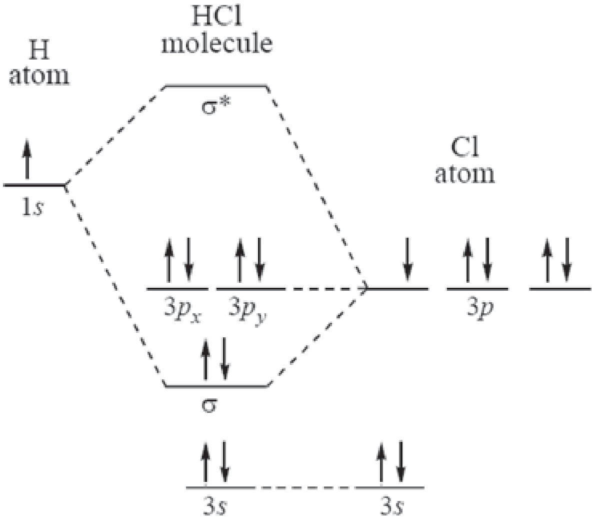
## Energy level diagram of CO molecule



### Energy Diagram of NO Molecule



### Energy Level diagram of HClMolecule

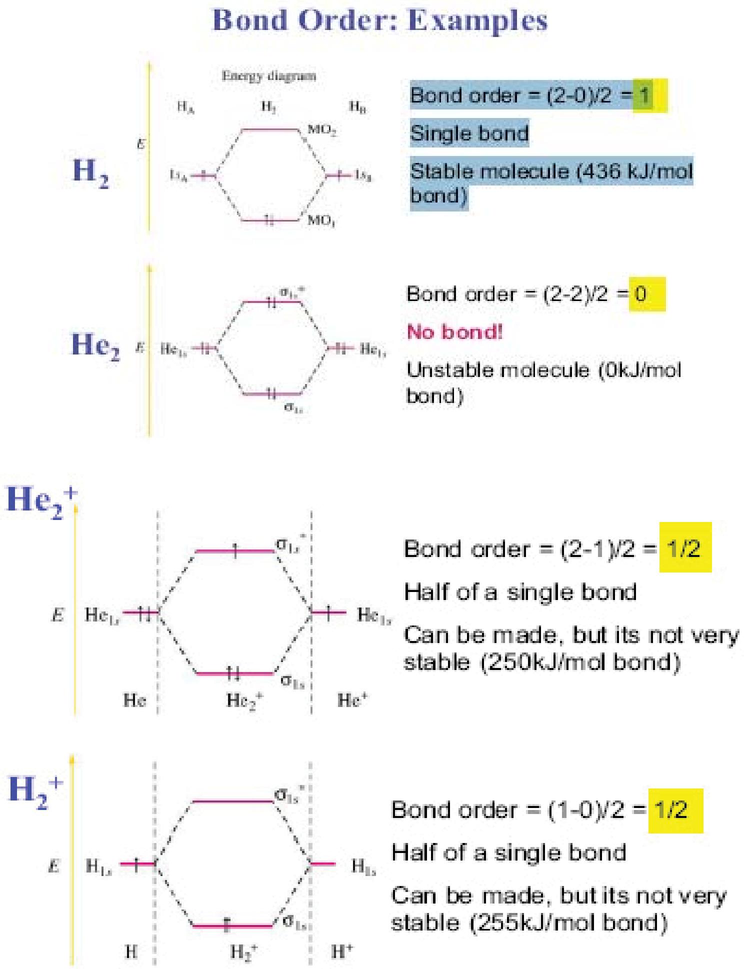


### Bond order

Bond order (b.o.) is defined as one half the difference between the number of electrons present in the bonding ($N_b$) and the antibonding orbitals (Na).

$$\text{Bond order (b.o)} = \frac{\text{Number of bonding orbitals } (N_a) - \text{Number of anti bonding orbitals } (N_b)}{2}$$

The rules discussed above regarding the stability of the molecule can be restated in terms of bond order as follows: A positive bondorder (i.e., $N_b > N_a$) means a stable molecule while a negative (i.e., $N_b < N_a$) or zero (i.e. $N_b = N_a$) bond order means an unstable molecule.



**Bond Order: Examples**

Bond order = (2-0)/2 = 1

Single bond

Stable molecule (436 kJ/mol bond)

Bond order = (2-2)/2 = 0

No bond!

Unstable molecule (0kJ/mol bond)

Bond order = (2-1)/2 = 1/2

Half of a single bond

Can be made, but its not very stable (250kJ/mol bond)

Bond order = (1-0)/2 = 1/2

Half of a single bond

Can be made, but its not very stable (255kJ/mol bond)

**Stability of molecules**

If $N_b$ is the numberof electrons occupying bonding orbitals and$N_a$ the number occupying the antibondingorbitals, then(i) the molecule is stable if $N_b$ is greater than$N_a$, and(ii) the molecule is unstable if $N_b$ is lessthan Na.

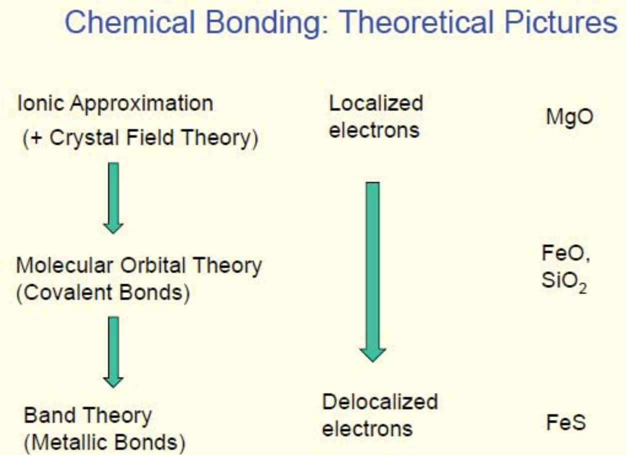
In the case of (i) more bonding orbitals are occupiedand so the bonding influence is stronger and astable molecule results. Similarly in the case of (ii) the antibondinginfluence is stronger and therefore the moleculeis unstable.

## Unit IV Metallic and Weak Bonds

### Syllabus

The Metallic bond: crystal structure of metals-ccp, hcp, metallic properties, band theory ofmetals – Alloys – mixture, interstitial- and substitutional solid solutions, Hume-Rothery rules,interstitial compounds - Weak bonds: hydrogen bonding-intra and intermolecular hydrogenbonding, influence on the physical properties of molecules, comparison of hydrogen bondstrength and properties of hydrogen bonded N, O and F compounds; associated moleculesethanoland acetic acid; crystalline hydrates and clathrates; van der waals forces, ion dipoledipoleinteractions.

## 4.1 The Metallic bond



Chemical Bonding: Theoretical Pictures

Ionic Approximation
(+ Crystal Field Theory)

Molecular Orbital Theory
(Covalent Bonds)

Band Theory
(Metallic Bonds)

Localized electrons

Delocalized electrons

MgO

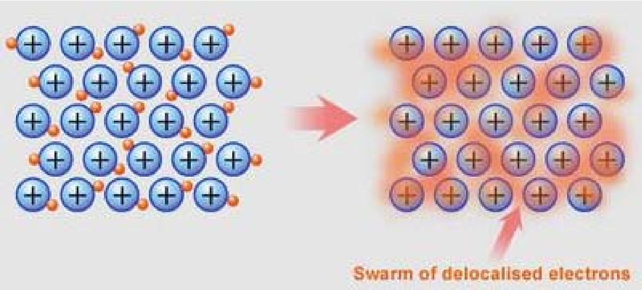
FeO, $SiO_2$

FeS

Metals are characterized by high thermal and electrical conductivities. Thus, neither covalent nor ionic bondings are realized because both types of bonding localize the valence electrons and preclude conduction. However, strong bonding does occur in metals. The valence electrons of metals also are delocalized.

Thus a***metallic bond may be defined as the bond formed as a result of simultaneous attraction of an electron by two or more than two positive ions of the metal.Thus a metallic bond is electrostatic in nature.***

Thus metallic bonding can be viewed as metal containing a periodic structure of positive ions surrounded by a sea or swarm of delocalized electrons. The attraction between the two provides the bond, which is non-directional.



### Crystal structure of metals

**Crystal:**
*Crystal is a solid composed of atoms, ions, or molecules arranged in a pattern that is repeated in three dimensions.A material in which atoms are situated in a repeating or periodic array over large atomic distances.*

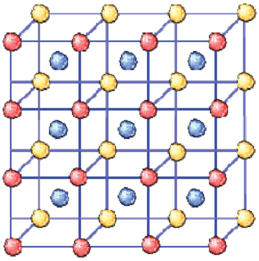
## Crystal structures

All metals, a major fraction of ceramics, and certain polymers acquire crystalline form when solidify, i.e. in solid state atoms self-organize to form *crystals*. Crystals possess a long-range order of atomic arrangement through repeated periodicity at regular intervals in three dimensions of space.

There is very large number of different crystal structures all having long-range atomic order; these vary from relatively simple structures for metals to exceedingly complex structures for ceramics and some polymers. To discuss crystalline structures it is useful to consider atoms as being hard spheres, with well-defined radii. In this scheme, the shortest distance between two like atoms is one diameter.

## Lattice:

A *lattice* is an infinite array of evenly spaced points which are all similarly situated. Each points are regarded as similarly situated in the rest of the lattice appears the same, and in the same orientation when viewed form themis used to represent a three-dimensional periodic array of points coinciding with atom positions.

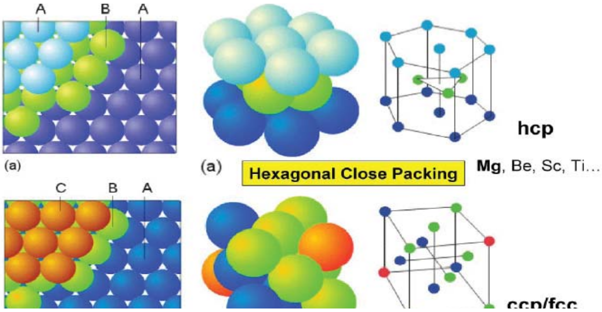


## Unit cell

It is smallest repeatable entity that can be used to completely represent a crystal structure. Thus it can be considered that a unit cell is the building block of the crystal structure and defines the crystal structure by virtue of its geometry and the atom positions within.

## Close Packed Crystal Structures

To build our 3-dimensional metal structures we now need to stack the close packed layers on top of each other.  There are several ways of doing this.

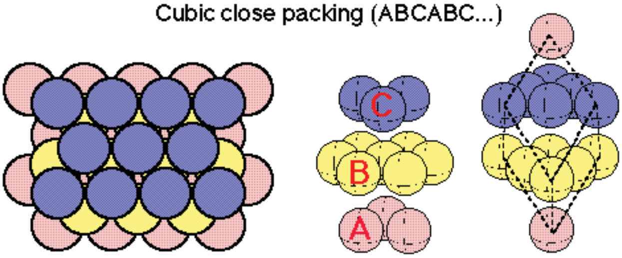


The most efficient space saving way is to have the spheres in one layer fit into the "holes" of the layer below.

The structures of many metals can be described as close packed arrays of spherical atoms. There are two alternative ways to maximize the packing efficiency of a collection of equally sized spheres.

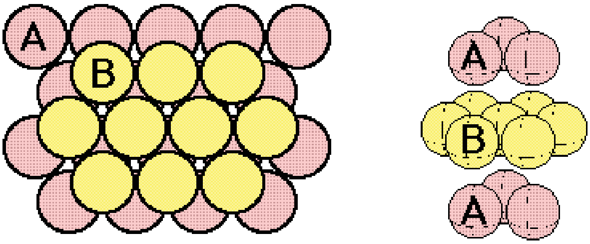
Cubic Close Packing (CCP) - ABCABC
Hexagonal Close Packing (HCP) - ABABAB

The figures below illustrates the two packing sequences. The spheres of the second layer can be centered over either the sites marked b or c. The symmetry is exactly the same regardless of the choice, however, when a third layer is added it now has a choice of packing over the spheres in the original layer or over the sites marked as c in the diagram of the first layer. The former option leads to the ABAB... stacking characteristic of hexagonal close packing, while the latter option leads to the ABCABC... packing which defines a cubic close packed (**ccp**) structure.


Cubic close packing (ABCABC...)

If we call the first layer "A", then the second layer ("B") is positioned as shown on the left of the diagram below. The third layer can then be added in two ways. In the first way the third layer fits into the holes of the B layer such that the atoms lie above those in layer A. By repeating this arrangement one obtains **ABABAB... stacking or <u>hexagonal close packing</u>**.

Hexagonal close packing (ABABAB...)



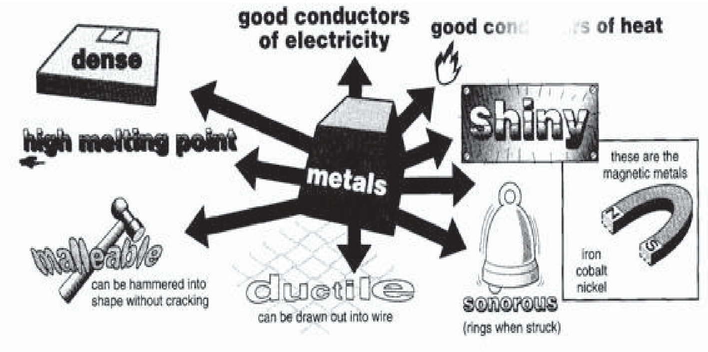
The packing efficiency (volume of space occupied by the spheres/total volume) is 74.05 % for both cubic and hexagonal close packing schemes. The number of (12) and distance between nearest neighbors is also identical for both HCP and CCP, but the second nearest neighbor coordination is different.

In addition to these two schemes a fair number of metals adopt a body centered cubic arrangement. In this structure type the number of nearest neighbors has been reduced from 12 to 8. This does not result in a close packed array of spheres, and the packing efficiency drops to 68.02%.

**Metallic properties**

**Physical properties of metals**

Metals show following general physical properties.

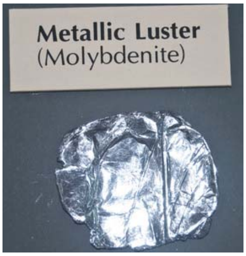


**1) Physical state**

Metals are solids at room temperature e.g. sodium, aluminium, potassium, magnesium. There are exceptions to this. Mercury and gallium are metals but they are in liquid state at room temperature.

**2) Luster**

Metals have a shining surface called luster when freshly prepared. They have a quality of reflecting light from their surface and they can be polished e.g. metals like gold, silver, copper show this property.



**3) Malleability**

Metals can be beaten into thin sheets. This property is called malleability. Due to this property, metals can be rolled into sheets e.g. aluminium, copper, zinc can be beaten into sheets.

### 4) Ductility

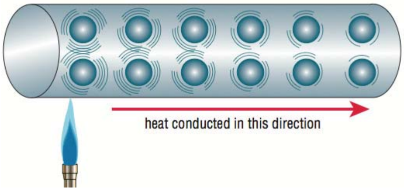
Metals can be drawn into thin wires. This property is called ductility. For example, 100 grams of silver can be drawn into a thin wire about 200 meters long.

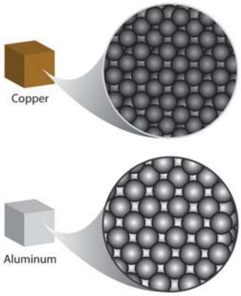
### 5) Hardness

Metals are generally hard e.g. iron, cobalt, nickel. There are few exceptions to this. Sodium and potassium are soft and they can be cut with a knife.

### 6) Conduction

Generally, metals are good conductors of heat and electricity because they have free electrons. Silver and copper are the two best conductors. Relatively, lead and bismuth are poor conductors of heat and electricity.





**7) Density**

Metals generally have high density and they are heavy. Iridium and osmium have the highest densities while lithium has the lowest density.

**8) Melting and boiling point**

Metals usually have high melting point and boiling point. For example, iron, cobalt and nickel have high melting and boiling point. Tungsten has the highest melting point. There are some exceptions to this. For example , most of the alkali metals have low melting and boiling point.

**9) Tensile strength**

Most of the metals possess high tensile strength i.e. tenacity. For example, iron, titanium, some alloys have high tensile strength. However, elements like sodium, potassium and mercury do not possess tenacity.

**Chemical properties of metals**

Metals show following general chemical properties.

**1) Electron configuration**

Metals usually have 1 to 3 electrons in the outermost shell of their atom. For example, sodium, magnesium and aluminium have 1, 2 and 3 electrons respectively in the outermost shell of their atom.

**2) Valency**

Metal atoms can lose 1 to 3 electrons in their outermost shell and show valencies1 to 3.

**3) Electrochemical nature**

Metal atoms have tendency to lose electrons and form cations. . This tendency is called the electropositive nature. Metals generally have moderate to high electropositive nature. For example, Na, Mg and Al have high electropositive character while Zn, Cd , Sn and Pb have moderate electropositive nature.

**4) Electronegativity**

Metals generally have low electronegativity i.e. tendency to attract electrons in the state of molecule. For example, metals like Ca, Mg, Al, Zn have low electronegativity.

### 5) Formation of oxides

Metals form oxides which are generally ionic and basic in nature. If this basic oxide dissolves in water, it forms an alkali. For example, oxides of Na, K and Ca viz. $Na_2O$, $K_2O$ and CaO are highly basic in nature and when dissolved in water, they form alkalies NaOH, KOH and $Ca(OH)_2$. The oxides react with acids to form salts. Oxides of metals like Pb, Zn, Al and Sn viz. $PbO_2$, ZnO, $Al_2O_3$ and $SnO_2$ are moderately basic and they react with acids as well as alkalies to form salt. So such oxides are called amphoteric oxides. The oxides $Sb_2O_3$ and $Cr_2O_3$ are exceptions and they are acidic in nature.

### 6) Reducing agent

All metals act as reducing agents. Strongly electropositive metals like Mg, Al and Cr act as strong reducing agents while moderately electropositive elements like Zn, Cd and Sn act as moderate reducing agents.

### 7) Reaction with water

Strongly electropositive metals like Na and K react even with cold water to produce their hydroxides and they evolve hydrogen gas. The heat evolved is not sufficient for the hydrogen to catch fire. Metals like Mg do not react with cold water. They react only with hot water to form hydroxide evolving hydrogen. The elements less electropositive than Na, K and Mg like Al, Fe and Zn do not react with cold or hot water. These hot metals react only with steam to form their oxides and hydrogen .However, metals like Cu, Ag and Au which are below hydrogen in the activity series do not react with water at all.

### 8) Reaction with acids

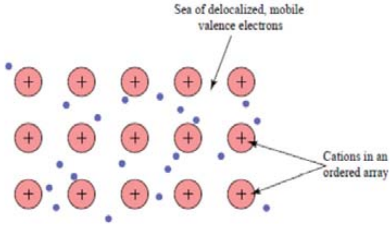
Highly reactive metals like Na, Mg and K react with dilute mineral acids like HCl or $H_2SO_4$ to form salt and hydrogen gas. These reactions are displacement reactions. If nitric acid is used, the hydrogen evolved gets oxidized to water and hence no hydrogen gas is evolved. Metals like Cu, Ag and Au which are below hydrogen in the reactivity series do not react with dilute mineral acids and do not evolve $H_2$.

### 9) Reaction with non-metals

Metals like Mg, Ca, Al, etc. react with non-metals like H, S, Cl, Br and I under different conditions of temperature to form their respective salts. However, all metals are not equally reactive so they require different conditions to react with non-metals.

### Band theory of metals

The first and simplest explanation of metallic bonding is often referred to as the **sea of electrons model**. The essential feature of this model is that the valence electrons of metal atoms are delocalized and move freely throughout the solid rather than being tied to any specific atom. This model accounts for several observed properties of metals.

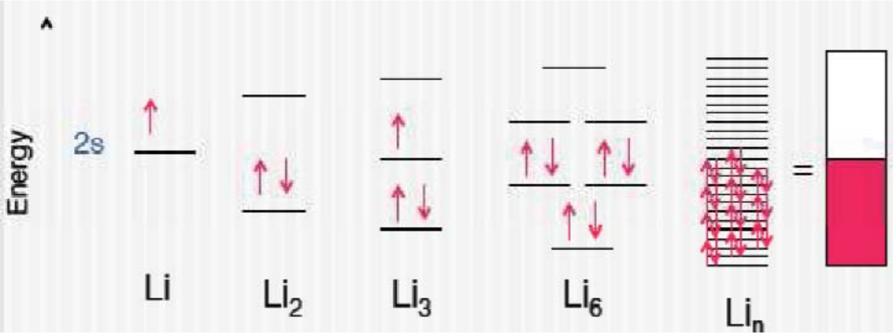


Finally, these delocalized electrons can move in response to any applied electrical field, so the conductivity of metals can also be understood from the model. The sea of electrons model provides qualitative understanding, but quantitative models for metallic bonding also exist. The most important such model is **band theory**.

Use lithium for the simplicity of the *s* orbital overlap, not because this is the most practical choice. Because the valence electron configuration of lithium is 1$s_2$ 2$s_1$, any bonding interactions between the metal atoms will have to be based on the 2*s* orbitals. Those orbitals, of course, are waves, and so we can use the concept of wave interference to think about how they will interact with one another. We'll start with the simplest case: two lithium atoms placed close enough together for their 2*s* orbitals to overlap one another and interact. Now recall that waves can interfere either constructively or destructively.

If the pair of 2*s* orbitals interacts in phase with one another, the interference will be constructive. The resulting wave, which will have increased amplitude (or electron density) between the nuclei, is referred to as a ***bonding molecular orbital***. On the other hand, if the pair of 2*s* orbitals interacts out of phase with one another, the resulting wave will have a node between the nuclei. This is known as an ***antibonding molecular orbital***. *The term "antibonding" is used because electrons in this orbital will actually weaken the bond between the atoms.* Rather than being associated with either atom individually, these new molecular orbitals can be thought of as belonging to the pair of lithium atoms together. Figure shows how the energies of these molecular orbitals are related to that of the original 2*s* orbitals. Looking at Figure, we can think through what would happen as more and more lithium atoms are loaded into them. With two atoms, there would be one bonding and one antibonding orbital. With four lithium atoms, there would be two bonding and two antibonding orbitals, as shown in the center panel of Figure.

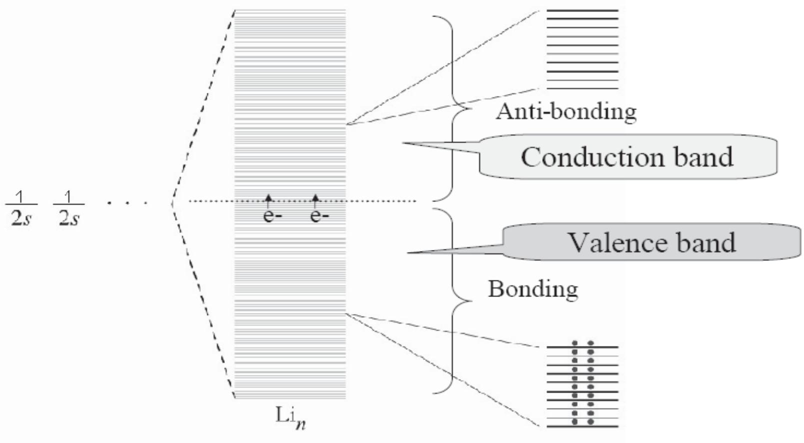
*(With an odd number of atoms, one nonbonding orbital would be formed, keeping the number of bonding and antibonding orbitals equal to each other.)*



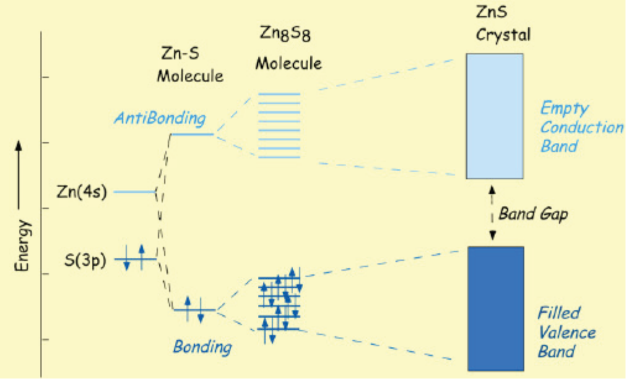
As we proceed further to very large numbers of atoms, the number of molecular orbitals formed becomes so large that there is virtually no energy difference from one orbital to the next. At this point, the orbitals have merged into a band of allowed energy levels, and this is the origin of the term *band theory*. Although our presentation here is entirely qualitative, it is important to note that a more thorough development of these ideas leads to a quantitative model.

A three-dimensional bulk metal is slightly more complicated, and the way that the orbitals will combine has some dependence on the structure of the solid. For metals with valence electrons beyond the *s* subshell, the orbitals that ultimately form bands will include *p* or *d* orbitals. These will form additional bands, and the energy of the resulting *s* bands, *p* bands, or *d* bands may overlap one another. To understand properties such as conductivity, the band structure of the material provides a very powerful model.

Band theory provides the most satisfactory explanation of the characteristics of the metallic properties in a very natural manner. The theory is an extension of molecular orbital (M.O.) treatment for a large number of atoms. For homonuclear diatomic species, the combination of two atomic orbitals gives rise to two molecular orbitals and these are two new energy levels for the electrons in the two joint fields of the nuclei. If the idea is extended to an aggregate of a large number of atoms (*n*), each offering one orbital for the combination with others, so there will be a total of *n* new energy levels similar to '*n*' number of molecular orbitals (M.O.s). These large numbers of energy levels form an energy band by spacing closely one upon another. The valence electrons from all the atoms will enter energy level and a metal thus consists of energy bands formed by merging of individual atomic orbitals. Let us illustrate the following cases:

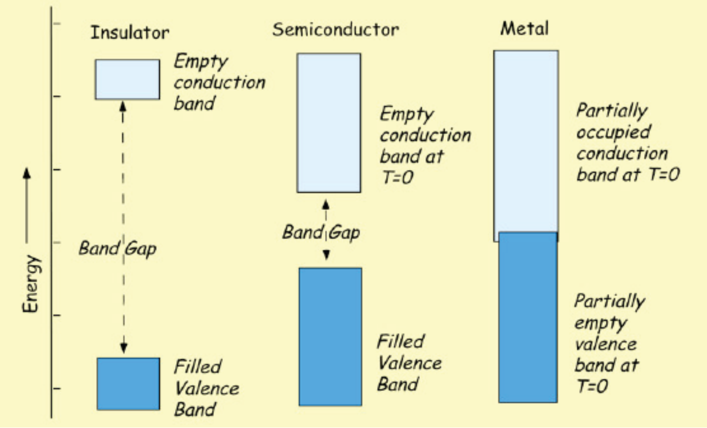


Let us consider Li as an example. The electronic configuration of a Li atom is $1s^2\ 2s^1$. So, two molecular orbitals are formed by two 2*s* atomic orbitals from two Li atoms. Similarly three or four Li atoms would give rise to the formation of three or four energy levels by combination of their 2*s*-atomic orbitals. Now extending this idea for '*n*' atoms, all 2*s* atomic orbitals will combine to give a 2*s*energy band with *n*-energy levels. Similar combination of the *p*-atomic orbitals will form a 2*p* energy band containing 3*n* energy levels. Each Li atom has only one valence electron and the total *n* electrons from *n* atoms will occupy doubly the lower *n*/2 energy levels in the 2*s* band. When the electrons gain thermal energy or are placed in an electric field, the electrons are raised to higher unfilled energy levels. This phenomenon explains the high thermal and electrical conductivities of metals. The conduction in metallic solids is depicted in the following illustration with zinc as an example.



## Band Theory and Conductivity

The band structure of a metal plays much the same role as atomic orbital energy level does for atoms. Just as the Aufbau principle dictates that electrons occupy the lowest energy orbitals, electrons in bulk materials fill the bands starting at the lowest energy. The highest energy with electron occupation and the energy gap between this energy level and the next available band provide a means for understanding the electrical conductivity of a material. Electrons carry a current by moving through a material, and this motion can be thought of in terms of electrons moving from one orbital to another. But electrons within a filled band cannot move readily to conduct electricity. To have mobile electrons, we will need to have an unfilled band or portion of a band that is close to a filled band or portion of a band.



## Alloys (Metallic mixtures)

An **alloy** is a material composed of two or more metals or a metal and a nonmetal. An **alloy** may be a solid solution of the elements (a single phase), a mixture of metallic phases (two or more solutions) or an intermetallic compound with no distinct boundary between the phases.

## Solid solutions

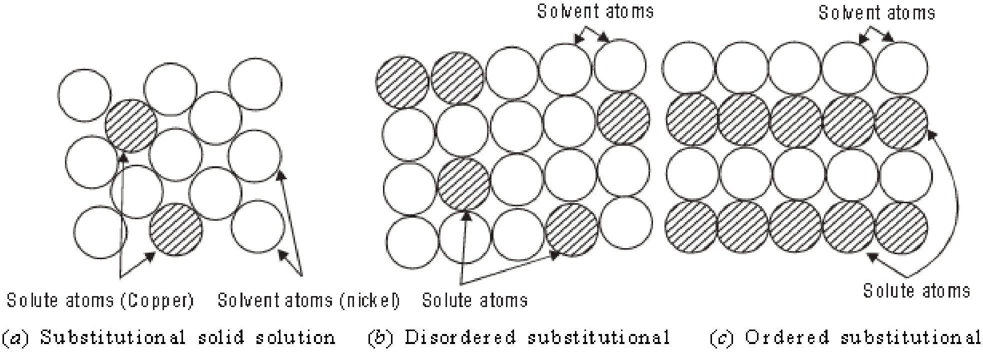
A solid solution is formed when two metals are completely soluble in liquid state and alsocompletely soluble in solid state. In other words, when homogeneous mixtures of two ormore kinds of atoms (of metals) occur in the solid state, they are known as solid solutions.The more abundant atomic form is referred as solvent and the less abundant atomic formis referred as solute. For example sterling silver (92.5 % silver and the remaindercopper) is a solid solution of silver and copper. In this case silver atoms are solvent atomswhereas copper atoms are solute atoms. Another example is brass. Brass is a solidsolution of copper (64 %) and zinc (36 %). In this case copper atoms aresolvent atoms whereas zinc atoms are solute atoms.

## Types of solid solutions

Solid solutions are of two types. They are

1. Substitutional solid solutions 2. Interstitial solid solutions.

**1. Substitutional Solid Solutions**: If the atoms of the solvent or parent metal are replaced in the crystal lattice by atoms of the olute metal then the solid solution is known as substitutional solid solution. For example, copper atoms may substitute for nickel atoms without disturbing the F.C.C. Structure of nickel is shown in the figure.



**Substitutional solid solutions**

In the substitutional solid solutions, the substitution can be either disordered or ordered. In the disordered substitutional solid solution, the solute atoms have substituted disorderly for the solvent atoms on their lattice site. In the ordered substitutional solid solution the solute atoms have substituted in an orderly manner for the solvent atoms on their lattice site.

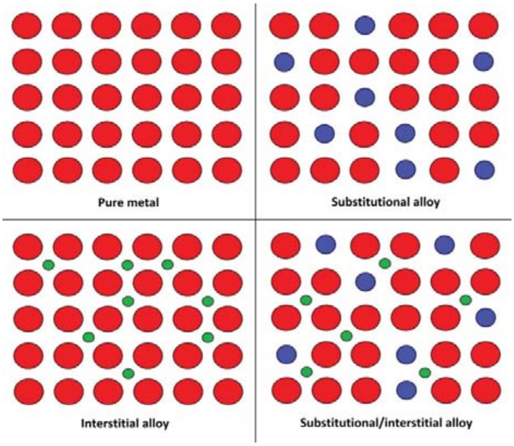
**Hume Rothery rules for the formation of substitutional solid solutions –** By studying a number of alloy systems, Hume Rothery formulated certain rules which govern the formation of substitutional solid solutions. These are:

a) *Crystal structure factor*: For complete solid solubility, the two elements should have the same type of crystal structure i.e., both elements should have eitherF.C.C. or B.C.C. or H.C.P. structure.

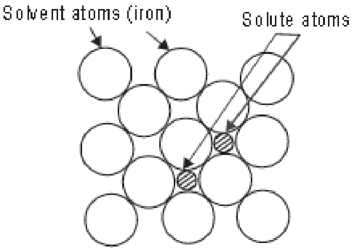
b) *Relative size factor*: As the size (atomic radii) difference between two elementsincreases, the solid solubility becomes more restricted. For extensive solidsolubility the difference in atomic radii of two elements should be less thanabout 15 percent. If the relative size factor is more than 15 percent, solidsolubility is limited. For example, both silver and lead have F.C.C. structureand the relative size factor is about 20 percent. Therefore the solubility of leadin solid silver is about 1.5 percent and the solubility of silver in solid lead isabout 0.1 percent. Copper and nickel are completely soluble in each other inall proportions. They have the same type of crystal structure (F.C.C.) and differin atomic radii by about 2 percent.

c) *Chemical affinity factor*: Solid solubility is favored when the two metalshave lesser chemical affinity. If the chemical affinity of the two metals isgreater then greater is the tendency towards compound formation. Generally,if the two metals are separated in the periodic table widely then they possessgreater chemical affinity and are very likely to form some type of compoundinstead of solid solution.

d) *Relative valence factor*: It is found that a metal of lower valence tends todissolve more of a metal of higher valence than vice versa. For example inaluminium-nickel alloy system, nickel (lower valance) dissolves 5 percent aluminiumbut aluminium (higher valence) dissolves only 0.04 percent nickel.



**2. Interstitial Solid Solutions**: In interstitial solid solutions, the solute atom does not displace a solvent atom, but rather it enters one of the holes or interstices between the solvent atoms. An excellent example is iron-carbon system which is shown in the figure.



**Interstitial solid solutions**

**Interstitial compounds**

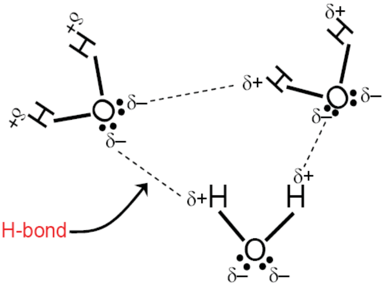
In the above system the carbon (solute atom) atom occupies an interstitial position between iron (solvent atom) atoms. Normally, atoms which have atomic radii less than one angstrom are likely to form interstitial solid solutions. Examples are atoms of carbon (0.77 A°), nitrogen (0.71 A°), hydrogen (0.46 A°), Oxygen (0.60 A°) etc.

## 4.2 Weak bonds

### Hydrogen bonding

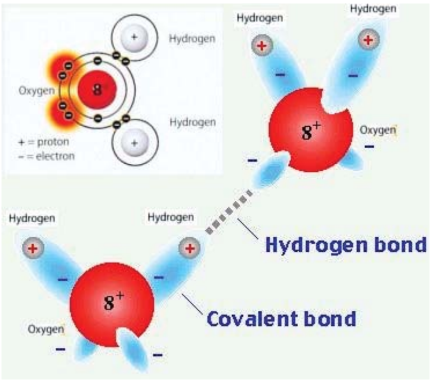
Nitrogen, oxygen and fluorine are the highlyelectronegative elements. When they areattached to a hydrogen atom to form covalentbond, the electrons of the covalent bond areshifted towards the more electronegativeatom. This partially positively chargedhydrogen atom forms a bond with the othermore electronegative atom. This bond isknown as hydrogen bond and is weaker thanthe covalent bond. For example, in HFmolecule, the hydrogen bond exists betweenhydrogen atom of one molecule and fluorineatom of another molecule as depicted below:

Here, hydrogen bond acts as a bridge betweentwo atoms which holds one atom by covalentbond and the other by hydrogen bond. Hydrogen bond is represented by a dotted line(- - -) while a solid line represents the covalentbond. **Thus, hydrogen bond can be definedas the attractive force which bindshydrogen atom of one molecule with theelectronegative atom (F, O or N) of anothermolecule.**



### Causes for hydrogen bonding

1) A hydrogen atom is covalently bonded to an electronegative atom like fluorine, oxygen or nitrogen, so that due to the polarisation of the bonded electron pair, it acquires a slightly positive charge.



2) A lone pair of nonbonded electrons is available on one of the atoms so that it can be donated to the positive hydrogen atom. Again such atoms are fluorine, oxygen,

nitrogen etc. It is found that of all the electronegative donor atoms, only fluorine, oxygen and nitrogen atoms enter into stable hydrogen bond formation. Other elements like chlorine or sulphur give extremely weak hydrogen bonds which are of no consequence in isolation.

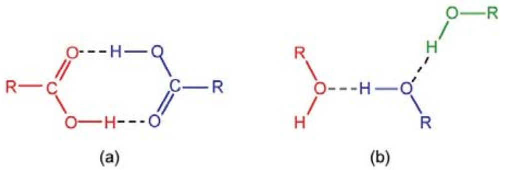
The weak electrostatic interaction leading to the hydrogen bond formation is shown by dotted lines. Thus X-H .....Y represents hydrogen bonding between hydrogen and Y atom.

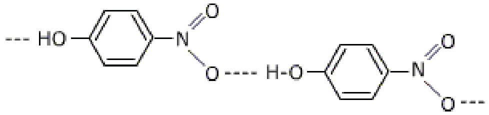
**Two Types of Hydrogen Bonds Exist:**

a) Intermolecular Hydrogen bonding b) Intra molecular Hydrogen bonding

### a) Intermolecular Hydrogen Bonding:

When hydrogen atoms acts as a bridge between two molecules as observed in water, carboxylic acids, alcohols, *p*-nitro phenol, ammonia, hydrogen fluoride, acetic acid etc.

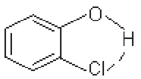




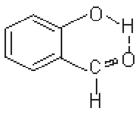
P- Nitrophenol with inter molecular hydrogen bonding

### b) Intramolecular Hydrogen Bonding:

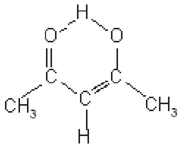
It is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. Some hydrogen bonded compounds, where the hydrogen bond is formed within the molecule such as in*o*-chlorophenol, salicylaldehyde, acetylacetone, ethylacetoacetate, etc., are shown in figure below.



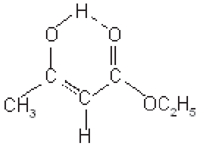
O – Chlorophenol



Salicylaldehyde



Acetylacetone



Ethyl acetoacetate

### Influence on physical properties of molecules

Though a weak bond, the hydrogen bond affects a large number of the physical properties of compounds, some of which are given below:

**1. Boiling points of liquids:** Hydrogen bonding tends to raise the boiling points of liquids and increases the heat of vaporization by increasing the intermolecular attractions and restricting the molecular rotations in liquid state. Hence, the hydrogen bonding results in greater entropy of vaporization. This is seen by considering a few examples.

a) Water, methanol and dimethyl ether: As the hydrogen atoms in water are replaced progressively by the methyl groups, the extent of the hydrogen bonding decreases as is reflected by the decreasing boiling points of the compounds: water (373 K) and dimethyl ether (268 K). For non-hydrogen bonded compounds, the change from hydrogen to methyl group results in the increase in the boiling points due to the increase in the molecular weights of the compounds.

b) Water and hydrogen sulphide: The hydrogen bonds in water raise its boiling points considerably in comparison with that of the non-hydrogen bonded hydrogen sulphide (B.P. 212.9 K).

c) Ammonia and phosphine: Ammonia is a hydrogen bonded compound with a higher boiling point (240 K) and higher melting point (195.5 K), higher heat of fusion and vaporization, than the non-hydrogen bonded phosphine.

d) Dimethyl sulphate, trimethyl phosphate and trimethyl borate have much lower boiling points (461 K, 466 K and 388 K, respectively) than the respective hydrogen compounds, i.e. sulphuric acid, phosphoric acid and boric acid which do not boil but decompose at 613 K, 485 K and 460 K, respectively with the loss of water. Further, a similar comparison can be made of hydrogen fluoride (B.P. 293.1 K) with methyl fluoride (B.P. 195 K); $HN_3$, hydrazoic acid (B.P. 310 K) and methyl azide, $CH_3N_2$ (B.P. 293 K).

**2. Solubility**: The solubility of organic compounds in water in attributed to hydrogen bond formation. Thus dimethyl ether, capable of forming hydrogen bonds with two water molecules is completely miscible with water, whereas dimethyl sulphide is partially miscible. Benzene is partially miscible with water but pyridine is miscible in all proportions due to the strong hydrogen bond formation through nitrogen atom. Sugars and dioxane also go into water completely due to the same reason.

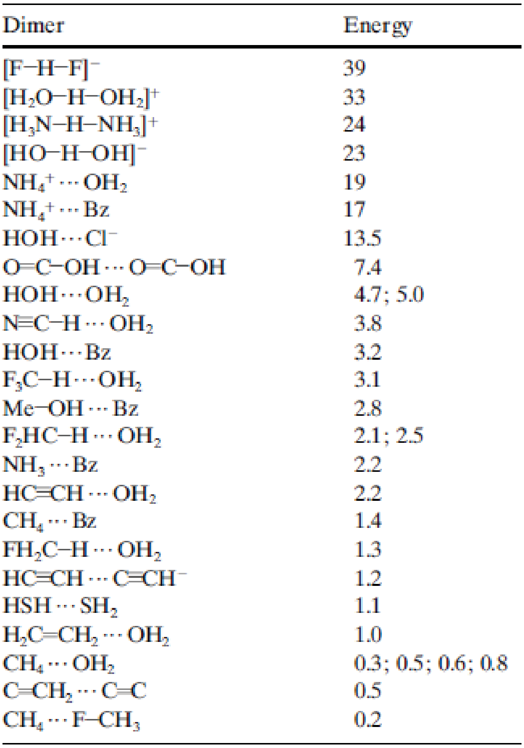
**3. Viscosity**: Intermolecular hydrogen bonding increases attractions between the molecules in the different layers of the hydrogen bonded liquids. This results in the increase in viscosity due to hindrance in the smooth flow of liquid layers over one another. This can be seen by comparing the viscosity of water (10.05 millipoise) on one hand, and with that of glycerol (about $10^4$ millipoise) on the other.

**4. Azeotropic behaviour**: There are many liquids which have no hydrogen bonding (e.g. halogenated hydrocarbons) but have slightly positively charged hydrogen atom. There are many other liquids which are also not hydrogen bonded, but have electron donor atoms, e.g. pyridine, ketones, esters, carboxylic acids or nitriles. If the liquids of these two classes are mixed, intermolecular hydrogen bonding is formed, and the mixtures show negative deviation from Raoult's law:

$$P = p_1 n_1 + p_2 n_2$$

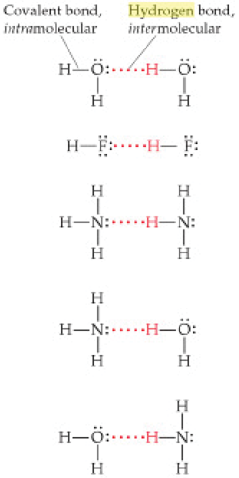
**5. Dielectric constants**: High dielectric constants of hydrogen bonded molecules may be due to the formation of polymeric species having enhanced dipole moments rather than the sum of the dipole moments of the constituent molecules. Substitution of a proton by a methyl group then reduces the dielectric constants, though in some cases where the methyl protons can take part in hydrogen bonding, the decrease in not much.

**Comparison of hydrogen bond strength**



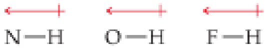
| Dimer | Energy |
|---|---|
| $[F{-}H{-}F]^-$ | 39 |
| $[H_2O{-}H{-}OH_2]^+$ | 33 |
| $[H_3N{-}H{-}NH_3]^+$ | 24 |
| $[HO{-}H{-}OH]^-$ | 23 |
| $NH_4^+ \cdots OH_2$ | 19 |
| $NH_4^+ \cdots Bz$ | 17 |
| $HOH \cdots Cl^-$ | 13.5 |
| $O{=}C{-}OH \cdots O{=}C{-}OH$ | 7.4 |
| $HOH \cdots OH_2$ | 4.7; 5.0 |
| $N{\equiv}C{-}H \cdots OH_2$ | 3.8 |
| $HOH \cdots Bz$ | 3.2 |
| $F_3C{-}H \cdots OH_2$ | 3.1 |
| $Me{-}OH \cdots Bz$ | 2.8 |
| $F_2HC{-}H \cdots OH_2$ | 2.1; 2.5 |
| $NH_3 \cdots Bz$ | 2.2 |
| $HC{\equiv}CH \cdots OH_2$ | 2.2 |
| $CH_4 \cdots Bz$ | 1.4 |
| $FH_2C{-}H \cdots OH_2$ | 1.3 |
| $HC{\equiv}CH \cdots C{\equiv}CH^-$ | 1.2 |
| $HSH \cdots SH_2$ | 1.1 |
| $H_2C{=}CH_2 \cdots OH_2$ | 1.0 |
| $CH_4 \cdots OH_2$ | 0.3; 0.5; 0.6; 0.8 |
| $C{=}CH_2 \cdots C{=}C$ | 0.5 |
| $CH_4 \cdots F{-}CH_3$ | 0.2 |

**Properties of hydrogen bonded N, O and F compounds**



In general the properties of hydrogen bonded compounds with N, O and F such as $NH_3$, $H_2O$ and HF has boiling points that are much higher than expected. In fact, these three compounds also have many other characteristics that distinguish them from other substances of similar molecular weight and polarity. For example, water has a high melting point, a high specific heat and a high heat of vaporization. Each of these properties indicates that the intermolecular forces are abnormally strong.

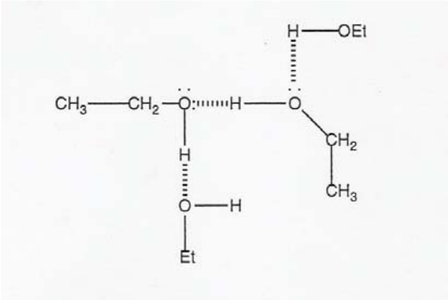
As discussed earlier, the strong intermolecular forces of attractions in the above three molecules results from hydrogen bonding. Hydrogen bonding can be considered as a type of dipole-dipole attraction. Because N, O and F are so electronegative, a bond between hydrogen and any of these elements is quite polar, with hydrogen at the positive end (remember the + sign on the right hand side):



The hydrogen atom has no inner electrons. Thus the positive side of the dipole has the concentrated charge of the nearly bare hydrogen nucleus. This positive charge is attracted to the negative charge of an electronegative atom in a nearby molecule. Because the electron-poor hydrogen is so small, it can approach an electronegative atom very closely and thus interact strongly with it.

Hydrogen bond (H-bond) is a weak bond, since it is merely electrostatic force of attraction and not a chemical bond. The strength of H-bond increases with increase of the electronegativity of the atom attached with H-atom by a covalent bond in N-H …. N, O-H … O and F-H … F. Now since the electronegativity of N, O and F is in the order of N < O < F, the strength of H-bond in N-H … N (e.g. in $NH_3$ molecules), O-H … O (e.g. in $H_2O$ molecules) and F-H … F (e.g. in HF molecules) is also in the same order, i.e. 8.37 kJ/mol, 29.29 kJ/mol and 41.85 kJ/mol respectively. H-bond is much stronger than van der Waals forces but weaker than a covalent bond and ionic bond.

**Hydrogen bonding in ethanol**



Hydrogen Bonding

Strong dipole-dipole interactions, usually involving the hydrogen (δ+) on an oxygen, nitrogen or fluorine interacting with another nitrogen, oxygen or fluorine are given the special name, hydrogen bond. Realize though, that hydrogen bonds are not **bonds,** they are interactions. The energy of a mole of hydrogen bonds is approximately 5 kcal joules, whereas a mole of RO-H covalent bonds has energy of 103 kcals. For comparison, a standard dipole-dipole interaction is approximately 2-3 kcal/mol joules.

Consider the following molecules and their respective boiling points to understand how profound an impact hydrogen-bonding can have.

$CH_3CH_2OH$ $CH_3$-$O$-$CH_3$

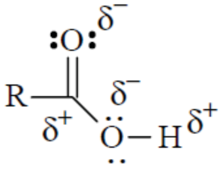
| | |
|---|---|
| ***B.P. 78.3°C*** | ***B.P. -25°C*** |
| ***Ethanol*** | ***Dimethyl Ether*** |

The above molecules are structural isomers and yet their boiling points differ by over 100°C! Why the big difference? Well, ethanol can hydrogen bond with itself and dimethyl ether can't. Ethanol forms a multiply hydrogen bonded network (illustrated on the next page) requiring a large input of energy to break up the cumulative interactions and vaporize the molecules.

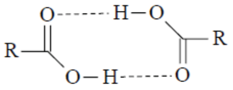
The dimethyl ether molecules do not have the requisite hydrogen on an electronegative N, 0 or F so they cannot act as hydrogen bond donors. Therefore, they do not hydrogen bond with each other. Though there are simple dipole-dipole interactions among the dimethyl ether molecules, they are much weaker as evidenced by the very low boiling point. Hydrogen bonding is extremely important in biological systems.

### Hydrogen bonding in acetic acid

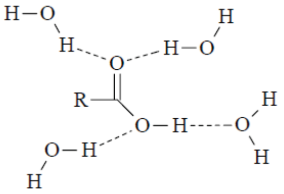
The carboxylic acid moiety is considered to be a highly polar organic functional group. This polarity results from the presence of a strongly polarized carbonyl (C=O) group and hydroxyl (O-H) group. Recall that oxygen is a relatively electronegative atom and when covalently bound to carbon and particularly hydrogen, a strong permanent dipole is created. In the case of carboxylic acids, the O-H group is even more strongly polarized than the O-H group of alcohols due to the presence of the adjacent carbonyl moiety.



The dipoles present in carboxylic acids allow these compounds to participate in energetically favorable hydrogen bonding (H-bonding) interactions with like molecules and water, functioning as both a H-bond donor and acceptor as shown below:

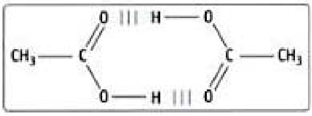


Intermolecular H-Bonding



H-Bonding with Water

When acetic acid is dissolved in benzene, the solute particles appear to have a relative molecular mass twice as large as expected. This is due to the formation of hydrogen-bonded dimers in benzene. The dimers are particularly stable because each pair of acid molecules is linked by two H-bonds. The presence of dimerised pairs of carboxylic acid molecules in benzene has been confirmed by electron diffraction measurements. Studies of the relative molecular mass of ethanoic acid in the vapor state also suggest the presence of dimers.



### 4.3 Crystalline hydrates [Metallic or Non-stoichiometric (**or Interstitial**) Hydrides]

Hydrates, i.e. crystal forms containing water as integral part of the crystal lattice, are frequent and well recognised. Of the total of 596 810 crystal structures filed in the Cambridge Structural Database (as of May 2012), 88 470 structures, *i.e.* 15%, contain water, more than any other solvent. Hydrates show a wide range of properties such as physical and chemical stability, intermolecular interactions and solubilities, and can be very different in this regard from the parent, anhydrous material.

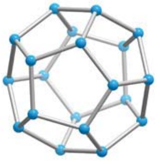
These are formed by many *d*-block and *f*-blockelements. However, the metals of group 7, 8and 9 do not form hydride. Even from group6, only chromium forms CrH. These hydridesconduct heat and electricity though not asefficiently as their parent metals do. Unlikesaline hydrides, they are almost always nonstoichiometric,being deficient in hydrogen.

**For example,**

$LaH_2$.YbH,TiH, ZrH,
VH, NiH, PdHetc.

In suchhydrides, the law of constant composition doesnot hold good.Earlier it was thought that in thesehydrides, hydrogen occupies interstices in themetal lattice producing distortion without anychange in its type. Consequently, they weretermed as interstitial hydrides. However, recentstudies have shown that except for hydridesof Ni, Pd, Ce and Ac, other hydrides of this classhave lattice different from that of the parentmetal. The property of absorption of hydrogenon transition metals is widely used in catalyticreduction / hydrogenation reactions for thepreparation of large number of compounds.Some of the metals (e.g., Pd, Pt) canaccommodate a very large volume of hydrogenand, therefore, can be used as its storagemedia. This property has high potential for**hydrogen storage** and as a **source of energy**

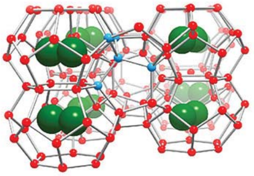
### 4.4 Clathrates



The clathrates can also be called a gas hydrate.Water forms into a different geometric shape than hexagonal ice when water and gas come into contact with each other at high pressure and low temperature. Frozen water' host, molecules form a cage that can hold a 'guest' gas molecule.

**Nature of Gas Hydrate**

1. It has less density than the original crystalline water structure due to the guest gas molecule.
2. It form differently shaped lattice to accommodate gas molecules.
3. The cage is held together by hydrogen bonds between water molecules and stabilized by van der walls forces. Van der Waals forces are the forces between the gas and water molecules. It is the Vader Waals force that makes the gas hydrate very stable, in fact the clathrate hydrate is more stable than hexagonal ice. Gas hydrates are characterised by the shape of their cages.



Clathrate Hydrate

The above illustration shows the model of a Clathrate with trapped guest molecules of gas inside the ice cages of the host molecule.

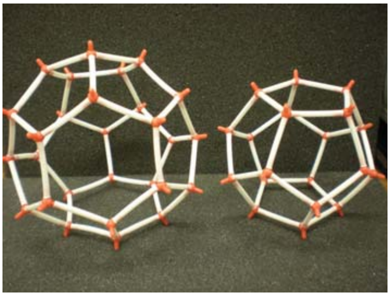
**There two types of Clathrates**

In type I where Methane molecule is trapped between the water molecules.

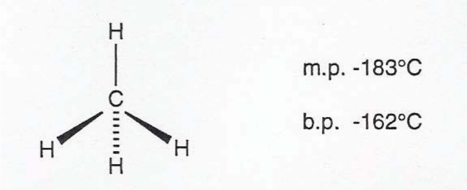
- Type I clathrate hydrates trap methane gas ($CH_4$)
- Methane rearranges host water molecules to form a cage and remains trapped inside the cage.
- Not every cage attracts a gas molecule. Some hosts remain empty. Placement is random and can be either of the two sized cages however larger the cage is preferred.
- When the clathrate hydrate melts, methane is released.

In type II

- Trap propane (C3H8) gas in their cages.
- Can only occupy the larger of the two cages.
- The dodecahedron cages are too small for their large propane molecules.



## 4.5 Van der Waals Forces



Why do non-polar substances have melting points or boiling points? Consider the physical properties given for methane.

Now these are very low numbers, but why would methane liquefy or solidify? What forces help to bind them together? The answer is Van-der Waals forces (also called induced dipole-induced dipole or London forces).

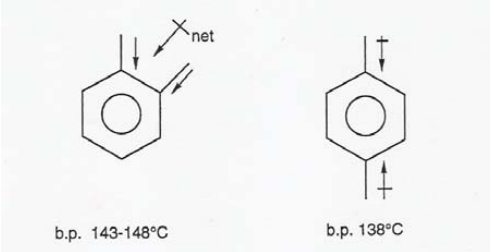
These relatively weak (but can be strong in large molecules) forces involve the cloud of electrons that encompasses any molecule. Even though we think of the methane (or any similarly symmetrical) molecule as being perfectly symmetrical, at any given moment in time the cloud is not. At any given moment, one side of the molecule might have a slight electron deficiency (δ+) and the other, a slight electron excess (δ -) due to repulsive interactions with surrounding methane molecules. This small dipole has an effect on the electron clouds of nearby molecules, inducing complimentary dipole moments. The small attractions between the dipoles lead to forces sufficient to allow methane to liquefy and solidify.

When molecules become larger, the Van der Waals forces become larger. This fact helps account for the nearly linear relationship between increases in boiling point with increasing numbers of carbons in a homologous series of organic compounds. For example, n-pentane boils at 36°C and n-hexane at 69°C.

**Dipole-Dipole Forces**

A **dipole** is a molecule that has both positive and negative regions. Although we talk as though electrons distribute their time evenly among all atoms in a molecule, some elements have more affinity for the electrons than others, and they hang out around that atom more. A **polar molecule** is a molecule with a slightly positive side and a slightly negative side. I always think about the North and South Poles of the earth to help me remember what a polar molecule is. A **dipole-dipole force** is when the positive side of a polar molecule attracts the negative side of another polar molecule. In order for this kind of bond to work, the molecules need to be very close to each other, like they are in a liquid.

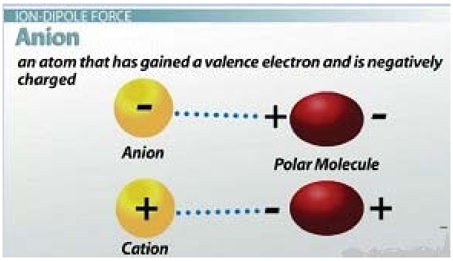
Dipole-dipole forces are considerably weaker than ion-ion forces, but if significant, can have a large influence on physical properties. Dipole-dipole forces are important for molecules having net dipole moments, i.e., molecules having atoms with differing electronegativities arranged in such a way that the center of positive charge is different from the center of negative charge. In other words, the electron cloud is distorted so that an area(s) of the molecule is richer in electron density and another area is depleted of electron density. When in close proximity, the molecules will align themselves in such a way that the poles are complementary, i.e., δ+ with δ - and δ - with δ +. As examples, consider hydrogen fluoride and chloromethane shown below.
If the dipole moments are large, the attraction between the δ + and δ- of different molecules is strong and can serve to tightly pack the molecules into a solid.



Consider the following example of how changes in dipole moment can influence the boiling points of position isomers. Ignoring the benzene rings which both of the illustrated compounds have in common, ortho-xylene has a small net dipole moment and para-xylene has none. As you may have surmised from the previous examples, net dipole moments are vector quantities which are determined by "resolving" the individual bond dipole moments. The direction of the net dipole moment is based on the direction and magnitude of the individual vectors. If you haven't encountered vector resolution in your previous studies and you don't understand it, you should see your instructor. The fact that ortho-xylene has a larger dipole moment than p-xylene means that its binding forces are stronger and that more energy is needed to separate the molecules and send them into the gas phase. Therefore, o-xylene has a higher boiling point than para-xylene.

### 4.6 Ion dipole – dipole interactions

An **ion-dipole force** is just what its name says. It is a force between an ion and a dipole molecule. Remember that an **ion** is an atom that has gained or lost one or more electrons and therefore has a negative or positive charge. A **cation** is an atom that has lost a valence electron and therefore has more positive protons than negative electrons, so it is positively charged. An **anion** is an atom that has gained a valence electron and is negatively charged.



So knowing that a dipole molecule has a slight charge on either side and that ions have charges, either negative or positive, you can understand how these would bond together. Cations would be attracted to the negative side of a polar molecule and anions would be attracted to the positive side.

# Unit V: Acids and Bases

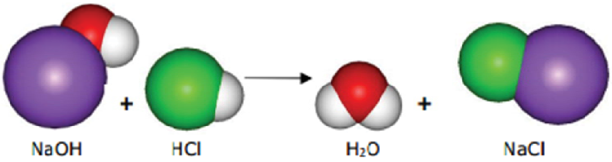
## Syllabus

Types of chemical reactions: acid-base, oxidation-reduction, electron transfer and doubledecomposition reactions; balancing chemical reactions by oxidation number and ion electronmethod - Theories of acids and bases: Arrhenius theory, acids and bases in protic solvents, Bronsted-Lowry theory, Lewis theory, the solvent system, Lux-Flood definition, Usanovichdefinition; hard and soft acids and bases-HSAB principle - Nonaqueous solvents: classificationprotonicand aprotic solvents, liquid ammonia as solvent-solutions of alkali and alkaline earthmetals in ammonia.

## 5.1 Types of chemical reactions

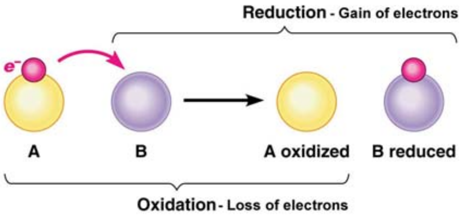
### Acid-base reactions

When an **acid** and a **base** are placed together, they **react** to neutralize the **acid** and **base** properties, producing a salt. The H(+) cation of the **acid** combines with the OH(-) anion of the **base** to form water. The compound formed by the cation of the **base** and the anion of the **acid** is called a salt.



### Oxidation-reduction reactions

An **oxidation-reduction** (**redox**) **reaction** is a type of chemical **reaction** that involves a transfer of electrons between two species. An **oxidation-reduction reaction** is any chemical **reaction** in which the **oxidation** number of a molecule, atom, or ion changes by gaining or losing an electron.

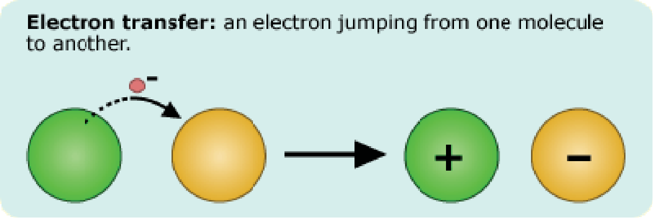


For example, when natural gas burns, for example, an oxidation-reduction reaction occurs that releases more than 800 kJ/mol of energy.

$$CH_4(g) + 2\ O_2(g) \longrightarrow CO_2(g) + 2\ H_2O(g)$$

### Electron transfer reactions

**Electron transfer** reaction (ET) occurs when an electron moves from an atom or a chemical species (e.g. a molecule) to another atom or chemical species.


**Electron transfer:** an electron jumping from one molecule to another.

Consider the following reaction,

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

With oxidation numbers insertedas superscripts, this reaction is written as:

$$4Al^{(0)} + 3O_2^{(0)} \rightarrow 2Al_2^{(+3)}O_3^{(-2)}$$

It is shown that both the elements aluminium and oxygen change its oxidation number. Because the oxidation numbers change as electrons are transferred between atoms. In the example, each oxygen atom has gained two electrons and eachaluminium has lost three electrons.

In an electron transfer reaction, an element undergoing oxidation lose electrons, where an element gaining electrons undergoes reduction. In the aluminium-Oxygen example, the aluminium was electron transfer reaction involves simultaneous oxidation and reduction. These reactions are frequently called redox reactions.

In the above reaction oxidising agent(in the example, oxygen) is reduced, whereas the reducing agent in the example, aluminium) is oxidised.

**Double decomposition reactions**

In **decomposition reactions**, one compound is converted into two or more simpler substances. The products can be either elements or compounds. For example, when an electric current is passed through liquid water or molten sodium chloride, these compounds decompose to form their elements.

$$2H_2O(l) \xrightarrow{\text{Electric current}} 2H_2(g) + O_2(g)$$

$$2NaCl(l) \xrightarrow{\text{Electric current}} 2Na(l) + Cl_2(g)$$

$$A \rightarrow B + C$$

**Example:**

The decomposition of mercury(II) oxide into its elements when the compound is heated. This is anoxidation–reduction reaction.

$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$

Another example is the preparation of oxygen by heating potassium chlorate with manganese(IV) oxide as a catalyst.

$$2KClO_3(s) \xrightarrow[MnO_2]{\Delta} 2KCl(s) + 3O_2(g)$$

Not all decomposition reactions are of the oxidation–reduction type.

**For example**

Calcium carbonate at high temperatures decomposes into calcium oxide and carbondioxide.

$$CaCO_{3(s)} \overset{\Delta}{\rightarrow} CaO_{(s)} + CO_{2(g)}$$

**Balancing chemical reactions**

Two methods are used to balance chemicalequations for redox processes. One of thesemethods is based on the change in theoxidation number of reducing agent and theoxidising agent and the other method is basedon splitting the redox reaction into two half reactions. Both these methodsare in use and the choice of their use rests withthe individual using them.

**1. Oxidation number method**

In writingequations for oxidation-reduction reactions,just as for other reactions, the compositionsand formulas must be known for thesubstances that react and for the products thatare formed. The oxidation number method isnow best illustrated in the following steps:

**Step 1:**

Write the correct formula for eachreactant and product.

**Step 2:**

Identify atoms which undergo changein oxidation number in the reaction byassigning the oxidation number to all elementsin the reaction.

**Step 3:**

Calculate the increase or decrease inthe oxidation number per atom and for theentire molecule/ion in which it occurs. If theseare not equal then multiply by suitablecoefficients so that these become equal. (If yourealise that two substances are reduced andnothing is oxidised or vice-versa, somethingis wrong. Either the formulas of reactants orproducts are wrong or the oxidation numbershave not been assigned properly).

**Step 4:**

Ascertain the involvement of ions ifthe reaction is taking place in water, add $H^+$ or$OH^-$ions to the expression on the appropriateside so that the total ionic charges of reactantsand products are equal. If the reaction iscarried out in acidic solution, use $H^+$ ions inthe equation; if in basic solution, use $OH^-$ions.

**Step 5:**

Make the numbers of hydrogen atomsin the expression on the two sides equal byadding water ($H_2O$) molecules to the reactantsor products. Now, also check the number ofoxygen atoms. If there are the same numberof oxygen atoms in the reactants andproducts, the equation then represents thebalanced redox reaction.Let us now explain the steps involved inthe method with the help of a few problems given below.

**Illustration**

Write the net ionic equation for the reaction of potassium dichromate (VI), $K_2Cr_2O_7$ with sodium sulphite, $Na_2SO_3$, in an acid solution to give chromium (III) ion and the sulphate ion.

**Step 1:**

The skeletal ionic equation is:

$$Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$$

**Step 2:**

Assign oxidation numbers for Cr and S

$$\overset{+6}{Cr}_2\overset{-2}{O}_7^{2-}(aq) + \overset{+4}{S}\overset{-2}{O}_3^{2-}(aq) \rightarrow \overset{+3}{Cr}(aq)+\overset{+6}{S}\overset{-2}{O}_4^{2-}(aq)$$

This indicates that the dichromate ion is the oxidant and the sulphite ion is the reductant.

**Step 3:**

Calculate the increase and decrease of oxidation number, and make them equal:

$$\overset{+6}{Cr}_2\overset{-2}{O}_7^{2-}(aq) + \overset{+4}{S}\overset{-2}{O}_3^{2-}(aq) \rightarrow \overset{+3}{Cr}(aq)+\overset{+6}{S}\overset{-2}{O}_4^{2-}(aq)$$

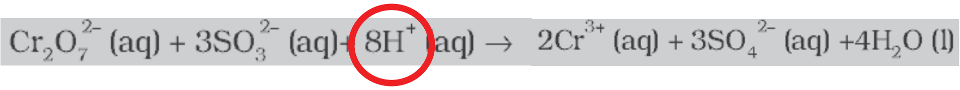
**Step 4:**

As the reaction occurs in the acidic medium, and further the ionic charges are not equal on both the sides, add $8H^+$ on the left to make ionic charges equal.

$$\overset{+6}{Cr}_2\overset{-2}{O}_7^{2-}(aq) + 3\overset{+4}{S}\overset{-2}{O}_3^{2-}(aq) \rightarrow 2\overset{+3}{Cr}^{3+}(aq) + 3\overset{+6}{S}\overset{-2}{O}_4^{2-}(aq)$$

**Step 5:**

Finally, count the hydrogen atoms, and add appropriate number of water molecules (i.e., $4H_2O$) on the right to achieve balanced redox change.

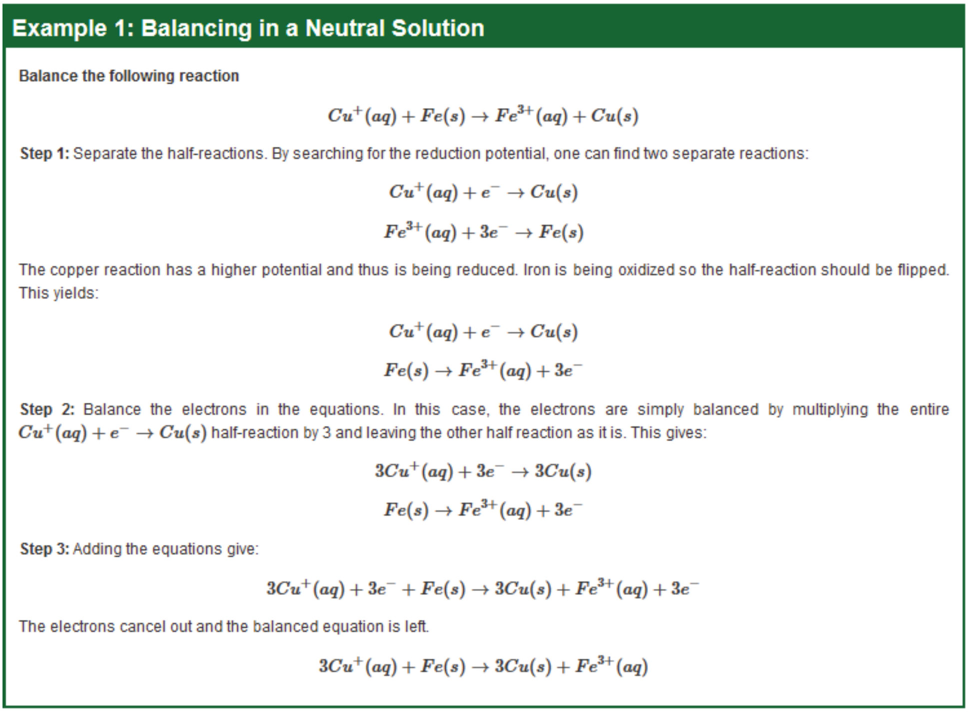


$$Cr_2O_7^{2-}\ (aq) + 3SO_3^{2-}\ (aq) + 8H^+\ (aq) \rightarrow 2Cr^{3+}\ (aq) + 3SO_4^{2-}\ (aq) + 4H_2O\ (l)$$

## 2. Half Reaction Method:

In this method,the two half equations are balanced separately and then added together to give balanced equation.

### 2a. Reactions in neutral medium



**Example 1: Balancing in a Neutral Solution**

**Balance the following reaction**

$$Cu^+(aq) + Fe(s) \rightarrow Fe^{3+}(aq) + Cu(s)$$

**Step 1:** Separate the half-reactions. By searching for the reduction potential, one can find two separate reactions:

$$Cu^+(aq) + e^- \rightarrow Cu(s)$$

$$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$$

The copper reaction has a higher potential and thus is being reduced. Iron is being oxidized so the half-reaction should be flipped. This yields:

$$Cu^+(aq) + e^- \rightarrow Cu(s)$$

$$Fe(s) \rightarrow Fe^{3+}(aq) + 3e^-$$

**Step 2:** Balance the electrons in the equations. In this case, the electrons are simply balanced by multiplying the entire $Cu^+(aq) + e^- \rightarrow Cu(s)$ half-reaction by 3 and leaving the other half reaction as it is. This gives:

$$3Cu^+(aq) + 3e^- \rightarrow 3Cu(s)$$

$$Fe(s) \rightarrow Fe^{3+}(aq) + 3e^-$$

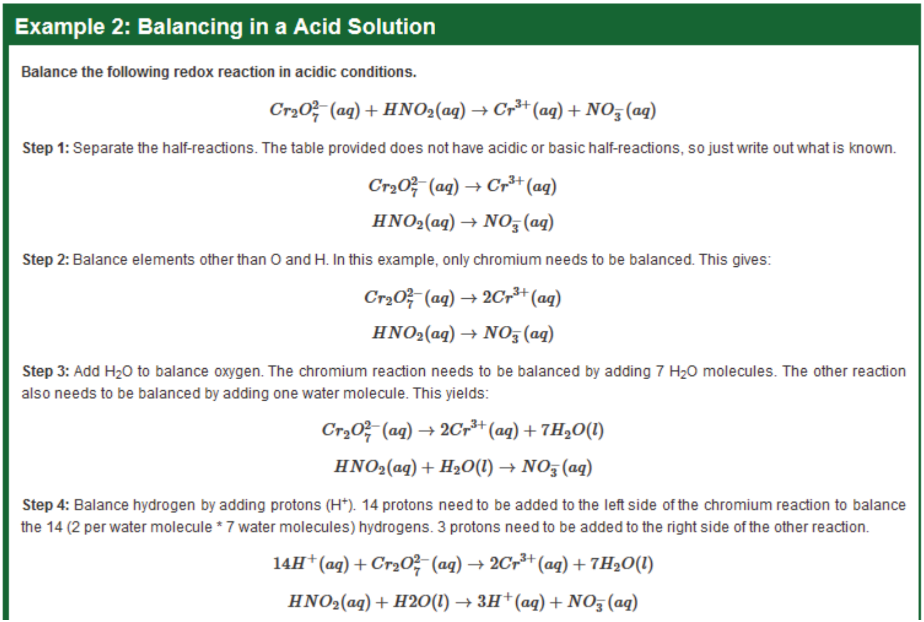
**Step 3:** Adding the equations give:

$$3Cu^+(aq) + 3e^- + Fe(s) \rightarrow 3Cu(s) + Fe^{3+}(aq) + 3e^-$$

The electrons cancel out and the balanced equation is left.

$$3Cu^+(aq) + Fe(s) \rightarrow 3Cu(s) + Fe^{3+}(aq)$$

### 2b. Reactions in acid medium



### Example 2: Balancing in a Acid Solution

**Balance the following redox reaction in acidic conditions.**

$$Cr_2O_7^{2-}(aq) + HNO_2(aq) \rightarrow Cr^{3+}(aq) + NO_3^-(aq)$$

**Step 1:** Separate the half-reactions. The table provided does not have acidic or basic half-reactions, so just write out what is known.

$$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$$

$$HNO_2(aq) \rightarrow NO_3^-(aq)$$

**Step 2:** Balance elements other than O and H. In this example, only chromium needs to be balanced. This gives:

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$$

$$HNO_2(aq) \rightarrow NO_3^-(aq)$$

**Step 3:** Add $H_2O$ to balance oxygen. The chromium reaction needs to be balanced by adding 7 $H_2O$ molecules. The other reaction also needs to be balanced by adding one water molecule. This yields:

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$HNO_2(aq) + H_2O(l) \rightarrow NO_3^-(aq)$$

**Step 4:** Balance hydrogen by adding protons ($H^+$). 14 protons need to be added to the left side of the chromium reaction to balance the 14 (2 per water molecule * 7 water molecules) hydrogens. 3 protons need to be added to the right side of the other reaction.

$$14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$HNO_2(aq) + H2O(l) \rightarrow 3H^+(aq) + NO_3^-(aq)$$

Acidic conditions usually implies a solution with an excess of $H^+$ concentration, hence making the solution acidic. The balancing starts by separating the reaction into half-reactions. However, instead of immediately balancing the electrons, balance all the elements in the half-reactions that are not hydrogen and oxygen. Then, add $H_2O$ molecules to balance any oxygen atoms. Next, balance the hydrogen atoms by adding protons ($H^+$). Now, balance the *charge* by adding electrons and scale the electrons (multiply by the lowest common multiple) so that they will cancel out when added together. Finally, add the two half-reactions and cancel out common terms.

**Step 5:** Balance the charge of each equation with electrons. The chromium reaction has (14+) + (2-) = 12+ on the left side and (2 * 3+) = 6+ on the right side. To balance, add 6 electrons (each with a charge of -1) to the left side:

$$6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

For the other reaction, there is no charge on the left and a (3+) + (-1) = 2+ charge on the right. So add 2 electrons to the right side:

$$HNO_2(aq) + H_2O(l) \rightarrow 3H^+(aq) + NO_3^-(aq) + 2e^-$$

**Step 6:** Scale the reactions so that the electrons are equal. The chromium reaction has 6e$^-$ and the other reaction has 2e$^-$, so it should be multiplied by 3. This gives:

$$3 * [HNO_2(aq) + H_2O(l) \rightarrow 3H^+(aq) + NO_3^-(aq) + 2e^-] \Rightarrow$$

$$3HNO_2(aq) + 3H_2O(l) \rightarrow 9H^+(aq) + 3NO_3^-(aq) + 6e^-$$

$$6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l).$$

**Step 7:** Add the reactions and cancel out common terms.

$$[3HNO_2(aq) + 3H_2O(l) \rightarrow 9H^+(aq) + 3NO_3^-(aq) + 6e^-] +$$

$$[6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)] =$$

$$3HNO_2(aq) + 3H_2O(l) + 6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 9H^+(aq) + 3NO_3^-(aq) + 6e^- + 2Cr^{3+}(aq) + 7H_2O(l)$$

The electrons cancel out as well as 3 water molecules and 9 protons. This leaves the balanced net reaction of:

$$3HNO_2(aq) + 5H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 3NO_3^-(aq) + 2Cr^{3+}(aq) + 4H_2O(l)$$

## 2c. Reactions in basic medium

### Example 3: Balancing in Basic Solution

**Balance the following redox reaction in basic conditions.**

$$Ag(s) + Zn^{2+}(aq) \rightarrow Ag_2O(aq) + Zn(s)$$

Go through all the same steps as if it was in acidic conditions.

**Step 1:** Separate the half-reactions.

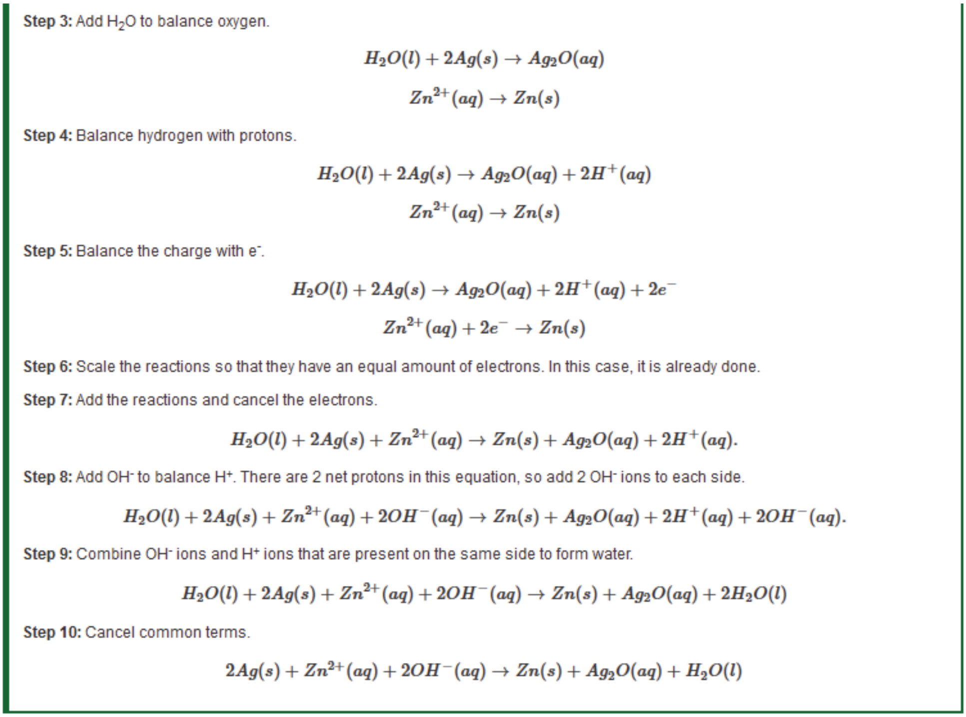
$$Ag(s) \rightarrow Ag_2O(aq)$$

$$Zn^{2+}(aq) \rightarrow Zn(s)$$

**Step 2:** Balance elements other than O and H.

$$2Ag(s) \rightarrow Ag_2O(aq)$$

$$Zn^{2+}(aq) \rightarrow Zn(s)$$



**Step 3:** Add $H_2O$ to balance oxygen.

$$H_2O(l) + 2Ag(s) \rightarrow Ag_2O(aq)$$

$$Zn^{2+}(aq) \rightarrow Zn(s)$$

**Step 4:** Balance hydrogen with protons.

$$H_2O(l) + 2Ag(s) \rightarrow Ag_2O(aq) + 2H^+(aq)$$

$$Zn^{2+}(aq) \rightarrow Zn(s)$$

**Step 5:** Balance the charge with $e^-$.

$$H_2O(l) + 2Ag(s) \rightarrow Ag_2O(aq) + 2H^+(aq) + 2e^-$$

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$$

**Step 6:** Scale the reactions so that they have an equal amount of electrons. In this case, it is already done.

**Step 7:** Add the reactions and cancel the electrons.

$$H_2O(l) + 2Ag(s) + Zn^{2+}(aq) \rightarrow Zn(s) + Ag_2O(aq) + 2H^+(aq).$$

**Step 8:** Add $OH^-$ to balance $H^+$. There are 2 net protons in this equation, so add 2 $OH^-$ ions to each side.

$$H_2O(l) + 2Ag(s) + Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Zn(s) + Ag_2O(aq) + 2H^+(aq) + 2OH^-(aq).$$

**Step 9:** Combine $OH^-$ ions and $H^+$ ions that are present on the same side to form water.

$$H_2O(l) + 2Ag(s) + Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Zn(s) + Ag_2O(aq) + 2H_2O(l)$$

**Step 10:** Cancel common terms.

$$2Ag(s) + Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Zn(s) + Ag_2O(aq) + H_2O(l)$$

## 5.2 Theories of acids and bases

### The Arrhenius theory

- Acids are substances that produce hydrogen ions in solution.
- Bases are substances that produce hydroxide ions in solution.

Neutralization happens because hydrogen ions and hydroxide ions react to produce water.

$$H^+_{(aq)} + OH^-(aq) \rightarrow H_2O_{(l)}$$

Hydrochloric acid is neutralized by both sodium hydroxide solution and ammonia solution. In both cases, you get a colorless solution which you can crystallize to get a white salt - either sodium chloride or ammonium chloride. These are clearly very similar reactions. The full equations are:

$$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

$$NH_{3(aq)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)}$$

In the sodium hydroxide case, hydrogen ions from the acid are reacting with hydroxide ions from the sodium hydroxide - in line with the Arrhenius theory. However, in the ammonia case, there do not appear to be any hydroxide ions! You can get around this by saying that the ammonia reacts with the water it is dissolved in to produce ammonium ions and hydroxide ions:

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

This is a reversible reaction, and in a typical dilute ammonia solution, about 99% of the ammonia remains as ammonia molecules. Nevertheless, there are hydroxide ions there, and we can squeeze this into the Arrhenius theory. However, this same reaction also happens between ammonia gas and hydrogen chloride gas.

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$$

In this case, there are no hydrogen ions or hydroxide ions in solution - because there is not any solution. The Arrhenius theory would not count this as an acid-base reaction, despite the fact that it is producing the same product as when the two substances were in solution.

**Acids and bases in protic solvents**

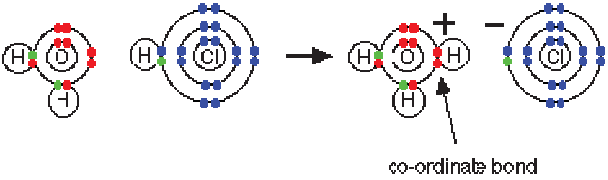
Protic solvents have hydrogen bound directly to electronegative atoms,such as oxygen or nitrogen. They are characterized by their abilityto form strong hydrogen bonds with suitable acceptors, particularlysimple anions. They include alcohols, formamide and other primaryand secondary amides, and formic acid. In methanol, dissociationconstants of carboxylic acids, phenols, and protonated nitrogen basesshow excellent correlations with corresponding values in water.

**The Brønsted-Lowry Theory of acids and bases**

- An acid is a proton (hydrogen ion) donor.
- A base is a proton (hydrogen ion) acceptor.

The Brønsted-Lowry theory does not go against the Arrhenius theory in any way - it just adds to it. Hydroxide ions are still bases because they accept hydrogen ions from acids and form water. An acid produces hydrogen ions in solution because it reacts with the water molecules by giving a proton to them.

When hydrogen chloride gas dissolves in water to produce hydrochloric acid, the hydrogen chloride molecule gives a proton (a hydrogen ion) to a water molecule. A coordinate (dative covalent) bond is formed between one of the lone pairs on the oxygen and the hydrogen from the $HCl$. Hydronium ions, $H_3O^+_{(aq)}$, are produced.

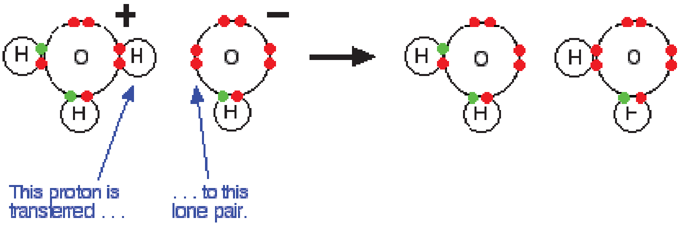


$$H_2O + HCl \rightarrow H_3O^+ + Cl^-$$

When an acid in solution reacts with a base, what is actually functioning as the acid is the hydronium ion. For example, a proton is transferred from a hydronium ion to a hydroxide ion to make water.

$$H_3O^+_{(aq)} + OH^-_{(aq)} \rightarrow 2H_2O_{(l)}$$

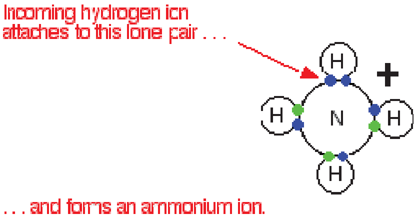
Showing the electrons, but leaving out the inner ones:



It is important to realize that whenever you talk about hydrogen ions in solution, $H^+_{(aq)}$, what you are actually talking about are hydronium ions.

**The hydrogen chloride / ammonia problem**

This is no longer a problem using the Brønsted-Lowry theory. Whether you are talking about the reaction in solution or in the gas state, ammonia is a base because it accepts a proton (a hydrogen ion). The hydrogen becomes attached to the lone pair on the nitrogen of the ammonia via a co-ordinate bond.



If it is in solution, the ammonia accepts a proton from a hydronium ion:

$$NH_{3(aq)} + H_3O^+_{(aq)} \rightarrow NH^+_{4(aq)} + H_2O_{(l)}$$

If the reaction occurs in the gas state, the ammonia accepts a proton directly from the hydrogen chloride:

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$$

Either way, the ammonia acts as a base by accepting a hydrogen ion from an acid.

### Conjugate pairs

When hydrogen chloride dissolves in water, almost 100% of it reacts with the water to produce hydronium ions and chloride ions. Hydrogen chloride is a strong acid, and we tend to write this as a one-way reaction:

$$H_2O + HCl \rightarrow H_3O^+ + Cl^-$$

In fact, the reaction between HCl and water is reversible, but only to a very minor extent. To generalize, consider an acid *HA*, and think of the reaction as being reversible.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

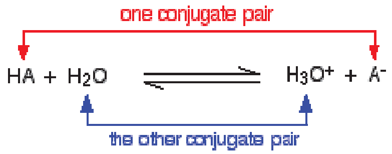
Thinking about the forward reaction:

- The *HA* is an acid because it is donating a proton (hydrogen ion) to the water.
- The water is a base because it is accepting a proton from the *HA*.

However, there is also a back reaction between the hydronium ion and the $A-$ ion:

- The $H_3O^+$ is an acid because it is donating a proton (hydrogen ion) to the $A-$ion.
- The$A^-$ ion is a base because it is accepting a proton from the $H_3O^+$.

The reversible reaction contains two acids and two bases. We think of them in pairs, called *conjugate pairs*.



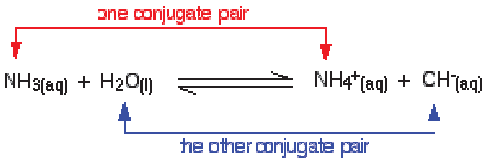
When the acid, *HA*, loses a proton it forms a base, $A-$, which can accept a proton back again to refom the acid, *HA*. These two are a *conjugate pair*. Members of a conjugate pair differ from each other by the presence or absence of the transferable hydrogen ion.

- If you are thinking about *HA* as the acid, then $A-$ is its conjugate base.
- If you are thinking about $A-$ as the base, then *HA* is its conjugate acid.

The water and the hydronium ion are also a conjugate pair. Thinking of the water as a base, the hydronium ion is its conjugate acid because it has the extra hydrogen ion which it can give away again. Thinking about the hydronium ion as an acid, then water is its conjugate base. The water can accept a hydrogen ion back again to reform the hydronium ion.

### A second example of conjugate pairs

This is the reaction between ammonia and water that we looked at earlier:

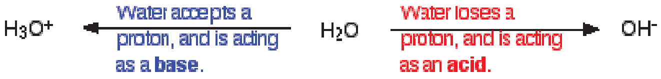


Think first about the forward reaction. Ammonia is a base because it is accepting hydrogen ions from the water. The ammonium ion is its conjugate acid - it can release that hydrogen ion again to reform the ammonia.

The water is acting as an acid, and its conjugate base is the hydroxide ion. The hydroxide ion can accept a hydrogen ion to reform the water. Looking at it from the other side, the ammonium ion is an acid, and ammonia is its conjugate base. The hydroxide ion is a base and water is its conjugate acid.

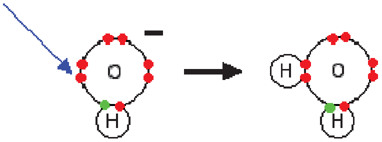
## Amphoteric substances

You may possibly have noticed (although probably not!) that in one of the last two examples, water was acting as a base, whereas in the other one it was acting as an acid. A substance which can act as either an acid or a base is described as being amphoteric.

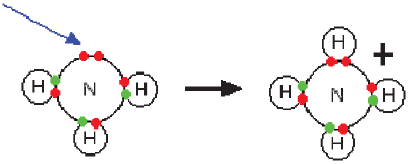


## The Lewis Theory of acids and bases

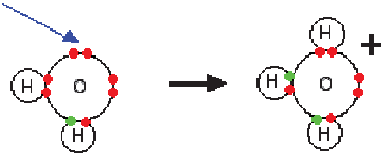
A hydroxide ion picks up a hydrogen ion by attaching it to one of the lone pairs on the oxygen.



Ammonia picks up a hydrogen ion by attaching it to the lone pair on the nitrogen.



Water picks up a hydrogen ion by attaching it to one of the lone pairs on the oxygen.



This theory extends well beyond the things you normally think of as acids and bases.

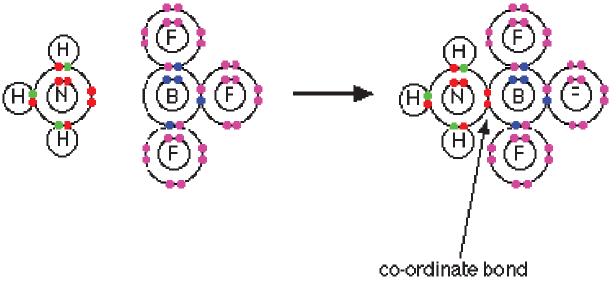
- An acid is an electron pair acceptor.
- A base is an electron pair donor.

### Lewis bases

It is easiest to see the relationship by looking at exactly what Brønsted-Lowry bases do when they accept hydrogen ions. Three Brønsted-Lowry bases we've looked at are hydroxide ions, ammonia and water, and they are typical of all the rest.

The Brønsted-Lowry theory says that they are acting as bases because they are combining with hydrogen ions. The reason they are combining with hydrogen ions is that they have lone pairs of electrons - which is what the Lewis theory says. The two are entirely consistent. So how does this extend the concept of a base? At the moment it doesn't - it just looks at it from a different angle.

But what about other similar reactions of ammonia or water, for example? On the Lewis theory, any reaction in which the ammonia or water used their lone pairs of electrons to form a co-ordinate bond would be counted as them acting as a base. Here is a reaction which you will find talked about on the page dealing with co-ordinate bonding. Ammonia reacts with $BF_3$ by using its lone pair to form a co-ordinate bond with the empty orbital on the boron.



As far as the ammonia is concerned, it is behaving exactly the same as when it reacts with a hydrogen ion - it is using its lone pair to form a co-ordinate bond. If you are going to describe it as a base in one case, it makes sense to describe it as one in the other case as well.

### Lewis acids

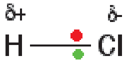
Lewis acids are electron pair acceptors. In the above example, the $BF_3$ is acting as the Lewis acid by accepting the nitrogen's lone pair. On the Brønsted-Lowry theory, the $BF_3$ has nothing remotely acidic about it. This is an extension of the term acid well beyond any common use.

What about more obviously acid-base reactions - like, for example, the reaction between ammonia and hydrogen chloride gas?

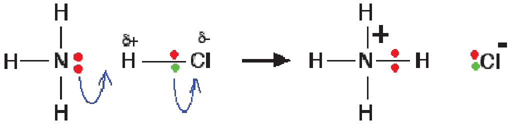
$$NH_{3(g)} + HCl_{g)} \rightarrow NH^{+}_{4(s)} + Cl^{-}_{(s)}$$

What exactly is accepting the lone pair of electrons on the nitrogen. Textbooks often write this as if the ammonia is donating its lone pair to a hydrogen ion - a simple proton with no electrons around it. That is misleading! You don't usually get free hydrogen ions in chemical systems. They are so reactive that they are always attached to something else. There aren't any uncombined hydrogen ions in HCl.

There isn't an empty orbital anywhere on the HCl which can accept a pair of electrons. Why, then, is the HCl a Lewis acid? Chlorine is more electronegative than hydrogen, and that means that the hydrogen chloride will be a polar molecule. The electrons in the hydrogen-chlorine bond will be attracted towards the chlorine end, leaving the hydrogen slightly positive and the chlorine slightly negative.



The lone pair on the nitrogen of an ammonia molecule is attracted to the slightly positive hydrogen atom in the HCl. As it approaches it, the electrons in the hydrogen-chlorine bond are repelled still further towards the chlorine. Eventually, a coordinate bond is formed between the nitrogen and the hydrogen, and the chlorine breaks away as a chloride ion.This is best shown using the "curly arrow" notation commonly used in organic reaction mechanisms.



The whole HCl molecule is acting as a Lewis acid. It is accepting a pair of electrons from the ammonia, and in the process it breaks up. Lewis acids don't necessarily have to have an existing empty orbital.

### 5.3 The solvent system

The concept of the solvent system as a means for explaining acid-base behavior had its origin with E.C. Franklin in 1905.

The solvent system definition applies to any solvent that can dissociate into a cation and an anion (autodissociation), where the cation resulting from this process of the solvent is acid and the anion is the base. Solutes that increase the concentration of the cation of the solvent are considered bases.

The classic solvent system is water, which undergoes autodissociation:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

By the solvent definition, the cation, $H^3O^+$, is the acid and the anion, $OH^-$ is the base. For example in the reaction,

$$H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO_4^-$$

Sulphuric acid increases the concentration of the hydronium ion and is an acid by any of the three definitions given. The solvent system approach can also be used with solvents that do not contain hydrogen. For example, $BrF_3$ also undergoes autodissociation.

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

Solution that increase the concentration of the acid, $BrF_4^-$, are considered acids. For example, $SbF_6$ is an acid in $BrF_3$:

$$SbF_5 + BrF_3 \longrightarrow BrF_2^+ + SbF_6^-$$

And solutes such as KF that increase the concentration of $BrF_4^-$ are considered bases:

$$F^- + BrF_3 \longrightarrow BrF_4^-$$

Acid-base reactions in the solvent system concept are reverse of autodissociation:

$$H_3O^+ + OH^- \longrightarrow 2H_2O$$
$$BrF_2^+ + BrF_4^- \longrightarrow 2Br\,F_3$$

The Arrhenius, Brønsted-Lowry and solvent system neutralization reactions can be compared as follows:

| | | |
|---|---|---|
| Arrhenius | : | Acid + Base → Salt + Water |
| Brønsted | : | Acid 1 + Base 2 → Base 1 + Acid 2 |
| Solvent system | : | Acid + Base → Solvent |

Following table gives some properties of common solvents. The $pK_{ion}$ is the autodissociation constant for the pure solvent, indicating that, among these acids, sulphuric acid dissociates much more readily than any of the others, and the acetonitrile is least likely to autodissociate. The boiling points are given to provide as estimate of the conditions under which each solvent might be used.

**Protic Solvents**

| *Solvent* | *Acid cation* | *Base anion* | *$pK_{ion}$ (25°C)* | *B.P. (°C)* |
|---|---|---|---|---|
| Sulfuric acid, $H_2SO_4$ | $H_3SO_4^+$ | $HSO_4^-$ | 3.4 (10°) | 330 |
| Hydrogen fluride, HF | $H_2F^+$ | $HF_2^-$ | –12 (0°) | 19.5 |
| Water, $H_2O$ | $H_3O^+$ | $OH^-$ | 14 | 100 |
| Acetic acid, $CH_3COOH$ | $CH_3COOH_2^+$ | $CH_3COO^-$ | 14.45 | 118.2 |
| Methanol, $CH_3OH$ | $CH_3OH_2^+$ | $CH_3O^-$ | 18.9 | 64.7 |
| Ammonia $NH_3$ | $NH_4^+$ | $NH_2^-$ | 27 | –33.4 |
| Acetonitrile $CH_3CN$ | $CH_3CNH^+$ | $CH_2CN^-$ | 28.6 | 81 |

Caution is needed in interpreting these reactions. For example, $SOCl_2$ and $SO_3^{2-}$ react as acid and base in $SO_2$ solvent, with the reaction apparently occurring as:

$$SOCl_2 + SO_3^{2-} \rightleftharpoons 2SO_2 + 2Cl^-$$

It was first believed that $SOCl_2$ dissociated and that the resulting $SO^{2+}$ reacted with $SO_3^{2-}$:

$$SOCl_2 \rightleftharpoons SO^{2+} + 2Cl^-$$

$$SO^{2+} + SO_3^{2-} \rightleftharpoons 2SO_2$$

However, the reverse reactions should lead to the exchange of oxygen atoms between $SO_2$ and $SOCl_2$, but none is observed. The details of the reaction $SOCl_2 + 2SO_3^{2-}$ are still uncertain, but may involve dissociation of only one chloride, as in:

$$SOCl_2 \rightleftharpoons SOCl^- + Cl^-$$

**Lux–Flood Definition:**

This acid–base theory was a revival of oxygen theory of acids and bases proposed by German chemist Hermann Lux in 1939, further improved by Håkon Flood circa 1947 and is still used in modern geochemistry and electrochemistry of molten salts. This definition describes an **acid** as an oxide ion ($O^{2-}$) acceptor and a **base** as an oxide ion donor. For example:

$$MgO_{\text{(base)}} + CO_{2\,\text{(acid)}} \rightarrow MgCO_3$$

$$CaO_{\text{(base)}} + SiO_{2\,\text{(acid)}} \rightarrow CaSiO_3$$

$$NO_3^-{}_{\text{(base)}} + S_2O_7^{2-}{}_{\text{(acid)}} \rightarrow NO_2^+ + 2\ SO_4^{2-}$$

**Usanovich Definition**

Mikhail Usanovich developed a general theory that does not restrict acidity to hydrogen-containing compounds, but his approach, published in 1938, was even more general than Lewis theory.

Usanovich's theory can be summarized as defining an acid as anything that accepts negative species or donates positive ones, and a base as the reverse. This pushed the concept of acid–base reactions to its logical limits, and even redefined the concept of redox (oxidation-reduction) as a special case of acid-base reactions, and so did not become widespread, despite being easier to understand than Lewis theory, which required detailed familiarity with atomic structure. Some examples of Usanovich acid-base reactions include:

$Na_2O_{\text{(base)}} + SO_{3\,\text{(acid)}} \rightarrow 2\ Na^+ + SO_4^{2-}$ (species exchanged: anion $O^{2-}$)

$3\ (NH_4)_2S_{\text{(base)}} + Sb_2S_{3\,\text{(acid)}} \rightarrow 6\ NH_4^+ + 2\ SbS_4^{2-}$ (species exchanged:anion $S^{2-}$)

$Na_{\text{(base)}} + Cl_{\text{(acid)}} \rightarrow Na^+ + Cl^-$ (species exchanged: electron)

### 5.4 Hard and soft acids and bases

The ease with which an acid-base reaction occurs depends on the strength of both the acid and the base. Strong acids and bases are generally more reactive than weak acids and bases. However, the direction of the reaction and the stability of the products often depend on another quality – the **hardness** or **softness** of the acid and base.

### Soft Acids

For soft acids, the electron-pair acceptor atoms are large, have a low positive **charge density**, and contain unshared pairs of electrons in their valence shells. The unshared pairs of electrons are in the *p* or *d* orbitals. Also, soft acids have a high **polarizability** and a low electronegativity. In organic chemistry, the soft acids usually include only the halogens, phosphorus, and sulfur compounds.

### Hard Acids

For hard acids, the acceptor atoms are small, have a high positive charge density, and contain no unshared pairs of electrons in their valence shells. They have a low polarizability and a high electronegativity. The hydrogen ion is a good example of a hard acid.

### Soft Bases

For soft bases, the donor atoms hold their valence electrons loosely. They have high polarizability, low negative charge density, and low electronegativity. Common soft bases are the cyanide ($CN^-$) and iodide ($I^-$) ions.

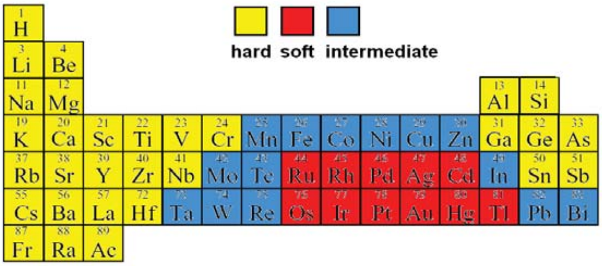
### Hard Bases

For hard bases, the donor atoms are small, have a high negative charge density, and hold their valence electrons tightly. They have a low polarizability and a high electronegativity. The hydroxide ion is a good example of a hard base.

| **Acids** | **Type** | **Bases** |
|---|---|---|
| $H^{\oplus}$, $Li^{\oplus}$, ${}^{\oplus}CH_3$, $Na^{\oplus}$, $K^{\oplus}$, $Mg^{2\oplus}$,$Ca^{2\oplus}$, $Al^{3\oplus}$, $BF_3$, $AlCl_3$, $RCO^{\oplus}$, $CO_2$ | *Hard* | $H_2O$, ${}^{\ominus}OH$, $F^{\ominus}$, $Cl^{\ominus}$, ${}^{\ominus}CH_3$, ${}^{\ominus}NH_2$, $RCOO^{\ominus}$, $CO_3{}^{2\ominus}$, ROH, $RO^{\ominus}$, $NH_3$, $RNH_2$ |
| $Fe^{2\oplus}$, $Zn^{2\oplus}$, $Sn^{2\oplus}$, $Sb^{3\oplus}$, $BR_3$, $SO_2$, $R_3C^{\oplus}$, $NO^{\oplus}$ | *Borderline* | $C_6H_5NH_2$, $N_3{}^{\ominus}$, $Br^{\ominus}$, $NO_2{}^{\ominus}$, $R^{\ominus}$ |
| $Cu^{\oplus}$, $Ag^{\oplus}$, $Hg^{2\oplus}$, $BH_3$, $I_2$, $Br_2$, $:CH_2$ (carbenes) | *Soft* | $RS^{\ominus}$, $I^{\ominus}$, ${}^{\ominus}CN$, RCN, CO, $C_6H_6$, ${}^{\ominus}SH$, $H^{\ominus}$ |

Hardness and softness are difficult to quantify. Rather than relying specifically on these types of sequences, chemists divide acids and bases into three groups: (1) hard acids or bases, (2) soft acids or bases, and (3) borderline acids or bases.

$H^+$ is a hard acid because it has no electrons and has a high positive charge density. The $H^-$ ion is a soft base because it has a pair of electrons and only one proton, so it holds the electrons rather loosely. Thus, it is quite polarizable and soft.



We have already pointed out that the affinity that metal ions have for ligands is controlled by size, charge and electronegativity. This can be refined further by noting that for some metal ions, their chemistry is dominated by size and charge, while for others it is dominated by their electronegativity. These two categories of metal ions have been termed by Pearson as hard metal ions and soft metal ions. Their distribution in the periodic table is as follows:

**HSAB principle**.

1965- Ralph Pearson introduced the hard-soft-acid-base(HSAB) principle.

“Hard acids prefer to coordinate the hard bases and soft acids to soft bases”.

This very simple concept was used by Pearson torationalize a variety of chemical information.1983 – the qualitative definition of HSAB wasconverted to a quantitative one by using the idea ofpolarizability.

**A less polarizable atom or ion is “hard” and a more easily polarized atom or ion is “soft”**

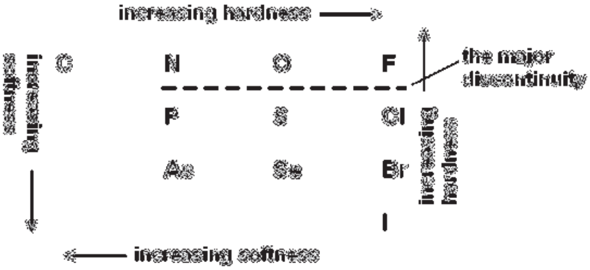


Figure above shows the distribution of hardness and softness for potential donor atoms for ligands in the Periodic Table. The diagram shows that hardness increases toward $F^-$, and softness increases away from $F^-$. However, this is not a smooth transition. There is, as shown, a major discontinuity between the lighter members of each group, namely, $F^-$, O, and N, and their heavier congeners. Thus, $Cl^-$, $Br^-$, and $I^-$ are far more like each other, and far different from $F^-$, in their bonding preferences, as can be seen in Table 1.

The hardness of ligands tends to show, as seen in the figure, a discontinuity between the lightest member of each group, and the heavier members. Thus, one finds that the metal ion affinities of $NH_3$ are very different from metal ion affinities for phosphines such as $PPh_3$ (Ph = phenyl), but that the complexes of $PPh_3$ are very similar to those of $AsPh_3$. A selection of ligands classified according to HSAB ideas are:

**Hard:**

$H_2O$, $OH^-$, $CH_3COO^-$, $F^-$,$NH_3$, oxalate ( $^-OOC\text{-}COO^-$).

**Intermediate:**

$C_6H_5N$ (pyridine), $N_3^-$ (azide), $^-N{=}C{=}S$ (thiocyanate, N-bound), $Cl^-$.

**Soft:**

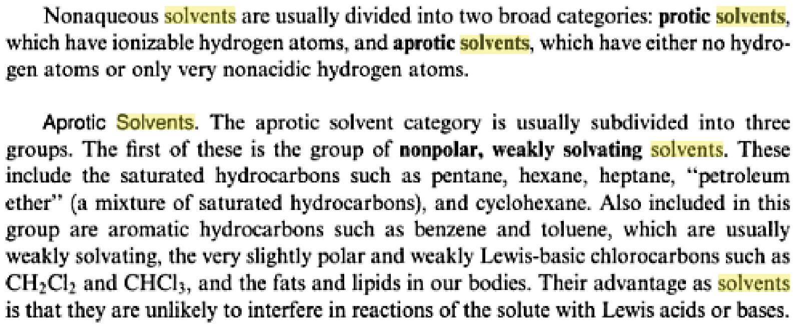
$Br^-$, $I^-$, $SH^-$, $(CH_3)_2S$, $S{=}C(NH_2)_2$, (thiourea), $P(CH_3)_3$, $PPh_3$, $As(CH_3)_3$, $CN^-$ , $S\text{-}C{\equiv}N$ (thiocyanate S-bound).

One can rationalize HSAB in terms of the idea that soft-soft interactions are more covalent, while hard-hard interactions are ionic. The covalence of the soft metal ions relates to their higher electronegativity, which in turns depends on relativistic effects.

### 5.5 Nonaqueous solvents

Many ionic compounds are insoluble in water, and many of those that are soluble undergo hydrolysis in water. Therefore, it is often very useful to find **nonaqueous** solvents for ionic (as well as polar and nonpolar covalent) compounds. The Lewis acid-base properties of many liquid substances allow them to be used as solvents for selected ionic and other compounds. There is a wide variety of such solvents; here we can only indicate categories and give a few examples.

Most of the titrations are performed in the aqueous media, means water is used as solvent. There may be difficulty if reactant is insoluble in water or reactant is reactive with water or the analyte (sample) is either too weak acid or too weak base.Those too weak acids or bases cannot be titrated in aqueous solution due to the amphoteric behavior of water (i.e. water can react as an acid on titration with a base and act as a base on titration with acid). So water will compete with the sample if it is weak acid or weak base.



Nonaqueous solvents are usually divided into two broad categories: **protic** solvents, which have ionizable hydrogen atoms, and **aprotic** solvents, which have either no hydrogen atoms or only very nonacidic hydrogen atoms.

Aprotic Solvents. The aprotic solvent category is usually subdivided into three groups. The first of these is the group of **nonpolar, weakly solvating** solvents. These include the saturated hydrocarbons such as pentane, hexane, heptane, "petroleum ether" (a mixture of saturated hydrocarbons), and cyclohexane. Also included in this group are aromatic hydrocarbons such as benzene and toluene, which are usually weakly solvating, the very slightly polar and weakly Lewis-basic chlorocarbons such as $CH_2Cl_2$ and $CHCl_3$, and the fats and lipids in our bodies. Their advantage as solvents is that they are unlikely to interfere in reactions of the solute with Lewis acids or bases.

Nonaqueous solvents are usually divided into two broad categories: **protic** solvents, which have ionizable hydrogen atoms, and **aprotic** solvents, which have either no hydrogen atoms or only very nonacidic hydrogen atoms.

**Protonic solvents:**

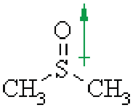
These solvents behave as acid as well as base depending on the substance dissolved in it. They can accept or donate protons.*Protic* refers to chemistry involving transfer of $H^+$ from one molecule to another. The speciesH$^+$ is also called a proton because it is what remains when a hydrogen atom loses itselectron. The hydronium ion, $H_3O^+$, is a combination of $H^+$ with $H_2O$. Although $H_3O^+$ is amore accurate representation than $H^+$ for the hydrogen ion in aqueous solution, $H_3O^+$ andH$^+$ are used interchangeably.

**Examples:**

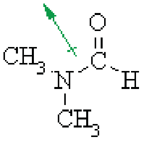
Water, Alcohol.

**Aprotic solvents**

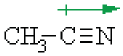
- Have dipoles due to polar bonds
- Do not have H atoms that can be donated into H-bond.
- Examples are acetone, acetonitrile, DMSO and DMF.



dimethylsulfoxide



N,N-dimethylformamide



acetonitrile

### 5.6 Liquid ammonia as solvent

1. $NH_{3(l)}$is a polar solvent, which can be conveniently handled in an insulated vessel(Dewar) owing to its relatively high heat of vaporization.

| | $NH_3(l)$ | $H_2O(l)$ |
|---|---|---|
| $H_{vap}$ (kJ/mol) | 23.3 | 40.7 |
| b.p. ($^oC$) | –33.35 | 100 |

2. Both ammonia and water are extensively hydrogen bonded.
3. Because of its high $\Delta H_{vap}$ liquid ammonia in a Dewar at –33.35 ºC evaporates slowly and smoothly, and the gaseous ammonia produced can easily be handled by a functioning fume hood.
4. Any room-temperature substance placed in liquid ammonia is “hot” and will causesignificant boiling and/or bumping.
5. **Be sure you are wearing nitrile gloves and safety goggles throughout thisexperiment, especially when handling the liquid ammonia.**

**Solutions of alkali and alkaline earth metals in ammonia**

Most metals are insoluble in virtually all solvents, but the alkali metals (and the heavier alkaline earth metals) dissolve readily in liquid ammonia to form solvated metal cations and solvated electrons, which give the solution a deep **blue** color.

A spectacular aspect of alkali metals chemistry is their solubility in liquid ammonia to give bright blue colored metastable solutions. Investigations in this area began with the discovery of T. Weyl in 1863, and subsequent studies revealed that even heavier alkaline earth metals and some divalent rare earth metals like europium and ytterbium also dissolved in liquid ammonia to give solutions with similar characteristic properties. The cause of solubility of alkali metals in liquid ammonia and other non-aqueous solvents are attributed to low metal lattice energy, low ionization energy and high solvation energy of the cation. These solutions are remarkable for their shining blue color, which implies that they originate due to common ionic species. At higher concentrations they assume bronze color. They have a higher degree of electrical conductivity than the corresponding aqueous solution. With increase in concentration the conductivity decreases and attains minimum at 0.04 M and then rise to value, which finally becomes equivalent to the liquid metal. All of them exhibit paramagnetism and in dilute solutions the susceptibility corresponds to one free electron per metal atom. At the concentration where the conductivity is minimum the solutions are diamagnetic, and turn feebly paramagnetic as the concentration of the metal atom increases.

It is believed that in liquid ammonia, the alkali metal atom is ionized to $M^+$ and the electron exists in a quasi free state solvated with 2-3 molecules of ammonia. The liquid ammonia solutions of alkali metals have been widely used for a variety of synthetic reactions. The solutions themselves are metastable and favor amide formation.

$$M + NH_3 \longrightarrow M\ddot{N}H_2 + \frac{1}{2}H_2$$

- Alkali metals (e.g., Na) in $NH_{3(l)}$ *produce bronze colored* solutions when oncentrated (> 1.0 M) and blue solutions when less concentrated.
- In both cases, the solution contains solvated electrons.

$$M(s) \; + \; NH_3(l) \longrightarrow [M(NH_3)]^+(l) \; + \; e^-(solvated)$$

- The more dilute blue solutions are strongly paramagnetic, becoming less so withincreasing concentration.
- In the concentrated solutions, extensive electron pairing occurs, making the bronze colored solutions less paramagnetic.
- Solutions of metals in liquid ammonia are very strong reducing agents and react very much like the free metals themselves.
- The reduction process appears to involve free solvated electrons.

**Reactions of alkali and alkaline earth metals in ammonia**

If alkali or alkaline earth metals are placed in liquid ammonia, they dissolve without initially generating hydrogen. The resulting blue solutions are stable for a long period, and are powerful reducing agents. In time they decompose, in the presence of catalysts like $FeCl_2$, and the reaction occurs rapidly.The products are metal amides and hydrogen, as shown below,

$$2\,Na + 2\,NH_3 \rightarrow 2\,NaNH_2 + H_2.$$

When alkali or alkaline earth metals dissolve in liquid ammonia, one of the reactions which is occurring is provided below:

$$\mathrm{Na} \xrightarrow{\text{liq. } \mathrm{NH_3}} \mathrm{Na\,(NH_3)_n^+} + \mathrm{e\,(NH_3)_m^-}$$

The solvated electrons, [$e(NH_3)_m^-$] are responsible for the blue color and the high electrical conductivity of the solution. At higher concentration of alkali metals, the solutions now also contain $Na(NH_3)_m^+$ and $e(NH_3)_m^-$, and are copper-colored with a metallic sheen; they have a very high electrical conductivity and thus indeed act like liquid metals.

When heated, amides are converted to imides; heating them to higher temperatures converts them to nitrides ($M^{II}$ = alkaline earth metal).

$$\mathrm{M^{II}(NH_2)_2} \rightarrow \mathrm{M^{II}NH} + \mathrm{NH_3}, \qquad 3\,\mathrm{M^{II}NH} \rightarrow \mathrm{M_3^{II}N_2} + \mathrm{NH_3}.$$

# NOTES