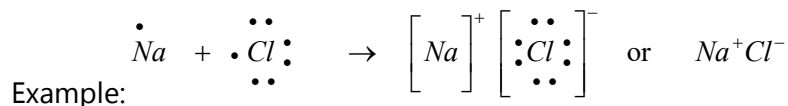# Electrovalent bond.

When a bond is formed by complete transfer of electrons from one atom to another so as to complete their outermost orbits by acquiring 8 electrons (i.e., octet) or 2 electrons (i.e., duplet) in case of hydrogen, helium etc. and hence acquire the stable nearest noble gas configuration, the bond formed is called ionic bond, electrovalent bond or polar bond. Compounds containing ionic bond are called ionic, electrovalent or polar compounds.

$$\overset{\bullet}{Na} \;+\; \bullet\,\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}\,\overset{\bullet}{\underset{\bullet}{}} \;\rightarrow\; \left[Na\right]^{+}\; \left[\overset{\bullet\bullet}{\underset{\bullet\bullet}{:Cl:}}\right]^{-} \quad \text{or} \quad Na^{+}Cl^{-}$$

Example:

Some other examples are: MgCl2, CaCl2, MgO, Na2S, CaH2, AlF3, NaH, KH, K_2O, KI, RbCl, NaBr, CaH2 etc.

(1) Conditions for formation of electrovalent bond

(i) Number of valency electrons: The atom which changes into cation (+ ive ion) should possess 1, 2 or 3 valency electrons. The other atom which changes into anion (– ive ion) should possess 5, 6 or 7 electrons in the valency shell.

(ii) Electronegativity difference: A high difference of electronegativity (about 2) of the two atoms is necessary for the formation of an electrovalent bond. Electrovalent bond is not possible between similar atoms.

(iii) Small decrease in energy: There must be overall decrease in energy i.e., energy must be released. For this an atom should have low value of Ionisation potential and the other atom should have high value of electron affinity.

(iv) Lattice energy: Higher the lattice energy, greater will be the ease of forming an ionic compound. The amount of energy released when free ions combine together to form one mole of a crystal is called lattice energy (U).

Magnitude of lattice energy $\propto \dfrac{\text{Charge of ion}}{\text{size of ion}}$

$$A^{+}(g) + B^{-}(g) \longrightarrow AB(s) + U$$
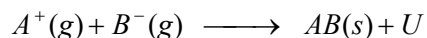
Determination of lattice energy (Born Haber cycle)

When a chemical bond is formed between two atoms (or ions), the potential energy of the system constituting the two atoms or ions decreases. If there is no fall in potential energy of the system, no

bonding is possible, the energy changes involved in the formation of ionic compounds from their constituent elements can be studied with the help of a thermochemical cycle called Born Haber cycle.

Example: The formation of 1 mole of $NaCl$ from sodium and chlorine involves following steps:

Step I: Conversion of metallic sodium into gaseous sodium atoms: $\underset{1\,mole}{Na(s) + S \rightarrow Na(g)}$, where S= sublimation energy i.e., the energy required for the conversion of one mole of metallic sodium into gaseous sodium atoms.

Step II: Dissociation of chlorine molecules into chlorine atoms: $Cl_2(g) + D \rightarrow 2Cl(g)$, where D = Dissociation energy of Cl_2 so the energy required for the formation of one mole of gaseous chlorine atoms $= D/2$.

Step III: Conversion of gaseous sodium atoms into sodium ions: $\underset{1\,mole}{Na(g) + IE \rightarrow Na^+(g) + e^-}$, where IE = Ionisation energy of sodium.

Step IV: Conversion of gaseous chlorine atoms into chloride ions: $\underset{1\,mole}{Cl(g) + e^- \rightarrow Cl^-(g) + EA}$, where EA = Electron affinity of chlorine.


(Born Haber Cycle)

Step V: Combination of gaseous sodium and chloride ions to form solid sodium chloride crystal.

$\underset{1\,mole}{Na^+(g) + Cl^-(g) \rightarrow NaCl(s) + U}$, where $U =$ lattice energy of $NaCl$

The overall change may be represented as: $Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s), \Delta H_f$, where ΔH_f is the heat of formation for 1 mole of $NaCl(s)$.

According to Hess's law of constant heat summation, heat of formation of one mole of $NaCl$ should be same whether it takes place directly in one step or through a number of steps. Thus,

$$\Delta H_f = S + \frac{1}{2}D + IE + EA + U$$
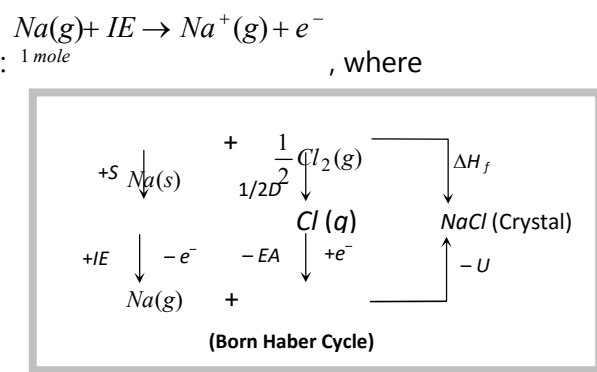
(2) Types of ions

The following types of ions are encountered:

(i) Ions with inert gas configuration: The atoms of the representative elements of group I, II and III by complete loss of their valency electrons and the elements of group V, VI, and VII by gaining 3,2 and 1 electrons respectively form ions either with ns^2 configuration or ns^2p^6 configuration.

(a) Ions with $1s^2$ (He) configuration: H^-, Li^+, Be^{2+} etc. The formation of Li^+ and Be^{2+} is difficult due to their small size and high ionisation potential.

(b) Ions with ns^2p^6 configuration: More than three electrons are hardly lost or gained in the ion formation

Cations: Na^+, Ca^{2+}, Al^{3+} etc.

Anions: Cl^-, O^{2-}, N^{3-}, etc.

(ii) Ions with pseudo inert gas configuration:The Zn^{2+} ; ion is formed when zinc atom loses its outer 4s electrons. The outer shell configuration of Zn^{2+} ions is $3s^2 3p^6 3d^{10}$. The $ns^2 np^6 nd^{10}$ outer shell configuration is often called pseudo noble gas configuration which is considered as stable one.

Examples: $Zn^{2+}, Cd^{2+}, Hg^{2+}, Cu^+ Ag^+, Au^+, Ga^{3+}$ etc

(iii) Exceptional configurations: Many d- and f block elements produce ions with configurations different than the above two. Ions like Fe^{3+}, Mn^{2+}, etc., attain a stable configuration half filled d-orbitals

Fe^{3+} $3s^2 3p^6 3d^5$; Mn^{2+} $3s^2 3p^6 3d^5$
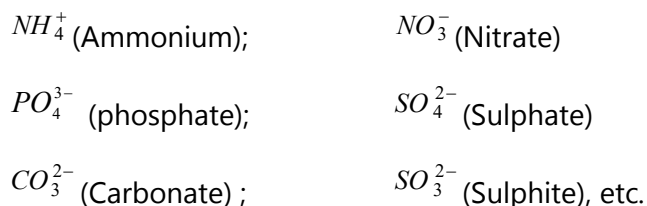
Examples of other configurations are many.

Ti^{2+} $(3s^2 3p^6 3d^2)$; V^{2+} $(3s^2 3p^6 3d^3)$

Cr^{2+} $(3s^2 3p^6 3d^4)$; Fe^{2+} $(3s^2 3p^6 3d^6)$

However, such ions are comparatively less stable

(iv) Ions with ns^2 configuration : Heavier members of groups III, IV and V lose p-electrons only to form ions with ns^2 configuration. $Tl^+, Sn^{2+}, Pb^{2+}, Bi^{3+}$ are the examples of this type. These are stable ions.

(v) Polyatomic ions : The ions which are composed of more than one atom are called polyatomic ions. These ions move as such in chemical reactions. Some common polyatomic ions are

NH_4^+ (Ammonium); NO_3^- (Nitrate)

PO_4^{3-} (phosphate); SO_4^{2-} (Sulphate)

CO_3^{2-} (Carbonate) ; SO_3^{2-} (Sulphite), etc.

(vi) Polyhalide ions : Halogens or interhalogens combine with halide ions to form polyhalide ions. I_3^-, ICl_4^-, ICl_2^- etc. Fluorine due to highest electronegativity and absence of d-oribitals does not form polyhalide ions.

The atoms within the polyatomic ions are held to each other by covalent bonds.

The electro valencies of an ion (any type) is equal to the number of charges present on it.

(3) Method of writing formula of an ionic compound

In order to write the formula of an ionic compound which is made up of two ions (simple or polyatomic) having electrovalencies x and y respectively, the following points are followed :

(i)   Write the symbols of the ions side by side in such a way that positive ion is at the left and negative ion at the right as AB.

(ii)   Write their electrovalencies in figures on the top of each symbol as $A^x B^y$

(iii)   Divide their valencies by H.C.F

(iv)   Now apply criss cross rule as $A^x \diagdown_y B$, i.e., formula $A_y B_x$

Examples :

Name of compound	Exchange of valencies	Formula	Name of compound	Exchange of valencies	Formula
Calcium chloride	$\overset{2}{Ca}\diagdown\overset{1}{Cl}$	$CaCl_2$	Aluminium oxide	$\overset{3}{Al}\diagdown\overset{2}{O}$	Al_2O_3
Potassium phosphate	$\overset{1}{K}\diagdown\overset{3}{PO_4}$	K_3PO_4	Magnesium nitride	$\overset{2}{Mg}\diagdown\overset{3}{N}$	Mg_3N_2
Calcium oxide	$\overset{2}{Ca}\overset{2}{O}$ or $\overset{1}{Ca}\diagdown\overset{1}{O}$	CaO	Ammonium sulphate	$\overset{1}{NH_4}\diagdown\overset{2}{SO_4}$	$(NH_4)_2SO_4$

(4) Difference between atoms and ions

The following are the points of difference between atoms and ions.

Atoms	Ions
Atoms are perfectly neutral in nature, i.e., number of protons equal to number of electrons. Na (protons 11, electrons 11), Cl (Protons – 17, electrons –17)	Ions are charged particles, cations are positively charged, i.e., number of protons more than the number of electrons. Anions are negatively charged, i.e., number of protons less than the number of electrons. Na+ (protons 11, electrons 10), Cl– (protons 17, electrons 18)
Except noble gases, atoms have less than 8 electrons in the outermost orbit Na 2,8,1; Ca 2,8,8,2 Cl 2,8,7; S 2,8,6	Ions have generally 8 electrons in the outermost orbit, i.e., ns2np6 configuration. Na+ 2,8; Cl– 2,8,8 Ca2+ 2,8,8
Chemical activity is due to loss or gain or sharing of electrons as to acquire noble gas configuration	The chemical activity is due to the charge on the ion. Oppositely charged ions are held together by electrostatic forces

(5) Characteristics of ionic compounds

(i) Physical state : Electrovalent compounds are generally crystalline is nature. The constituent ions are arranged in a regular way in their lattice. These are hard due to strong forces of attraction between oppositely charged ions which keep them in their fixed positions.

(ii) Melting and boiling points : Ionic compounds possess high melting and boiling points. This is because ions are tightly held together by strong electrostatic forces of attraction and hence a huge amount of energy is required to break the crystal lattice. For example order of melting and boiling points in halides of sodium and oxides of IInd group elements is as,

$$NaF > NaCl > NaBr > NaI, \ MgO > CaO > BaO$$

(iii) Hard and brittle : Electrovalent compounds are har in nature. The hardness is due to strong forces of attraction between oppositely charged ion which keep them in their alloted positions. The brittleness of the crystals is due to movement of a layer of a crystal on the other layer by application of external force when like ions come infront of each other. The forces of repulsion come into play. The breaking of crystal occurs on account of these forces or repulsion.

(iv) Electrical conductivity : Electrovalent solids donot conduct electricity. This is because the ions remain intact occupying fixed positions in the crystal lattice. When ionic compounds are melted or dissolved in a polar solvent, the ions become free to move. They are attracted towards the respective electrode and act as current carriers. Thus, electrovalent compounds in the molten state or in solution conduct electricity.

(v) Solubility : Electrovalent compounds are fairly soluble in polar solvents and insoluble in non-polar solvents. The polar solvents have high values of dielectric constants. Water is one of the best polar solvents as it has a high value of dielectric constant. The dielectric constant of a solvent is defined as its capacity to weaken the force of attraction between the electrical charges immersed in that solvent. In solvent like water, the electrostate force of attraction between the ions decreases. As a result there ions get separated and finally solvated.

The values of dielectric constants of some of the compounds are given as :

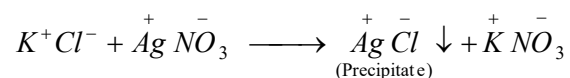| Compound	Water	Methyl Alc	Ethyl Alc.	Acetone	Ether
Dielectric constant	81	35	27	21	4.1

Capacity to dissolve electrovalent compounds decreases →

Lattice energy and solvation energy also explains the solubility of electrovalent compounds. These compounds dissolve in such a solvent of which the value of solvation energy is higher than the lattice energy of the compound. The value of solvation energy depends on the relative size of the ions. Smaller the ion more of solvation, hence higher the solvation energy.

Note: Some ionic compounds e.g., $BaSO_4, PbSO_4, AgCl, AgBr, AgI, Ag_2CrO_4$ etc. are sparingly soluble in water because in all such cases higher values of lattice energy predominates over solvation energy.

(vi) Space isomerism :The electrovalent bonds are non-rigid and non-directional. Thus these compound do not show space isomerism e.g. geometrical or optical isomerism.

(vii) Ionic reactions : Electrovalent compounds furnish ions in solution. The chemical reaction of these compounds are ionic reactions, which are fast. Ionic bonds are more common in inorganic compounds.

$$K^+Cl^- + \overset{+}{Ag}\ \overset{-}{NO}_3 \longrightarrow \overset{+}{Ag}\ \overset{-}{Cl} \downarrow + \overset{+}{K}\ \overset{-}{NO}_3$$
$$\text{(Precipitate)}$$

(viii) Isomorphism : Electrovalent compounds show isomorphism. Compound having same electronic structures are isomorphous to each other.

(ix) Cooling curve : Cooling curve of an ionic compound is not smooth, it has two break points corresponding to time of solidification.
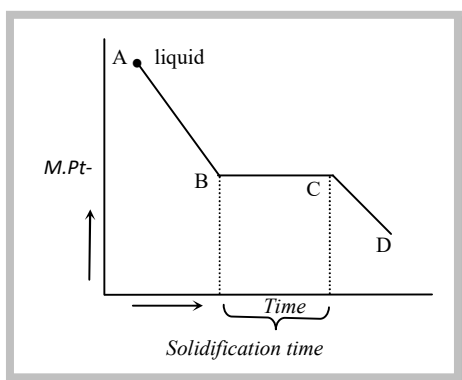
(x) Electrovalency and Variable electrovalency : The capacity of an element to form electro-valent or ionic bond is called its electro-valency or the number of electrons lost or gained by the atom to form ionic compound is known as its electro-valency.

Certain metallic element lose different number of electrons under different conditions, thereby showing variable electrovalency. The following are the reasons:

(a) Unstability of core : The residue configuration left after the loss of valency electrons is called kernel or core. In the case of the atoms of transition elements, ions formed after the loss of valency electrons do not possess a stable core as the configuration of outermost shell is not $ns^2 np^6$ but $ns^2 np^6 d^{1\ to\ 10}$. The outer shell lose one or more electrons giving rise to metal ions of higher valencies.

Example : $Fe^{2+} = 3s^2\,3p^6\,3d^6, 4s^0$ (not stable)

$Fe^{3+} = 3s^2\,3p^6\,3d^5, 4s^0$ (stable)

(b) Inert pair effect : Some of heavier representative elements of third, fourth and fifth groups having configuration of outermost shell $ns^2\ np^1$, $ns^2\ np^2$ and $ns^2\ np^3$ show valencies with a difference of 2, i.e., (1 : 3) (2 : 4) (3 : 5) respectively. In the case of lower valencies, only the electrons present in p–subshell are lost and ns2 electrons remain intact. The reluctance of s-electron pair to take part in bond formation is known as the inert pair effect.