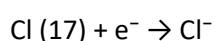
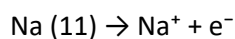


Ionic Bond

An **ionic bond** is a type of chemical bond formed due to the electrostatic attraction between oppositely charged ions. It occurs when one atom **transfers** electrons to another atom, leading to the formation of **cations** and **anions**.

The metal atom **loses electrons** to form a **cation**. The non-metal atom **gains electrons** to form an **anion**.

Example: **Sodium chloride (NaCl)**



Na^+ and Cl^- are held together by electrostatic forces, forming NaCl.

Factors Favouring the Formation of Ionic Bonds

The formation of an ionic bond depends on several factors that influence the stability and strength of the bond.

1. Low Ionization Energy of the Metal

Metals with **low ionization energy** (e.g., alkali and alkaline earth metals) can easily lose electrons to form cations.

Example: **Na, K, Mg, Ca** readily form Na^+ , K^+ , Mg^{2+} , and Ca^{2+} .

2. High Electron Affinity of the Non-Metal

Non-metals with **high electron affinity** readily accept electrons to form anions.

Example: **Cl, O, F** easily gain electrons to form Cl^- , O^{2-} , and F^- .

3. Large Difference in Electronegativity

A large difference (>1.7 on the Pauling scale) between metal and non-metal favors ionic bond formation.

Example: **Na (0.93) and Cl (3.16)** have a large difference in electronegativity, making NaCl an ionic compound.

4. High Lattice Energy

A **high lattice energy** increases the stability of the ionic compound.

Example: **NaCl, MgO, and CaF₂** have high lattice energies and are stable ionic compounds.

5. Small Cation and Large Anion

A **small cation** has a high charge density, making the electrostatic attraction stronger.

A **large anion** is easily polarized and enhances bond strength.

Example: **Mg²⁺ (small cation) and O²⁻ (large anion) form a strong ionic bond in MgO.**

6. Solvent Effect

Ionic bonds form more easily in **polar solvents** (like water) because they stabilize the ions.

Example: **NaCl dissolves in water due to the strong attraction between water molecules and ions.**

Lattice Energy

Lattice energy is the energy released when one mole of an ionic compound forms from its gaseous ions. It is a measure of bond strength in an ionic solid.



Lattice energy increases with **higher ionic charge** and **smaller ionic radius** (Coulomb's law). It is indirectly calculated using the **Born-Haber cycle** or theoretically estimated using the **Born-Landé equation**. Higher lattice energy results in **stronger ionic bonds** and lower solubility in polar solvents.

Born-Haber Cycle

The **Born-Haber cycle** is a thermodynamic cycle used to determine the **lattice energy** of an ionic compound.

It applies **Hess's Law**, which states that the total enthalpy change of a reaction is the same regardless of the pathway taken. This cycle breaks down the formation of an ionic solid into multiple steps involving measurable enthalpy changes.

Consider the formation of **sodium chloride (NaCl)** from its elements **sodium (Na)** and **chlorine (Cl₂)** using standard enthalpy values (approximate values in kJ/mol).

Step 1: Sublimation of Sodium ($\Delta H_s = +108$ kJ/mol)

Sodium metal (Na) is converted from a solid to a gas.



Step 2: Ionization of Sodium ($\Delta H_i = +496$ kJ/mol)

The gaseous sodium atom loses an electron to form a sodium ion (Na⁺). This is the **ionization energy**.



Step 3: Dissociation of Chlorine ($\Delta H_d = +122$ kJ/mol)

Diatomic chlorine gas (Cl₂) is split into individual chlorine atoms. Since we need one chlorine atom, we take half the bond dissociation enthalpy.



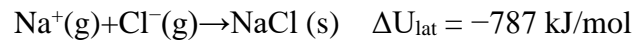
Step 4: Electron Affinity of Chlorine ($\Delta H_e = -349$ kJ/mol)

The chlorine atom gains an electron to form a chloride ion (Cl⁻). This is **electron affinity**.



Step 5: Formation of NaCl Crystal ($\Delta U_{\text{lat}} = ?$)

The gaseous sodium and chloride ions combine to form a solid lattice, releasing lattice energy.



Step 6: Enthalpy of Formation ($\Delta H_f = -411 \text{ kJ/mol}$)

The overall enthalpy change when NaCl is formed directly from its elements:



According to Hess's Law:

$$\Delta H_f = \Delta H_s + \Delta H_i + \Delta H_d + \Delta H_e + \Delta U_{\text{lat}}$$

Substituting the values:

$$-411 = (108 + 496 + 122 - 349 + \Delta U_{\text{lat}})$$

$$\Delta U_{\text{lat}} = -787 \text{ kJ/mol}$$

Fajan's Rules

Fajan's rules help predict whether a given chemical bond will be more ionic or covalent in nature. It was proposed by Kazimierz Fajan in 1923 and is based on the concept of polarization.

Conditions for Covalent Character

A compound that is expected to be ionic (formed between a metal and a non-metal) may show covalent character due to polarization. The extent of covalent character depends on three main factors:

1. Small Cation with High Charge (High Polarizing Power)

A smaller and highly charged cation has a strong positive field that attracts and distorts the electron cloud of the anion.

Example: AlCl_3 (Al^{3+} is small and highly charged, making AlCl_3 more covalent than NaCl).

2. Large Anion with High Polarizability

A large anion has loosely held outer electrons, which can be easily distorted by a cation.

Example: PbI_2 is more covalent than PbF_2 because I^- is larger and more polarizable than F^- .

3. Pseudo noble Gas Configuration in Cation

Transition metal cations with pseudo noble gas configuration (18-electron outer shell) have more covalent character than alkali or alkaline earth metal cations with a noble gas configuration (8 electrons).

○ Example: CuCl is more covalent than NaCl because Cu^+ has a pseudo noble gas configuration ($[\text{Ar}]3d^{10}$), whereas Na^+ has a noble gas configuration (Ne).

Polarising power of cation = charge on cation(z) / Radius of cation(r)

Topic - Periodicity (Ionisation Energy)

Ionisation Potential OR Ionisation Energy OR Ionisation Enthalpy

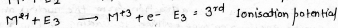
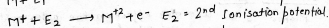
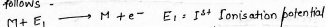
Definition:-

Minimum energy required to remove most loosely held outer most shell electron (e^-) in ground state from an isolated gaseous atom is known as ionisation potential.

(Isolated means without any bonding with other atom).

Successive Ionisation Energy

- a) For an atom M, successive ionisation energies are as follows -



Order of Successive Ionisation Energy

$1^{st} \text{ ionisation potential} < 2^{nd} \text{ ionisation potential} < 3^{rd} \text{ ionisation potential}$

- b) Electron can not be removed from solid state of an atom. It has to convert in gaseous form. Energy required for conversion from solid state to gaseous state is called Sublimation energy.
- c) Ionisation potential is always an exothermic process ($\Delta H = +ve$)
- d) It is measured in eV/atom (electronvolt/atom) or kcal/mole or kJ/mole.

Factors affecting Ionisation potential

a) Atomic size

Larger the atomic size, smaller is the Ionisation potential. It is due to the fact that when the size of atom increases the outermost electrons (e^-) farther away from the nucleus and nucleus loses the attraction on the electrons and hence can be easily removed.

$$\text{Ionisation potential} \propto \frac{1}{\text{Atomic size}}$$

b) Effective nuclear charge (Z_{eff})

Ionisation potential increases with the increase in nuclear charge between outermost electrons and nucleus.

$$\text{Ionisation potential} \propto \text{effective nuclear charge}$$

c) Screening effect

Higher is the screening effect on the outermost electrons causes less attraction from the nucleus and can be easily removed, which is leading to lower value of Ionisation potential.

$$\text{Ionisation potential} \propto \frac{1}{\text{screening effect}}$$

d) Penetration power of subshell

Penetration power describes the proximity to which an electron can approach to the nucleus. Order of attraction of subshells towards nucleus (penetration power) is $s > p > d > f$.

So, higher the penetration power of outermost orbital higher will be Ionisation energy.

Stability of half filled and fully filled orbitals ³

Half filled p^3, d^5, f^7 or fully filled s^2, p^6, d^{10}, f^{14} are more stable than others. so it requires more energy.

Periodic variation of ionisation energy —

Variation in period among the representative elements

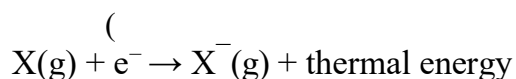
Ionisation energy generally increases along the period because in moving left to right, in a period the effective nuclear charge per outermost electron increases while the corresponding principal quantum number remains same.

Variation in a group among the representative elements

The ionisation energy generally decreases in moving from top to bottom because the size increases due to the increase of the principal quantum number. On the other hand the effective nuclear charge Z_{eff} for the outermost electron remains the same along the group.

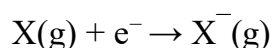
Electron Affinity

Definition: Electron affinity is defined as the change in energy (in kJ/mole) of a neutral gaseous atom, when an electron is added to the atom to form a negative ion.

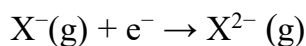


When an electron is added to a neutral atom (i.e., first electron affinity) energy is released; thus, the first electron affinities are **negative**. However, more energy is required to add an electron to a negative ion (i.e., second electron affinity) which overwhelms any the release of energy from the electron attachment process and hence, second electron affinities are **positive**.

First Electron Affinity (negative energy because energy released):



Second Electron Affinity (positive energy because energy needed is more than gained):



Periodicity in electron affinity:

In Period : In general E.A value increases on moving from left to right in a period because effective nuclear charge increases.

In group : In a group, E.A value decreases on moving from top to bottom because the atomic size increases.

Factors affecting E.A

1. Atomic Size: The electron affinity decreases with increase in atomic size and increases with decrease in atomic size.

2. Effective Nuclear Charge (Z_{eff}):

Atomic size decreases with increase in effective nuclear charge because, higher the effective nuclear charge stronger will be the attraction of the nucleus towards the electron of the outermost orbit and higher will be the E.A.

3. Shielding Effect : An increase in shielding effect decrease the nuclear charge. This result in decreased E.A.

4. Stability of half filled and fully filled orbitals :

Elements having half filled and fully filled electronic configuration have almost zero or negligible E.A.

Electronegativity

Def: The tendency of an atom to attract shared pair of electrons towards itself in a covalently bonded molecule.

Factors affecting the magnitude of electronegativity

- i) **Atomic radius:** As the atomic radius of the element increases the electronegativity value decrease.
- iii) **Effective nuclear charge:** The electronegativity value increases as the effective nuclear charge on the atomic nucleus increases.
- iii) **Oxidation state of the atom:** The electronegativity value increases as the oxidation state (i.e. the number of positive charge) of the atom increases.
- iv) **Hybridisation state of an atom in a molecule: (Reference : Chemical Bonding)** If the s- character in the hybridisation state of the atom increases electronegativity increases because s-electrons are comparatively nearer to the nucleus. For example the electronegativity values of C- atom in various hybridisation states are as under:

Hybridisation states	sp ³	sp ²	sp
Character	25%	33.33%	50%
Electronegativity	2.48	2.75	3.25

s-character is increasing. So the electronegativity value is increasing

1. **Electronegativity scale:** Some arbitrary scales for the quantitative measurement of electronegativities are as under

- i) **Pauling's scale:** Pauling related the resonance energy(Δ_{AB}) of a molecule AB with the electronegativities of the atoms A and B. If x_A and x_B are the electronegativities of atoms A and B respectively then

$$0.208 \sqrt{\Delta_{AB}} = x_A - x_B \text{ if } x_A > x_B \quad \text{or } \Delta_{AB} = 23.06 (x_A - x_B)^2$$

$\Delta_{AB} = E_{A-B(\text{experimental})} - E_{A-B(\text{theoretical})}$ where E_{A-B} is the energy of A-B bond. In a purely covalent molecule, AB, the experimental and theoretical values of bond energy A-B are equal.

$$\text{So } \Delta_{AB} = 0$$

$$\text{or } 0 = 23.06 (x_A - x_B)^2 \quad \text{or } x_A = x_B$$

In an ionic molecule AB, $E_{A-B(\text{experimental})}$ is more than $E_{A-B(\text{Theoretical})}$. Pauling assumed the electronegativity value of Hydrogen as 2.1 and calculated the electronegativity values of other elements from this value.

- ii) **Mulliken's electronegativity:** According to Mulliken, the electronegativity of an element is the average value of its ionisation potential and electron affinity.

$$\text{Electro-negativity} = \frac{\text{Electron affinity} + \text{Ionisation potential}}{2}$$
$$= \frac{\text{Electron affinity} + \text{Ionisation potential}}{5.6} \quad \text{(on pauling scale)}$$

Thus, Mulliken's values are 2.8 times larger than the Pauling's values. i.e.

$$EN_{\text{Pauling}} = \frac{EN_{\text{Mulliken}}}{2.8}$$

Allred Rochow's Electronegativity: According to Allred- Rochow, electronegativity is the force exerted by the nucleus of an atom on its valence electrons.

$$EN_{(AR)} = \frac{0.359 \times Z_{\text{effective}}}{r^2} + 0.744$$

Where, $Z_{\text{effective}}$ = Effective nuclear charge.

r = the covalent radius (in \AA)

Mulliken scale is limited to monovalent atoms and does not cover multivalent atoms.

Periodicity in Electronegativity

i) In a period moving from left to right, the electronegativity increases due to the increase in effective nuclear charge.

In a period the electronegativity value of IA alkali metal is minimum and that of VIIA halogen is maximum.

ii) In a group moving from top to bottom, the electronegativity decreases because atomic radius increases.

The electronegativity value of F is maximum and that of Cs is minimum in the periodic table.