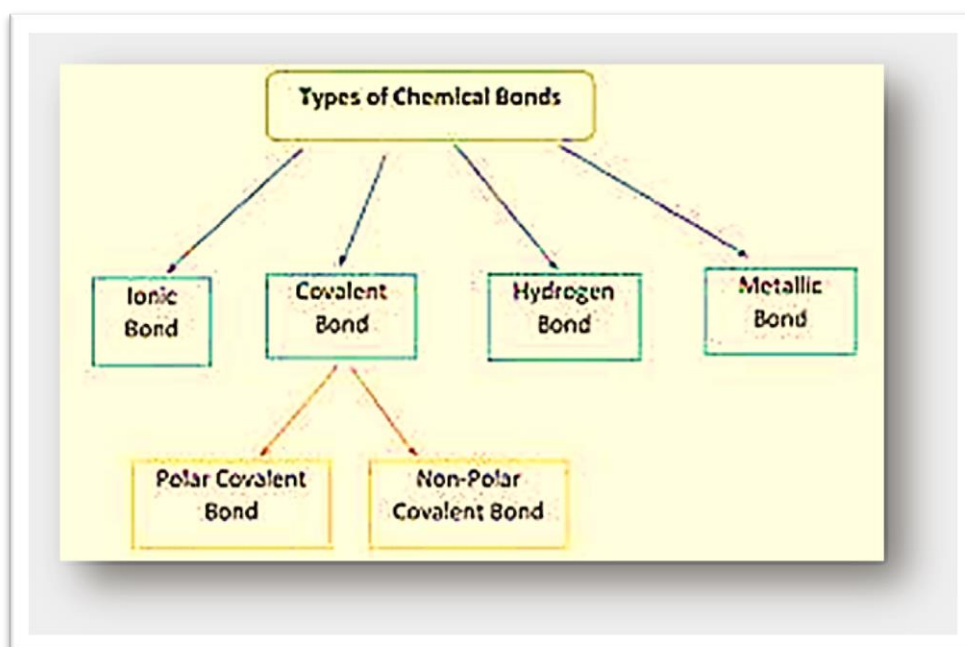


## Chemical compound

**Chemical bonds** are the forces that hold the atoms together in a compound.

1. Transferring electrons from one element to another to form **ionic compounds**
2. Sharing electrons between atoms of different elements to form **covalent compounds**



### Requirements For the formation of Ionic Compounds:

- 1- The two elements must be different (Metal & Nonmetal), and have an opposite charges (cation & anion).
- 2- One of the two atoms (Metal) should have low ionization potential and low electron affinity.
- 3- Another atom (Nonmetal) should have high ionization potential and high electron affinity.
- 4- Difference of electronegativity between two Elements (Metal & Nonmetal) must be greater than or equal to 1.7

5- The formed ionic compound must be having high lattice energy.

### Note

Ionic compounds are composed of ions, charged particles that form when an atom (or small group of atoms) gains or loses one or more electrons. The simplest type of ionic compound is a binary ionic compound, one composed of two elements.

**It typically forms when a metal reacts with a nonmetal:**

- Each metal atom loses one or more electrons and becomes a **cation**, a positively charged ion.
- Each nonmetal atom gains one or more of the electrons lost by the metal atom and becomes an **anion**, a negatively charged ion.

### Note

In effect, the metal atoms transfer electrons to the nonmetal atoms. The resulting large numbers of cations and anions attract each other and form the ionic compound. A cation or anion derived from a single atom is called a monatomic ion.

### Note

In general, when an element located near a noble gas forms a monatomic ion,

**Which is the type of element can formation ionic compound?**

• **Metals lose electrons:**

- 1- Elements in Group 1A(1) lose one electron,
- 2- Elements in Group 2A(2) lose two,
- 3- Elements in Group 3A (13) loses three such as aluminum.

- **Nonmetals gain electrons:** elements in Group 7A(17) gain one electron, oxygen and sulfur in Group 6A(16) gain two, and nitrogen in Group 5A(15) gains three.

### Problem

What monatomic ions do the following elements form? (a) Iodine ( $Z = 53$ ) (b) Calcium ( $Z = 20$ ) (c) Aluminum ( $Z = 13$ )

Solution (a)  $I_2$  Iodine ( ${}_{53}I$ ) is in Group 7A(17), the halogens. Like any member of this group, it gains 1 electron to attain the same number as the nearest Group 8A(18) member, in this case,  ${}_{54}Xe$ . (b) Calcium ( ${}^{20}Ca$ ) is in Group 2A(2), the alkaline earth metals. Like any Group 2A member, it loses 2 electrons to attain the same number as the nearest noble gas, 18Ar. (c)  $Al_{31}$  Aluminum (13Al) is a metal in the boron family (Group 3)

For example

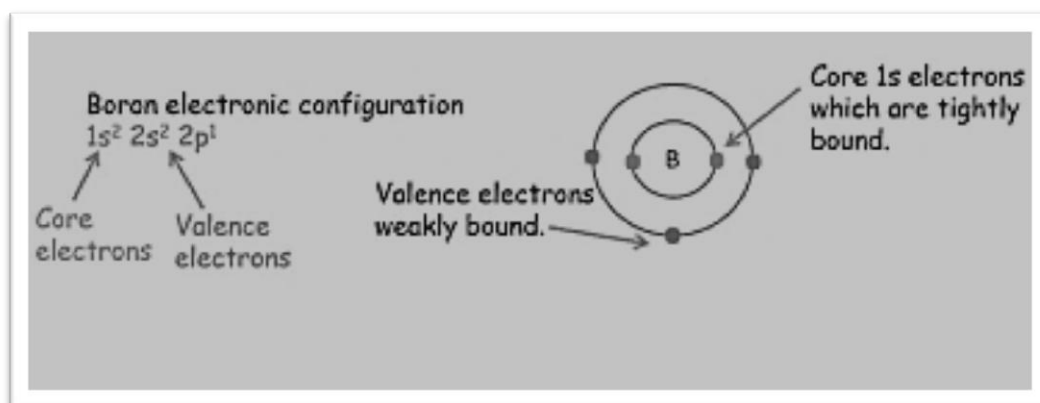
- Lithium fluoride:  $Li^+$  and  $F^-$  combine to form LiF.
- Calcium chloride:  $Ca^{2+}$  and  $Cl^-$  combine to form  $CaCl_2$ .
- Iron (II) oxide:  $Fe^{2+}$  and  $O^{2-}$  combine to form FeO.

### Note

In order to know which electron gain or loss to form ionic compound or shared electron to form covalent compound we need to know about the type of electrons in atom.

There are two types

- 1- Inner shell or core electron
- 2- Outermost shell or valence electron



The differences between core electron and valence electron

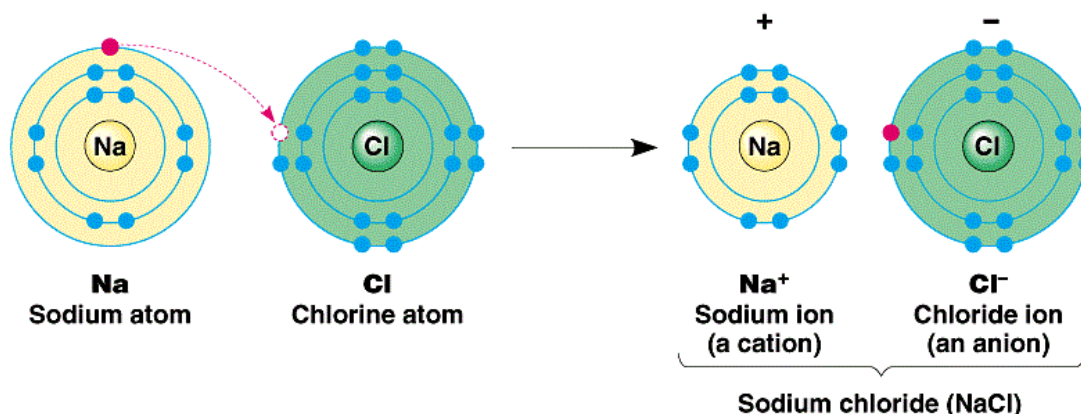
Core electron	Valence electron
1- Occupy the filled and lowest energy levels	1- Electrons of the outermost shell occupy the partly filled and highest energy levels.
2- Increase in the group	2- Increase in the period.
3- Does not represent the group number in main group elements	3- Represent the group number in main group elements.
4- Effect strongly in atomic size, because it screening the outer electron from nuclear charge.	4- Not effect strongly in atomic size
5- Never involved in hybridization and chemical bonding.	5- Involved in hybridization and chemical bonding.

## Ionic bond

**Ionic bond:** Is a chemical bond results from the electrostatic force of attraction between two oppositely charged ions.

The binding arises from the electrostatic attraction between two oppositely charged ions (positive metal and negative non-metal), If the difference in electronegativity between two atoms is equal or greater than (1.7). The electron of metallic atom completely transferred to nonmetallic one. The electrons are not shared at all between two atoms.

For example, consider the bond between Na (Electronegativity=0.93) and Cl (Electronegativity=3.16) in sodium chloride (NaCl).

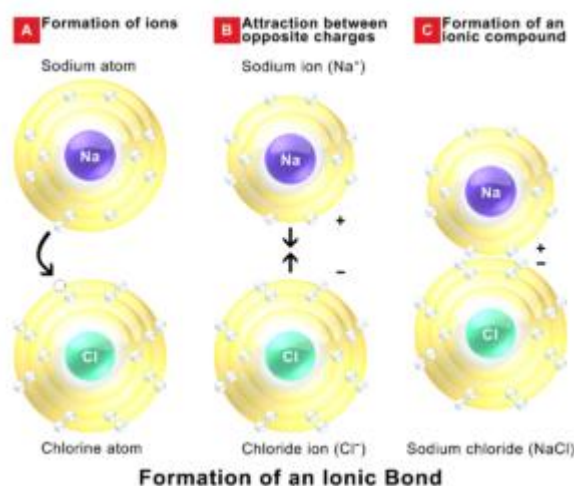


There are three steps to form ionic compound

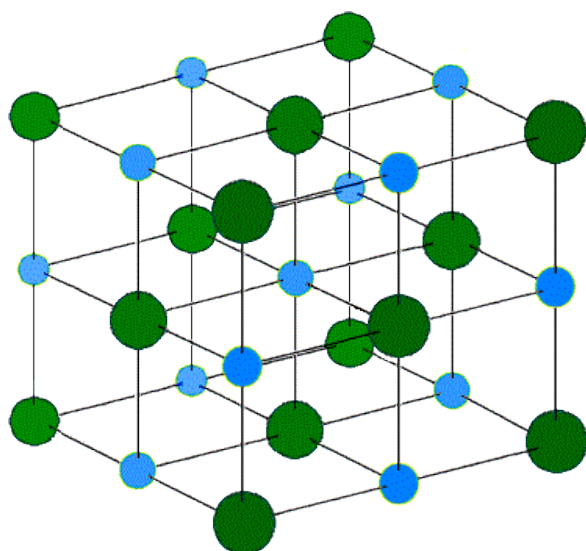
First step: formation of ions

Second step: attraction between opposite charges

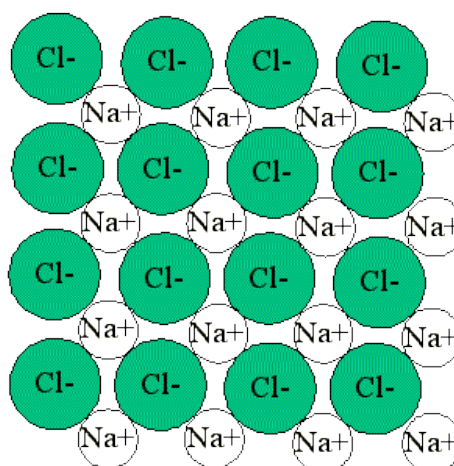
Third step: formation of ionic compound



Ionic Lattices Sodium Chloride is a typical ionic compound. Each sodium ion is surrounded by six chloride ions and each chloride ion is surrounded by six sodium ions. In this arrangement, each ion is strongly attracted to each of its neighbours. The large attractive forces result in a very stable structure. Cl - Na +



Slice through a NaCl crystal

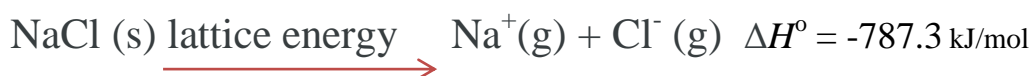


### Characteristic properties of ionic compounds:

1. Ionic compounds are solid (rigid) but (brittle) due to strong forces of attraction between the oppositely charged ions.
2. Ionic compounds have high melting and boiling points, due to strong forces of attraction between the ions.
3. Ionic compounds dissolve easily in water.
4. Solid Ionic compounds do not conduct electricity because their constituent ions are fixed in their positions. But, when melted or dissolved in water, they conduct electricity because the ions become free in a solution.
5. Ionic compounds are crystalline due to the orderly distribution of ions in them. This gives characteristic geometrical shapes to the ionic compounds.

### Definition of Lattice Energy

Lattice energy is an estimate of the bond strength in ionic compounds. It is defined as the heat of formation for ions of opposite charge in the gas phase to combine into an ionic solid. As an example, the lattice energy of sodium chloride, NaCl, is the energy released when gaseous  $\text{Na}^+$  and  $\text{Cl}^-$  ions come together to form a lattice of alternating ions in the NaCl crystal.



Or can define the **lattice energy as the energy required to separate a mole of an ionic solid into the gaseous form of its ions** (that is, the reverse of the reaction shown above).

### Note

Lattice energy cannot be determined experimentally due to the difficulty in isolating gaseous ions. The energy value can be estimated using the Born-Haber cycle, or it can be calculated theoretically with an electrostatic examination of the crystal structure.

### Factors Affecting Lattice Energy

Two main factors that contribute to the lattice energy of an ionic solid: **the charge on the ions**, and **the radius, or size**, of the ions. The effect of those factors is:

- as the charge of the ions increases, the lattice energy increases
- as the size of the ions increases, the lattice energy decreases

### Note

Lattice energies are also important in predicting the solubility of ionic solids in H<sub>2</sub>O. Ionic compounds with smaller lattice energies tend to be more soluble in H<sub>2</sub>O.

### 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 equation proposed by Max Born and Alfred Landé states that lattice energy can be derived from ionic lattice based on electrostatic potential and the potential energy due to repulsion.

To solve for the Born-Landé equation, you must have a basic understanding of lattice energy:

- Lattice energy decreases as you go down a group (as atomic radii goes up, lattice energy goes down).
- Going across the periodic table, atomic radii decreases, therefore lattice energy increases.

The Born-Landé equation was derived from these two following equations. The first is the electrostatic potential energy:

$$\Delta U = \frac{N_A M |Z^+| |Z^-| e^2}{4\pi\epsilon_0 r} \quad \text{-----1}$$

with

- $N_A$  is Avogadro's constant ( $6.022 \times 10^{23}$ )
- $M$  is the Madelung constant (a constant that varies for different structures)
- $e$  is the charge of an electron ( $1.6022 \times 10^{-19}$  C)
- $Z^+$  is the cation charge
- $Z^-$  is the anion charge
- $\epsilon_0$  is the permittivity of free space
- $4\pi\epsilon_0 = 1.112 \times 10^{-10} \text{ C}^2/(\text{J}\cdot\text{m})$

The second equation is the repulsive interaction:

$$\Delta U = \frac{N_A B}{r^n} \quad \text{-----2}$$

with

- $B$  is the repulsion coefficient and
- $n$  is the Born Exponent (typically ranges between 5-12) that is used to measure how much a solid compresses

These equations combine to form:

$$\Delta U(0K) = \frac{N_A M |Z^+| |Z^-| e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right) \dots \dots \dots -3$$

with

- $r_0$  is the distance to closest ion
- $n$  = the number of ions in the formula unit.

<b>n value</b>	<b>5</b>	<b>7</b>	<b>9</b>	<b>10</b>	<b>12</b>
<b>Symbol</b>	He	Ne	Ar	Kr	Xe

## Problems

1. Which compound has the greatest lattice energy?
  - $\text{AlF}_3$
  - $\text{NaCl}$
  - $\text{LiF}$
  - $\text{CaCl}_2$
2. What is the lattice energy of  $\text{NaCl}$ ? (Hint: you must look up the values for the constants for this compound)
3. Calculate the lattice energy of  $\text{NaCl}$ .

## Solution

1. This question requires basic knowledge of lattice energy. Since  $\text{F}_3$  gives the compound a +3 positive charge and the Al gives the compound a -1 negative charge, the compound has large electrostatic attraction. The bigger the electrostatic attraction, the greater the lattice energy.
2. -756 kJ/mol (again, this value is found in a table of constants)
- 3.

$$\text{Lattice Energy of NaCl} = -\frac{\frac{6.022 \times 10^{23}}{\text{mole}} (1.6022 \times 10^{-19}) \times 1.747}{4\pi \times 8.85 \times 10^{-12} \frac{\text{C}^2}{\text{m}} \times 282 \times 10^{-12} \text{m}} \left(1 - \frac{1}{9}\right) \approx -756 \frac{\text{kJ}}{\text{mol}}$$

## Born Haber cycle

Born Haber process or more commonly referred to as Born Haber cycle is a method that allows us to observe and analyze energies in a reaction. It mainly helps in describing the formation of ionic compounds from different elements

### What is Born Haber Cycle?

Born Haber cycle is a cycle of enthalpy change of process that leads to the formation of a solid crystalline ionic compound from the elemental atoms in their standard state and of the enthalpy of formation of the solid compound such that the net enthalpy becomes zero.

### Note

Hess's Law: The total change in enthalpy of the complete course of a chemical reaction is the same, weather the reaction is made in one step or in several steps

Standard Molar Enthalpy of Formation ( $\Delta H_f^0$ ):- The change in enthalpy when one mole of a substance formed from its pure elements in standard state (pressure= 1 atm, Temp= 298K).

### Example 1: Born Haber cycle of sodium chloride NaCl, (or any AB-type Mono-valent ionic solid).

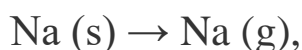
The heat of formation of sodium chloride ( $\Delta H_f^0$ ) from the sodium metal and chlorine gas can be experimentally measured.



The formation of ionic solid sodium chloride from solid sodium metal and gaseous chlorine is not a single step process but goes through several processes. Heat changes of all the processes except the lattice energy can be experimentally measured.

The processes or steps in the formation of sodium chloride are-

**1.** Solid sodium atom sublimates to gaseous atom by absorbing heat energy ( $\Delta H_{\text{sub}}$ ).



Sublimation energy  $\Delta H_{\text{sub}} = + 107\text{kJ/mol}$

**Note:** Heat of atomization ( $\Delta H_{\text{Am}}$  or  $\Delta H_{\text{Sub}}$ ): The energy change when the metal atom turns directly to a gas.

**2.** Gaseous sodium atom absorbs the ionization energy to release one electron and forms gaseous sodium ion.



Ionization energy  $\Delta H_{\text{IE}} = +502\text{kJ/mol}$

Note: Ionization energy is the energy required to remove an electron from a gaseous atom or ion.

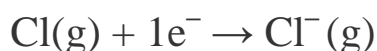
**3.** Diatomic gaseous chlorine breaks into two individual atoms by absorbing bond energy, such that each chlorine atom absorbs half of the bond energy of chlorine molecule.



Bond dissociation energy of chlorine =  $1/2 \Delta H_{\text{diss}} = 1/2(242) = +121\text{kJ/mol}$

Note: Heat of dissociation ( $\Delta H_{\text{D}}$ ): The energy required for breaking one mole of a bond to give separate atoms

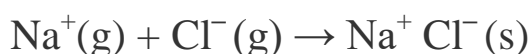
**4.** Chlorine atom accepts an electron to form chloride ion and releases energy equivalent to electron affinity.



Electron affinity =  $\Delta H_{\text{EA}} = -355\text{kJ/mol}$

Note: electron affinity of an atom or molecule is defined as the amount of energy released when an electron is added to a neutral atom or molecule to form a negative ion

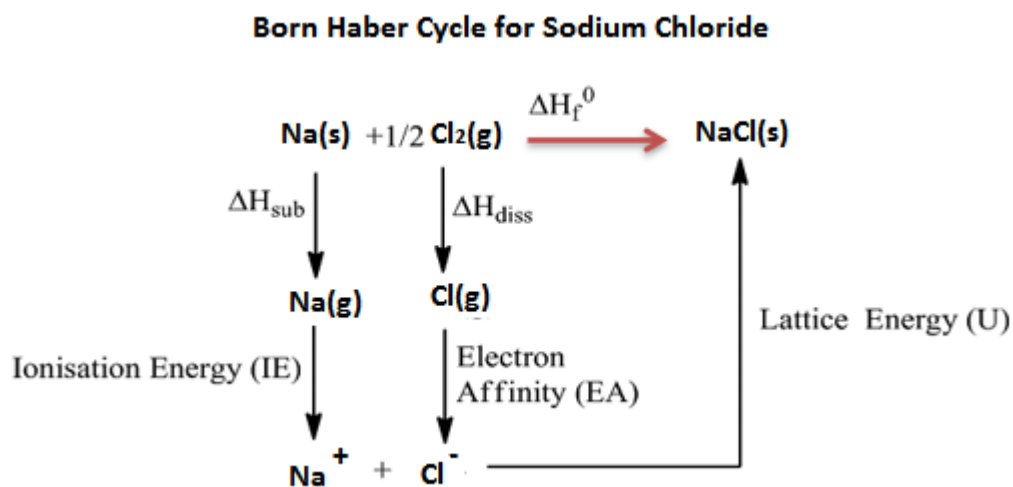
5. Gaseous sodium ion and gaseous chloride ion combine to form solid sodium chloride molecule and releases energy equivalent to lattice energy.



Lattice energy =  $\Delta H_{\text{LE}} = U = ?$

Summation of enthalpy of all the processes from step 1 to step 5) give the net enthalpy of formation of solid crystalline sodium chloride from sodium and chlorine in their standard conditions of solid and gas respectively. This should be equal to the experimentally measured enthalpy of formation of solid sodium chloride.

The enthalpies are represented as a cycle in the figure.



So,  $\Delta H_f^0 = \Delta H_{\text{sub}} + \Delta H_{\text{IE}} + \Delta H_{\text{dis}} + \Delta H_{\text{EA}} + U$  or  $\Delta H_f^0 - (\Delta H_{\text{sub}} + \Delta H_{\text{IE}} + \frac{1}{2}\Delta H_{\text{dis}} + \Delta H_{\text{EA}} + U) = 0$

$$411 + 107 + 502 + 121 - 355 + U = 0$$

Here, except lattice energy, all other enthalpies can be experimentally measured.

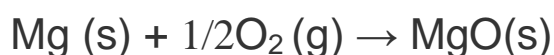
Lattice energy of the sodium chloride solid =  $U = \Delta H_f^0 - (\Delta H_{\text{sub}} + \Delta H_{\text{IE}} + \frac{1}{2} \Delta H_{\text{dis}} + \Delta H_{\text{EA}})$ .

$$= -411 - 107 - 502 - 121 + 355$$

$$= -786\text{kJ/mol}$$

**Example 2: Lattice energy of magnesium oxide (or any AB-type Divalent ionic solid).**

The heat of formation of magnesium oxide ( $\Delta H_f^0$ ) from the magnesium metal and oxygen gas can be experimentally measured.



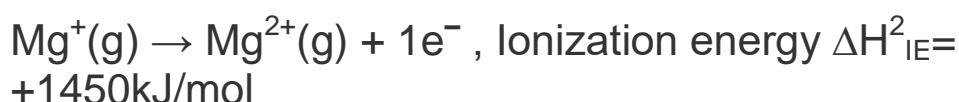
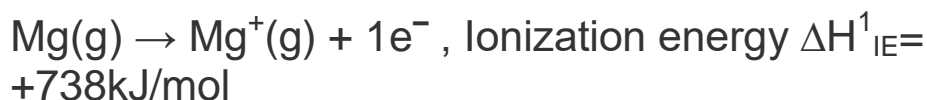
$$\Delta H_f^0 = -602\text{kJ/mol}$$

The processes or steps in the formation of magnesium oxide are-

1. Solid magnesium atom sublimates to gaseous atom by absorbing heat energy ( $\Delta H_{\text{sub}}$ ).

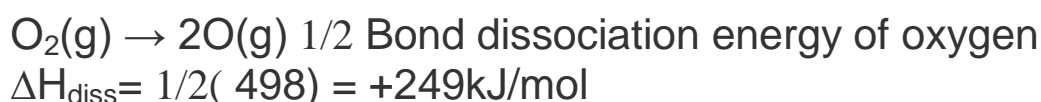


2. Gaseous magnesium atom releases two electrons in two steps with corresponding ionization energies.

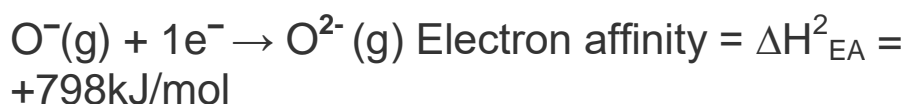


So energy of ionization =  $\Delta H_{\text{IE}} = 738 + 1450 = 2188\text{kJ/mol}$

3. Diatomic oxygen breaks into two individual atoms by absorbing bond energy, such that each chlorine atom absorbs half of the bond energy of the chlorine molecule.

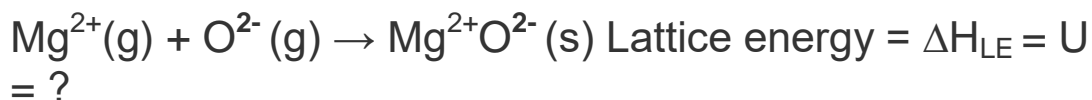


4. Oxygen atom accepts two electrons to form oxide ion and releases energy equivalent to two-electron affinities.



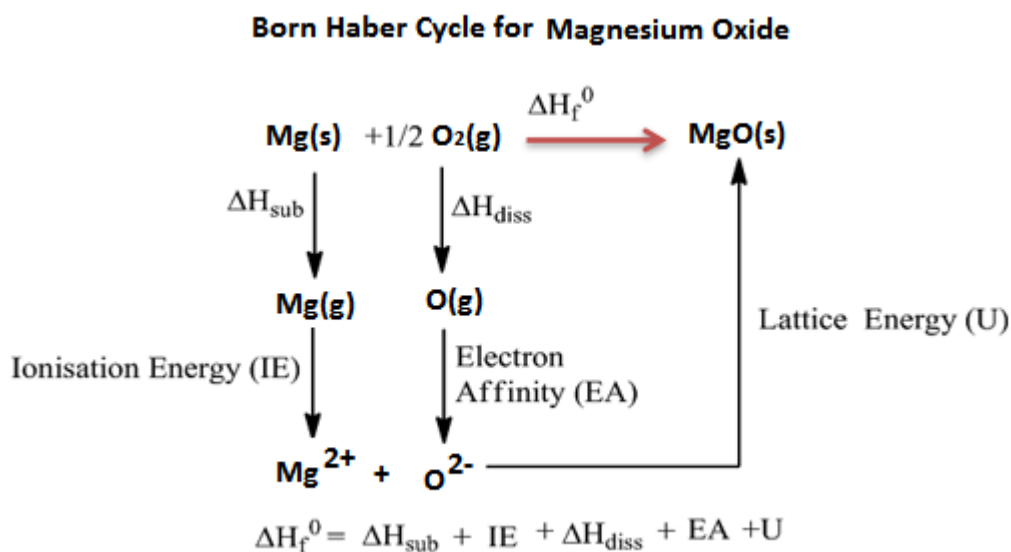
Total energy released as electron affinity by the oxygen atom is  $= \Delta H_{EA} = +656 \text{ kJ/mol}$

5. Gaseous magnesium ion and gaseous oxide ion combine to form solid magnesium oxide molecule and releases energy equivalent to lattice energy.



Summation of enthalpy of all the processes from the starting step to the final step gives the net enthalpy of formation of solid crystalline magnesium oxide from magnesium and oxygen in their standard conditions of solid and gas respectively. This should be equal to the experimentally measured enthalpy of formation of solid magnesium oxide.

The enthalpies are represented as a cycle in the figure.



So,  $\Delta H_f^0 = \Delta H_{\text{sub}} + \Delta H_{\text{IE}} + 1/2 \Delta H_{\text{dis}} + \Delta H_{\text{EA}} + U$  or  $\Delta H_f^0 - (\Delta H_{\text{sub}} + \Delta H_{\text{IE}} + 1/2 \Delta H_{\text{dis}} + \Delta H_{\text{EA}} + U) = 0$

$$602 + 136 + 2188 + 249 + 656 + U = 0$$

Here, except lattice energy, all other enthalpies can be experimentally measured.

Lattice energy of the magnesium oxide solid  $= U = \Delta H_f^0 - (\Delta H_{\text{sub}} + \Delta H_{\text{IE}} + 1/2 \Delta H_{\text{dis}} + \Delta H_{\text{EA}})$ .

$$= -602 - 136 - 2188 - 249 - 656 = -3831 \text{ kJ/mol}$$

Q: Calculate the lattice enthalpy for lithium fluoride, given the following information:

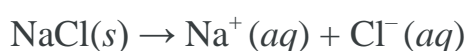
- Enthalpy of sublimation for solid lithium = 161 kJ/mol
- First ionization energy for lithium = 520 kJ/mol
- F-F bond dissociation energy = 154 kJ/mol
- Enthalpy of formation for F(g) = 77 kJ/mol
- Electron affinity for fluorine = -328 kJ/mol
- Enthalpy of formation for solid lithium fluoride = -617 kJ/mol

### Solubility of ionic compounds

An ionic crystal lattice breaks apart when it is dissolved in water.

**Dissociation is the separation of ions that occurs when a solid ionic compound dissolves.**

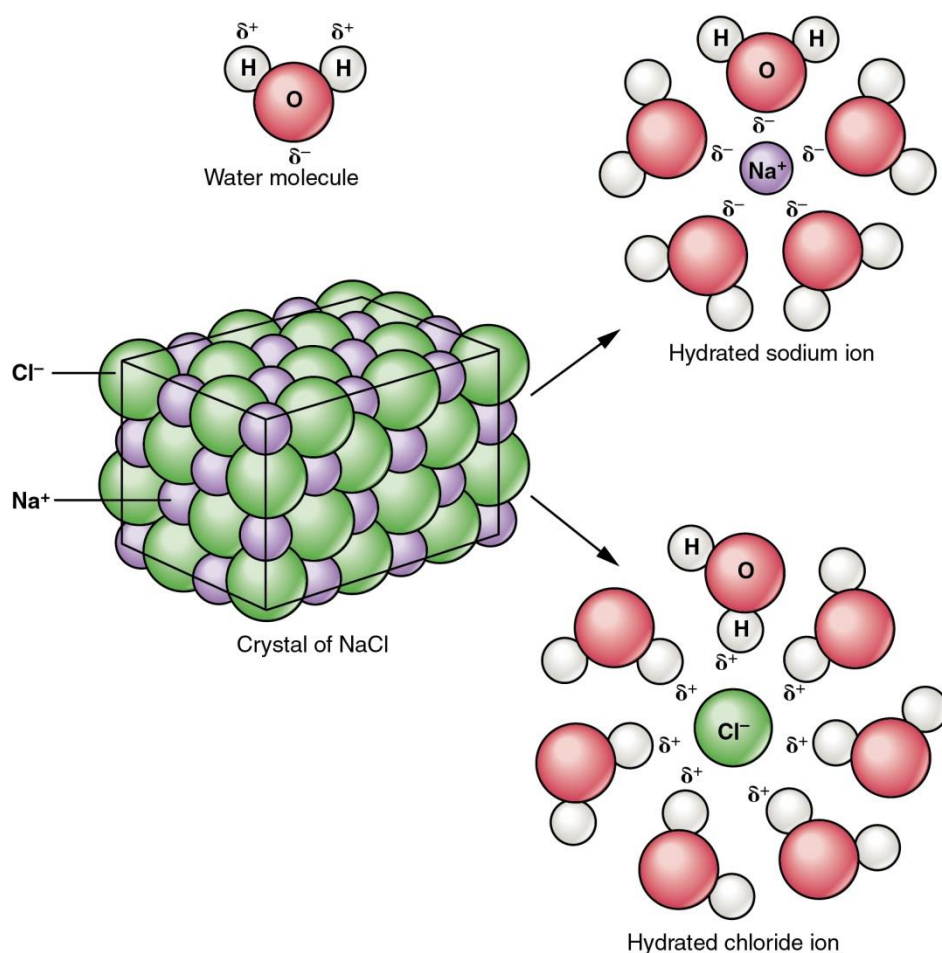
. Shown below are dissociation equations for NaCl, Ca(NO<sub>3</sub>)<sub>2</sub>, and (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>.



The tendency for a compound to dissolve in water depends on the strength of the bonds holding the compound together compared to the strength exerted on the individual ions by the water molecules. Highly soluble compounds, such as NaCl, break apart completely, while compounds with low solubilities, such as lead sulfate (PbSO<sub>4</sub>) do so only partially. Compounds with nonpolar molecules do not dissolve.

The concept of solubility versus insolubility in ionic compounds is a matter of degree. Some ionic compounds are very soluble, some are only moderately soluble, and some are soluble so little that they are considered insoluble. For most ionic compounds, there is also a limit to the amount of compound can be dissolved in a sample of water. For example, you can dissolve a maximum of 36.0 g of NaCl in 100 g of water at room temperature, but you can dissolve only 0.00019 g of AgCl in 100 g of water.

Water typically dissolves many ionic compounds and polar molecules. The process that occurs when an ionic compound such as (sodium chloride) dissolves in water, water molecules move about continuously due to their kinetic energy. When a crystal of sodium chloride is placed into water, the water's molecules collide with the crystal lattice. Recall that the crystal lattice is composed of alternating positive and negative ions. Water is attracted to the sodium chloride crystal because water is polar and has both a positive and a negative end. The positively charged sodium ions in the crystal attract the oxygen end of the water molecules because they are partially negative. The negatively charged chloride ions in the crystal attract the hydrogen end of the water molecules because they are partially positive. The action of the polar water molecules takes the crystal lattice apart (see image below).



After coming apart from the crystal, **the individual ions are then surrounded by solvent particles in a process called solvation.**

Note that the individual  $\text{Na}^+$  ions are surrounded by water molecules with the oxygen atom oriented near the positive ion. Likewise, the chloride

ions are surrounded by water molecules with the opposite orientation. **Hydration is the process of solute particles being surrounded by water molecules arranged in a specific manner.** Hydration helps to stabilize aqueous solutions by preventing the positive and negative ions from coming back together and forming a precipitate.

### Relating Hydration Energy to Lattice Enthalpy

In the discussion of lattice energy, we consider the ions separated into a gas form whereas in the dissolution process, the ions are also separated, but this time into ions dispersed in a medium with solvent molecules between ions. The medium or solvent has a dielectric constant. The molar enthalpy of solution,  $\Delta H_{\text{sol}}$ , is the energy released when one mole solid is dissolved in a solvent. This quantity, the enthalpy of crystallization, and energy of hydration forms a cycle. Taking the salt NaCl as an example,

The following relationship is obvious

$$\Delta H_{\text{sol}} = \Delta H_{\text{lattice}} + \Delta H_{\text{hydration}}$$

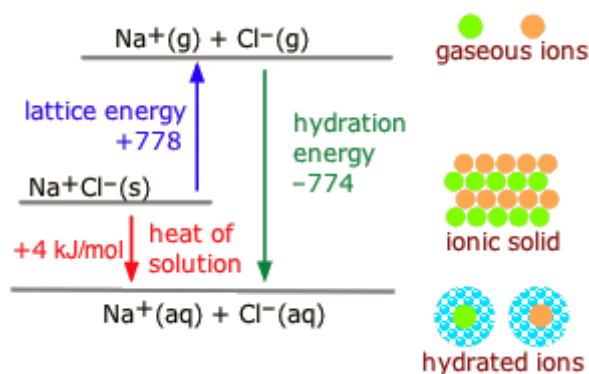


Figure 2: cycle for dissolving NaCl in water

### Note

The enthalpies of solution for some salts can be positive values, in these cases the temperatures of the solution decrease as the

substances dissolve; the dissolving is an endothermic reaction. The energy levels of solids and solutions reverse in order of height.

Example: The lattice energy of NaCl calculated using the Madelung constant of the NaCl structure type is +788 kJ/mol. The estimated enthalpy of hydration for sodium and chloride ions are -406 and -363 kJ/mol respectively. Estimate the enthalpy of solvation for NaCl.

### Solution

Using the cycle in Figure 2 and Equation 6,

$$\Delta H_{\text{hyd}} = \Delta H_{\text{lattice}} + \Delta H_{\text{sol}}$$

$$\Delta H_{\text{sol}} = -769 - (788) \text{ kJ} = -19 \text{ kJ/mol}$$

### Factors that affect ion solubility Solutions Solubility

- 1) Ion charge - Ions with small charges tend to be soluble - Increasing the charge increases the force that holds the ions together - (i.e. phosphates,  $\text{PO}_4^{3-}$ , tend to be insoluble).
- 2) Ion size - Small ions tend to be less soluble than large ions - Small ions bond more closely together than large ions - Thus the bond between small ions is stronger than the bond between large ions with the same charge.

### Polarization

The **polarising power** of a positive ion (cation) depends on its size and charge and is larger the larger the charge and the smaller the radius.

The **polarisability** of the negative ion (anion) also depends on its size and charge. The larger the anion radius and the lower its charge the more polarisable it is.

### NOTE

The breakdown of the ionic model occurs because one ion is much smaller than the other.

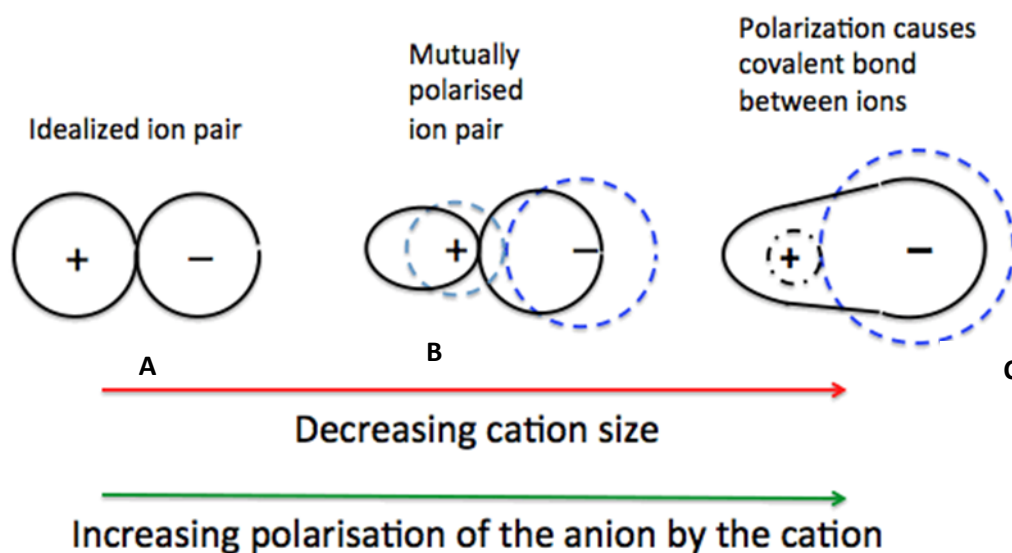
More specifically, the breakdown in the ionic model for some compounds occurs when the positive ion is much smaller than the negative ion.

The suggestion is that the small positive ion **polarises** the larger negative ion.

Also the suggestion is that this **process of polarisation** is more effect at distortion of the ionic model if the positive ion is small and highly charged and the negative ion is large with a low charge.

We see in the graphic below a stylised picture of how the polarization of an anion by a cation can happen.

This figure show that A is idealized ion pair and no polarizing B is exchange polarized of ion pair and C refer to enough polarizing to form covalent bond.



### Fajans' rules

Fajans' rules was formulated by Kazimierz Fajans in 1923 **It is used to predict whether a chemical bond will be covalent or ionic.**

#### Postulates of Fajans' Rule

The rule can be stated on the basis of 3 factors, which are:

1. **Size of the ion:** Smaller the size of cation, the larger the size of the anion, greater is the covalent character of the ionic bond.
2. **The charge of Cation:** Greater the charge of cation, greater is the covalent character of the ionic bond.

3. **Electronic configuration:** For cations with same charge and size, the one, with  $(n-1)d^n ns^0$  which is found in transition elements have greater covalent character than the cation with  $ns^2 np^6$  **electronic configuration**, which is commonly found in alkali or alkaline earth metals.

## Explanation of Fajans' Rule

### Rule 1:

The **first rule** speaks about the polarising power of the cation. If the cation is smaller, then we can say that the volume of the ion is less. If the volume is less, we can conclude that the **charge density** of the ion would be high.

Since the charge density is high, the polarising power of the ion would be high. This makes the compound to be more covalent.

This explains why LiBr is more covalent than KBr (Li<sup>+</sup> 90 pm cf. K<sup>+</sup> 152 pm).

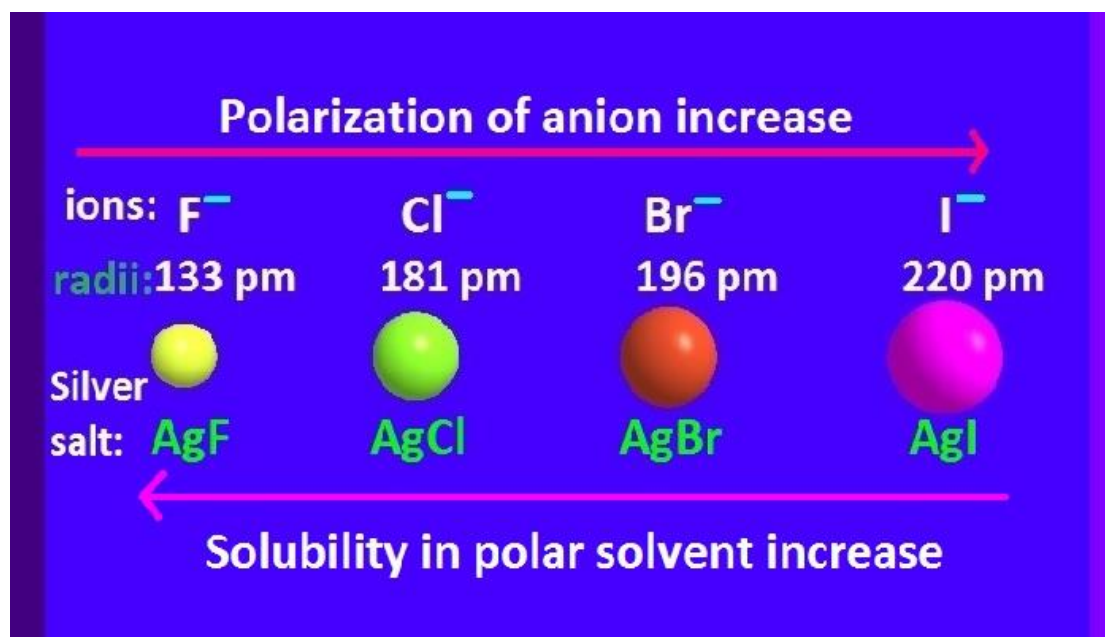
### Rule 2:

The **second rule** speaks about the polarizability of the anion. Larger the anion, less is the effective nuclear charge that holds the **valence electron** of the ion in place. Since the last electron is loosely bound in large anions, it can easily be polarised by a cation, thereby making the compound more covalent.

Polarizability of an anion increase with increase in anionic size or anionic charge

For example, the polarizability of I<sup>-</sup> ion is higher than F<sup>-</sup> ion, due to large size of iodide ion

If the polarizability of an anion increase, then covalent character of the resulting compound increases. Such as, AgI is more covalent than AgF



### Rule 3:

The **third rule** is a special case. Let us use an example to explain this point.

**Example:** If we want to find the more covalent compound among  $HgCl_2$  and Calcium Chloride we cannot use size as a factor to conclude. This is because both  $Hg^{2+}$  and  $Ca^{2+}$  are of almost equal size. To explain this, we employ the **third rule**.

The electronic configuration of  $Hg^{2+}$  is  $6s^0 5d^{10}$ . This configuration is called pseudo-octet because d-orbital is fully filled, but the element does not have 8 electrons or an octet.

We know that d orbitals are not good at shielding, so we can say that the anion ( $Cl^-$ ) would be more polarised because the d orbital is poor at shielding making  $HgCl_2$  more covalent than  $CaCl_2$  because  $Ca^{2+}$  ion has a noble gas configuration.

Now to answer the question that we asked first, amongst the alkali chlorides, which one is the most covalent?

Since the anion is the same, we have to compare the cations. According to **Fajans' rules**, smaller the cation, more is the covalency. Therefore,  $LiCl$  is the most covalent.

### Examples on Fajans' rule

**Illustration 1:** Which compound should theoretically be the most ionic and the most covalent amongst the metal halides?

**Solution:**

The smallest metal ion and the largest anion should technically be the most covalent

Therefore, LiI is the most covalent.

The largest cation and the smallest anion should be the most ionic.

Therefore, CsF should be the most ionic.

**Illustration 2:** Arrange the following according to the increasing order of covalency:

- NaF, NaCl, NaBr, NaI
- LiF, NaF, KF, RbF, CsF

**Solution:**

1. Since the cation is the same, compare the anions. Amongst the anions, larger the size more would be the covalency. Therefore the order is: NaF < NaCl < NaBr < NaI

2. Here the anion is the same, so we compare with cations. Smaller the cation more is the covalency. Therefore, the order is: CsF < RbF < KF < NaF < LiF

Fajans' Rule can be summarized as:

Ionic Characteristic	Covalent Characteristic
Large Cation	Small Cation
Small Anion	Large Anion
Small-charge	Large Charge

**Note**

1- THE CATION IS SMALL AND/OR HAS A HIGH CHARGE - HIGHLY POLARISING.

2- THE ANION IS LARGE AND/OR HAS A HIGH CHARGE - HIGHLY POLARISABLE.

