Born - Haber Cycle

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The Born-Haber cycle is a classic approach to measure the reaction energies. The cycle is mostly concerned with the formation of an ionic solid from the metals (Group I or Group II) when reacted with a halogen or a non-metallic element like oxygen.

Applications of Born – Haber Cycle

Born-Haber cycles are primarily used in calculating the lattice energy, which cannot be measured otherwise. The lattice energy is the enthalpy change involved in the formation of ionic solids from gaseous ions or the energy involved in breaking the ionic solids into gaseous ions. A Born-Haber cycle applies Hess' law to calculate the lattice energy by comparing the standard enthalpy change in the formation of the ionic solid from the elements to the enthalpy that is required to form the gaseous ions from the elements.

Born – Haber Cycle Definition

There are several other concepts that one has to understand before getting to the Born – Haber cycle and applying it to determine the lattice energy of an ionic solid. Some of them are:

Ionization Energy

The energy required to take off an electron from the neutral ion/atom. In order to do this, there should be an input of energy, which is why it is always positive. Ionization energy is noted to be increasing across the periodic table from left to right and decreasing from top to bottom. However, there are some exceptions due to the unpredictable stability of completely filled/half-filled orbitals.

Electron Affinity

The energy released when an electron is added to a neutral ion/atom. The energy released is known to have a negative value, but due to the definition of affinity, it is denoted as a positive value. When used to calculate the lattice energy, one has to subtract the electron affinity and not add it because of the positive value. The electron affinity is known for increasing from left to right and decreasing from top to bottom in a periodic table.

Dissociation Energy

The energy needed to break a compound apart. Dissociation is an endothermic process that requires an input of energy. Therefore, its value is always positive. The magnitude of it is dependent on the electronegativity of the atoms involved in the compound.

Sublimation Energy

Known as the energy of atomization, it is required to turn the compound from solid to gas while passing through the liquid phase. It is again an input of energy and is always positive.

The heat of Formation

It is the change in energy when a particular compound is formed from elements. It can be either positive or negative based on the atoms involved and their interaction.

Hess's Law

The overall change in energy is determined by breaking the process into steps and adding changes in each step. The Born – Haber cycle is based on Hess' law and its application of ionic solid.

Step 1

Determine the energy of all the metals and nonmetals in the elemental forms. Subtract the heat of formation of the ionic solid by combining these elements. This will be used as the energy of ionic solids in the equation.

Step 2

According to the Born–Haber cycle, the elements shall be in gaseous forms. Add the enthalpy change by turning the elements into the gaseous states.

Step 3

Metals usually exist as single atoms, which is why there won't be any dissociation energy for them. But nonmetals are polyatomic species. Calculate the dissociation energy for the nonmetals and add them to the value obtained in step 2.
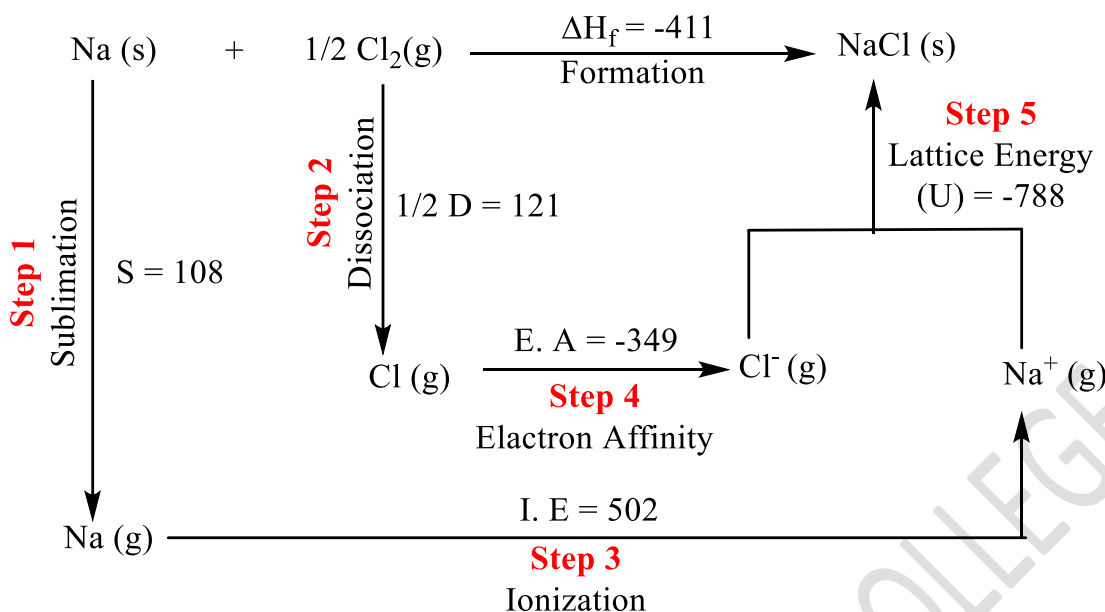
Step 4

Both metals and nonmetals are now to be changed to ionic solids. To do this, add the ionization energy of the metal to the value of step 3. Following that, subtract the electron affinity of nonmetal from the value of step 3.

Step 5

Now, the metal and nonmetal will be combined to release an energy called lattice energy. The value of this energy is the difference of values from Step 1 and Step 4.

Born – Haber Cycle Equation

Heat of formation= Dissociation Energy + Sublimation Energy + Ionization Energies – Electronic Affinities + Lattice Energy.
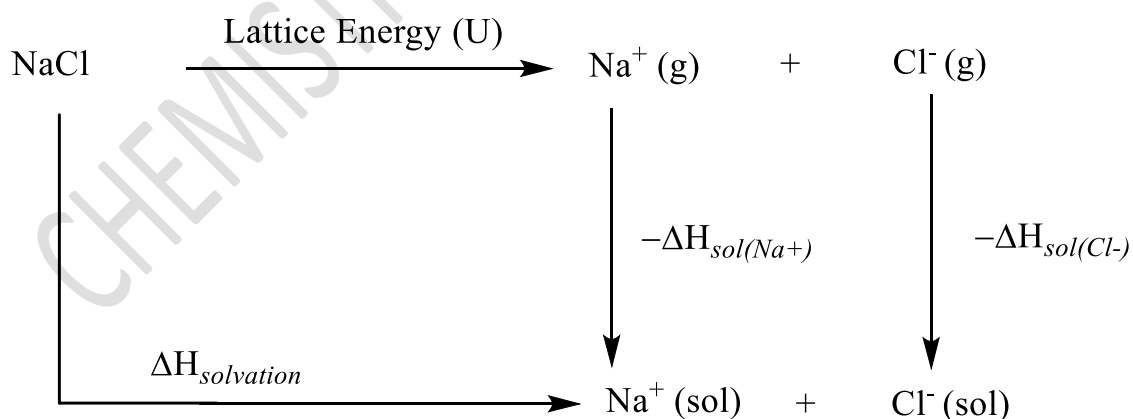
Na (s) + 1/2 Cl$_2$(g) $\xrightarrow[\text{Formation}]{\Delta H_f = -411}$ NaCl (s)

Step 1 Sublimation S = 108

Step 2 Dissociation 1/2 D = 121

Step 5 Lattice Energy (U) = -788

Cl (g) $\xrightarrow[\textbf{Step 4}]{\text{E. A} = -349}$ Cl$^-$ (g) Na$^+$ (g)

Electron Affinity

Na (g) $\xrightarrow{\text{I. E} = 502}$

Step 3 Ionization

Born Haber Cycle of NaCl.

Q. CaF does not exist- why?

Ans. We know that the energy required to produce Ca+ from Ca (IE1) is less than the energy required to produce Ca2+ from Ca (IE1+IE2), but the lattice energy caused by Ca2+ is very high. This high lattice energy favors the two IEs of Ca. Hence, CaF does not exist and can be considered to undergo following disproportionation reaction where more stable CaF2 is produced. CaF→ CaF2 + Ca

Lattice Energy and Solubility

Born Haber cycle for dissolution of NaCl in water is

NaCl $\xrightarrow{\text{Lattice Energy (U)}}$ Na$^+$ (g) + Cl$^-$ (g)

$-\Delta H_{sol(Na+)}$ $-\Delta H_{sol(Cl-)}$

$\Delta H_{solvation}$

Na$^+$ (sol) + Cl$^-$ (sol)

So, according to Hess's law,

$\Delta H_{solvation} = U - \Delta H_{sol(Na+)} - \Delta H_{sol(Cl-)}$

If the solvent is water, the solvation energy will be hydration energy.

Condition for solubility of an ionic salt in water is : |Lattice Energy|< < |Hydration Energy|

It has been seen that for a typical MX type of salt:

$U = K/(r_+ + r_-)$

And hydration energy, $\Delta H_{hyd} = k_1/r_+ + k_2/r_-$

Where, K, k1, k2 are constants and r+ and r- represents the radius(size) of cation and anion respectively.

Case-1: if r+ << r- , then $U = K/r_-$ and $\Delta H_{hyd} = k_1/r_+$

In this case, solubility increases with increasing hydration energy of the cation.

Example: $LiClO_4 > NaClO_4 > KClO_4$ (here, the size of ClO_4^- ion is very large)

Case -2: if r+ >> r- , then $U = K/r_+$ and $\Delta H_{hyd} = k_2/r_-$

In this case, solubility increases with decreasing lattice energy of the salt.

 Example: LiF< NaF< KF (here the size of F ion is very small)