

# ***Radius ratio rule for ionic compounds***

- (1) In crystals, cations tend to get surrounded by the largest possible number of anions around it.
- (2) If  $r_+$  and  $r_-$  are the radii of cation and anion respectively , then  $r_+/r_-$  represents the radius ratio.
- (3) Greater the radius ratio, greater is the coordination number of cation.
- (4) The geometry of the unit cell depends upon the coordination numbers of cation and anion.
- (5) If the cation is extremely small and anion is extremely large, then radius ratio is very small and packing of anions may be very close to each other, and system will be unstable due to repulsion and hence the structure changes into another suitable and stable arrangement.

# *Radius ratio rule*

- Radius ratio (Rr) :

Radius ratio (Rr) is defined as the ratio of the radius of a cation ( $r_{c+}$ ) to that of an anion ( $r_{a-}$ ). Thus Radius ratios is given by

$$Rr = r_{c+}/r_{a-}$$

- Radius ratio rules :

The limiting radius ratio values which determined the coordination number of the cation and the anion and thus can predict the geometry of ionic crystals are called Radius ratio rules .

# *Limiting radius ratios*

<i>Limiting Radius ratio values</i>	<i>CN</i>	<i>Geometry</i>	<i>Example</i>
0-0.155	2	Linear	UO <sub>3</sub> , CoO <sub>3</sub>
0.155-0.225	3	Triangular Planar	B <sub>2</sub> O <sub>3</sub>
0.225-0.414	4	Tetrahedral	ZnO, CuCl
0.414-0.732	6	Octahedral	NaCl, MgO
0.732-1.00	8	Body Centered Cubic (BCC)	CsCl, NH <sub>4</sub> Br
	12	Hexagonal or cubic closest packing	Metals

## *Limitation of radius ratio rule*

This **rule** is applicable when all the cations and anions are perfectly sphere but in maximum cases the atoms or ions are not perfectly sphere. Hence deviation arises.

# Born Haber Cycle

- 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.
- Born Haber Cycle Examples
- **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.
- $\text{Na (s)} + 1/2 \text{Cl}_2 \text{(g)} \rightarrow \text{NaCl(s)} \quad \Delta H_f^0 = -411\text{kJ/mol}$

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

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



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

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.



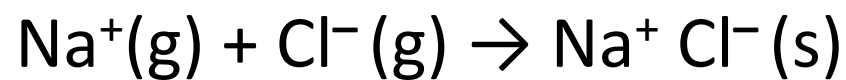
Bond dissociation energy of chlorine  $= 1/2 \Delta H_{\text{diss}} = 1/2 * 242 = +121\text{kJ/mol}$

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



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

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

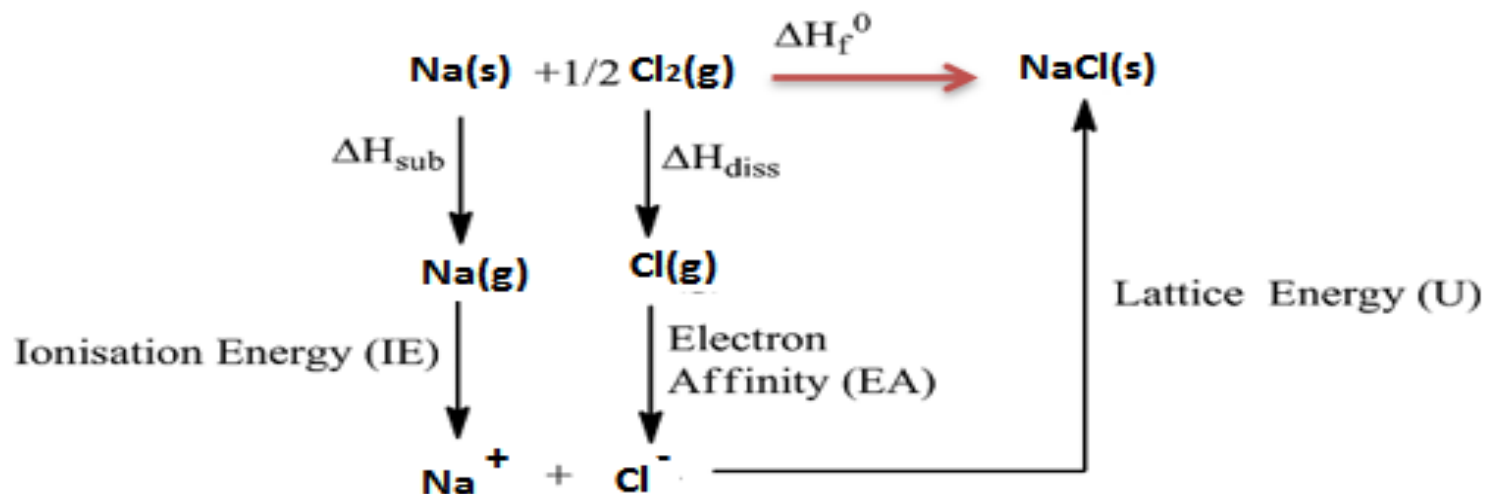


$$\text{Lattice energy} = \Delta H_{\text{LE}} = U = ?$$

➤ 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.

**Born Haber Cycle for Sodium Chloride**



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

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

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

= -411 -107 -502 -121 +355

= -786 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.



- 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.

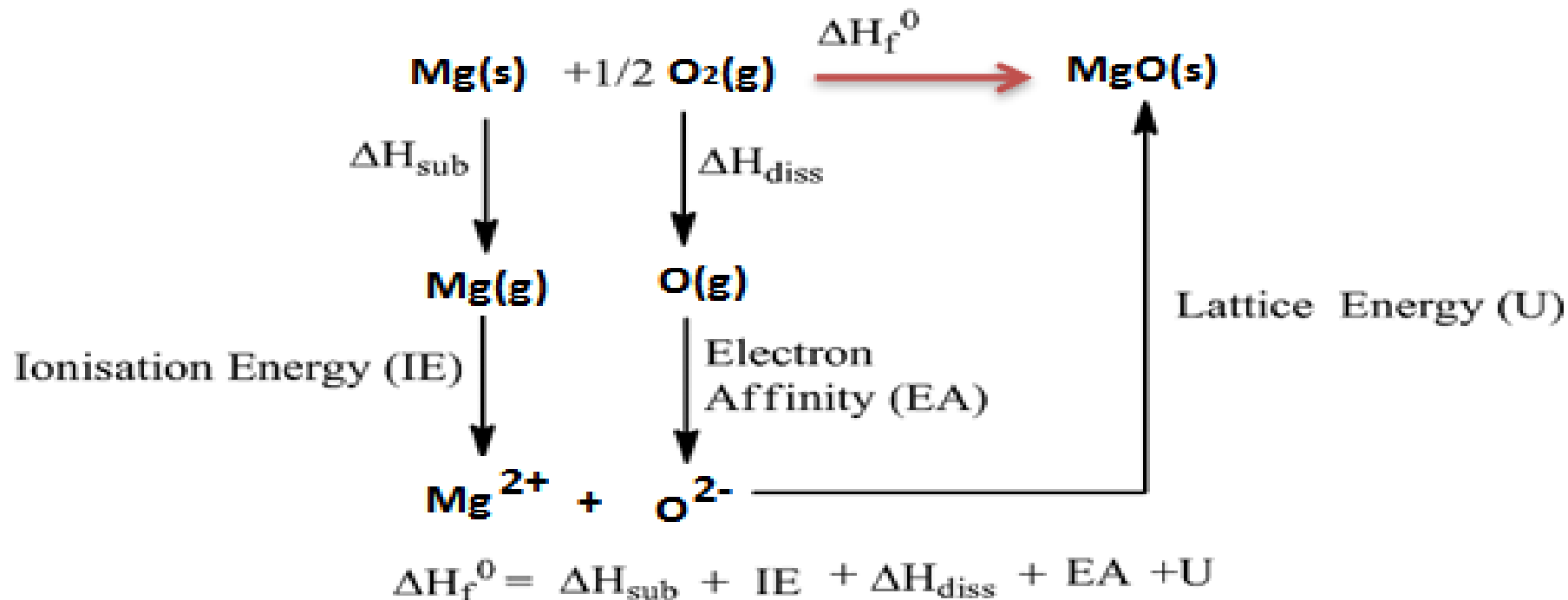


- So energy of ionization =  $\Delta H_{\text{IE}} = 738 + 1450 = 2188\text{kJ/mol}$

- **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.
- $O_2(g) \rightarrow 2O(g)$  ,  $1/2$  Bond dissociation energy of oxygen =  $\Delta H_{\text{diss}} = 1/2 * 498 = +249\text{kJ/mol}$
- **4.** Oxygen atom accepts two electrons to form oxide ion and releases energy equivalent to two-electron affinities.
- $O(g) + 1e^- \rightarrow O^-(g)$  Electron affinity =  $\Delta H_{\text{EA}}^1 = -142\text{kJ/mol}$
- $O^-(g) + 1e^- \rightarrow O^{2-}(g)$  Electron affinity =  $\Delta H_{\text{EA}}^2 = +798\text{kJ/mol}$
- Total energy released as electron affinity by the oxygen atom is =  $\Delta H_{\text{EA}} = +656\text{kJ/mol}$
- **5.** Gaseous magnesium ion and gaseous oxide ion combine to form solid magnesium oxide molecule and releases energy equivalent to lattice energy.
- $Mg^{2+}(g) + O^{2-}(g) \rightarrow Mg^{2+}O^{2-}(s)$  Lattice energy =  $\Delta H_{\text{LE}} = U = ?$

- 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.

## Born Haber Cycle for Magnesium Oxide



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

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

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

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