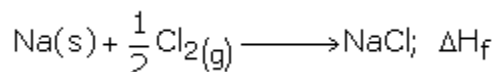


Based on Hess's law born and Haber in 1919 developed a simplified and cyclic method to correlate lattice energies of ionic crystals to other thermodynamic data.

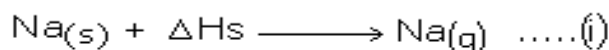
For example, the net energy changes during the formation of sodium chloride from metallic sodium and chlorine gas can be represented by ΔH_f .



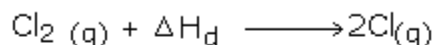
The overall process is thought to take place in following intermediate steps:

Intermediate steps:

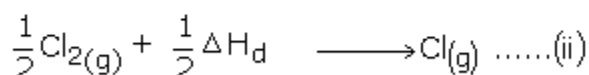
(i) Metallic sodium into gaseous sodium atom: The energy required per mole of sodium is 'enthalpy of sublimation' which is represented by (ΔH_s). This step is energy consuming process.



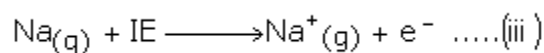
(ii) Dissociation of chlorine molecule into chlorine atoms: The energy required per mole of chlorine is 'enthalpy of dissociation' represented by (ΔH_d)



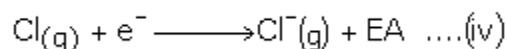
or



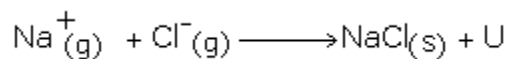
(iii) Gaseous sodium atom into gaseous cat ion: The energy required in this process is called Ionization energy (IE).



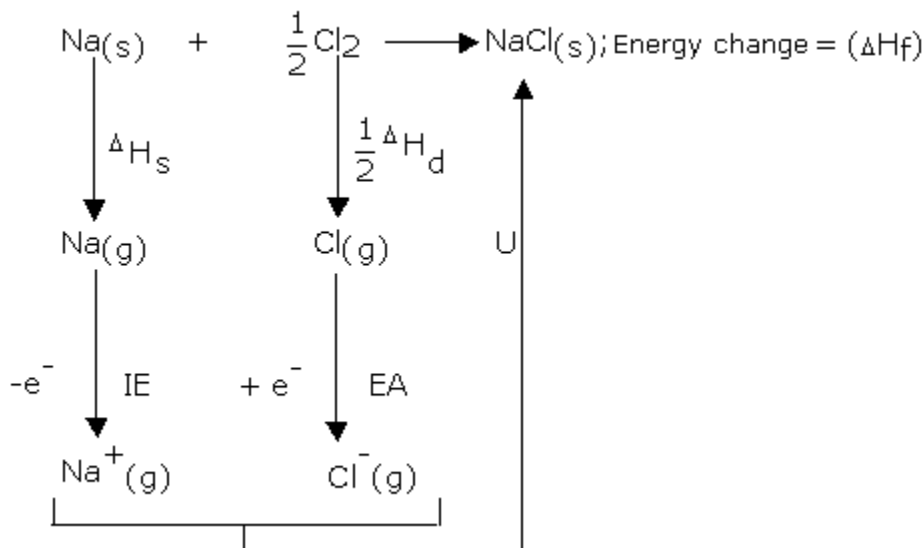
(iv) Gaseous chlorine atom into gaseous anion: This step involves the release of energy referred as Electron Affinity (E.A)



(v) Combination of oppositely charged gaseous ions to form solid crystal: This involves the release of energy referred as lattice energy (U).



The various energy changes in different steps are as shown:



Born Haber Cycle for NaCl: The sum of the energy changes taking place during various steps is equal to ΔH_f i.e., heat of formation of $\text{NaCl}(\text{s})$ according to Hess' Law.

$$\Delta H_f = \Delta H_s + \frac{1}{2} \Delta H_d + \text{IE} + \text{EA} + U \quad \dots(v)$$

Various values for NaCl are as follows:

Heat of sublimation of sodium (ΔH_s) = $108.5 \text{ kJ mol}^{-1}$

Dissociation energy of chlorine (ΔH_d) = $243.0 \text{ kJ mol}^{-1}$

IE of sodium (IE) = $495.8 \text{ kJ mol}^{-1}$, EA of chlorine (EA) = -349 kJ mol^{-1} ,

Lattice energy of NaCl (U) = $-769.8 \text{ kJ mol}^{-1}$

Substituting these values in equation (v) we get

$$\begin{aligned} \Delta H_f(\text{NaCl}) &= \Delta H_s + \frac{1}{2} \Delta H_d + \text{IE} + \text{EA} + U \\ &= 108.5 + \frac{1}{2}(243) + 495.8 + (-349) + (-769.8) \\ &= 393.0 \text{ kJ mol}^{-1} \end{aligned}$$

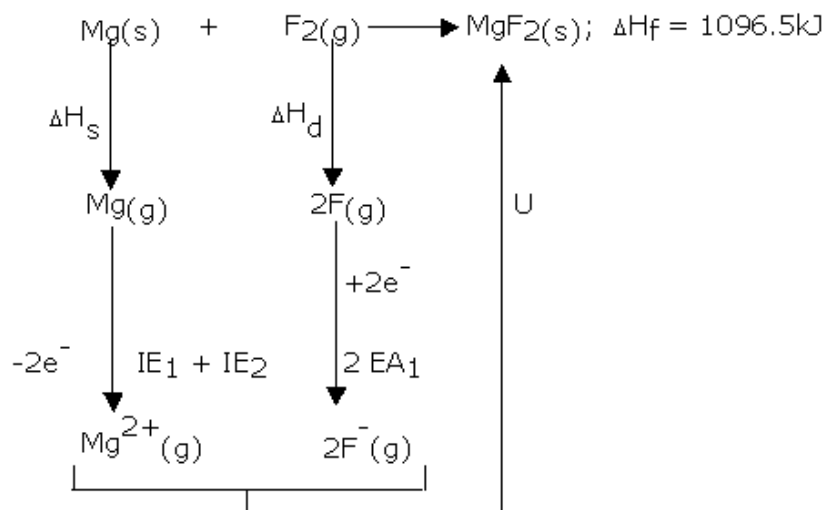
Applications of Born Haber Cycle:

Lattice energy of ionic solids: Born Haber Cycle helps us to calculate the lattice energy of ionic solid, provided other thermodynamic data is known.

For example, the lattice energy of magnesium fluoride (MgF_2) can be calculated when the sublimation energy (S) of $\text{Mg} = 146.4 \text{ kJ mol}^{-1}$; IE_1 and IE_2 values of $\text{Mg} = 737$ and 1449 kJ mol^{-1} Dissociation energy (D) of fluorine = $158.8 \text{ kJ mol}^{-1}$, EA of fluorine = -328 kJ mol^{-1} and

ΔH_f of $\text{MgF}_2 = -1096.5 \text{ kJ mol}^{-1}$.

Born Haber Cycle for MgF_2 is as shown:



Born Haber Cycle for MgF_2

$$\Delta H_f = \Delta H_s + \Delta H_d + (\text{IE}_1 + \text{IE}_2) + 2 \text{EA}_1 + U$$

$$U = \Delta H_f - \Delta H_s - \Delta H_d - (\text{IE}_1 + \text{IE}_2) - 2 \text{EA}_1$$

$$U = -1096.5 - 146.4 - 158.8 - (737 + 1449) - 2(-328) = -2931.7 \text{ kJ mol}^{-1}$$

ΔH_f values

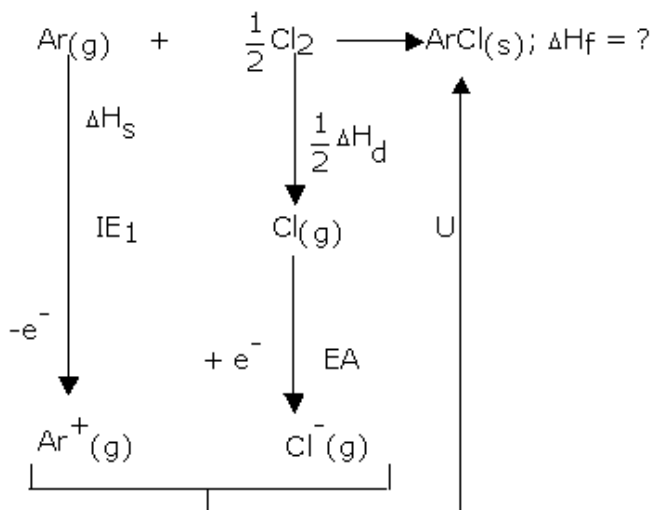
Born Haber cycle can help us to calculate the values of ΔH_f for unknown compounds. From the calculated values of ΔH_f one can predict whether the compound is stable or not.

- If ΔH_f value is negative, the compound is stable.
- If ΔH_f is positive, the formation of compound is highly unfavorable.

For example, to calculate the value of ΔH_f for hypothetical compound ArCl the data given is:

IE_1 for Ar = $526.3 \text{ kJ mol}^{-1}$, Dissociation energy of chlorine (D) = 243 kJ mol^{-1} ; EA of chlorine is - 349 kJ mol^{-1} ; Lattice energy (U) of $\text{ArCl}_{(s)}$ is -703 kJ mol^{-1} .

In the cycle below:



Born Haber cycle for $\text{ArCl}_{(s)}$

$$\Delta H_f = IE_1 + \frac{1}{2} \Delta H_d + EA + U = 526.3 + \frac{1}{2}(243) - 349.0 - 703$$

$$= 595.5 \text{ kJ mol}^{-1}$$

The +ve value of ΔH_f indicates that net energy is required for this process. Hence, formation ArCl is energetically unfavorable.

Electron affinities: The Born Haber cycle can be used for the calculation of electron affinities of some elements that are otherwise very difficult to measure. Heat of formation of a compound may be expressed as:

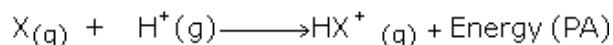
$$\Delta H_f = \Delta H_s + \frac{1}{2} \Delta H_d + IE + EA + U$$

On rearranging:

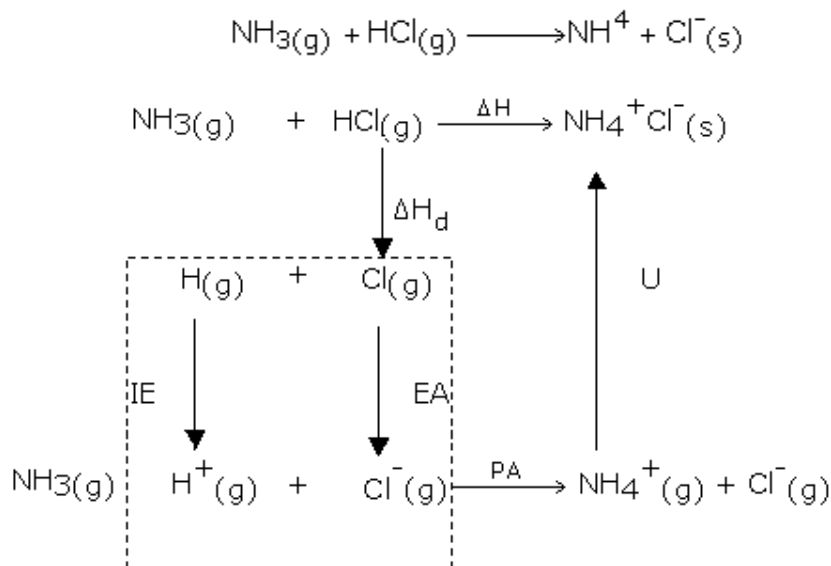
$$EA = \Delta H_f - \Delta H_s - \frac{1}{2} \Delta H_d - IE - U$$

S, ΔH_f , D, and IE are experimentally determined and lattice energy, U may be calculated by using other equation (Born Lande equation). Using the above equation, electron affinity may be calculated.

Proton affinities: The Born Haber cycle can also be used to calculate the proton affinities (PA) of some bases. The proton affinity of a species X is defined as the energy released in the reaction:



To calculate the proton affinity of NH_3 using Born Haber Cycle for the process,



According to Born Haber cycle,
 $\Delta H = \Delta H_d + IE + EA + PA + U$

$$PA = DH - DH_d - IE - EA - U \text{ -----(i)}$$

The thermodynamic data is as:

$$DH = - 144.5 \text{ kJ mol}^{-1}$$

$$IE = 1312 \text{ kJ mol}^{-1}$$

$$EA = -349.0 \text{ kJ mol}^{-1}$$

$$DH_d = 433.0 \text{ kJ mol}^{-1}$$

$$U = -649.0 \text{ kJ mol}^{-1}$$

Substituting the values,

$$PA = - 144.5 - (433.0) - (1313.0) - (-349.0) - (-649.0)$$

$$PA = -891.5 \text{ kJ mol}^{-1}$$