Born Haber's Cycle

Section - 5

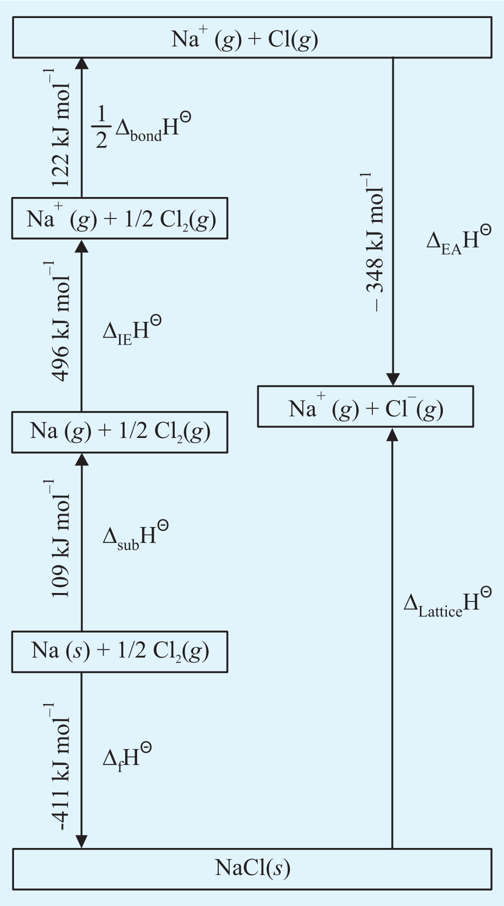
The energy binding ions together in a crystal is called as *lattice energy* ($\Delta_{\text{Lattice}}H^{\ominus}$). Lattice energy is defined as the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state which means $\Delta_{\text{Lattice}}H^{\ominus}$ is +ve i.e., $\text{NaCl}(s) \longrightarrow \text{Na}^{+}(g) + \text{Cl}^{-}(g) \quad \Delta_{\text{Lattice}}H^{\ominus} = +790 \text{ kJ mol}^{-1}$

These crystal lattice energies cannot be measured directly. By applying Hess's Law to a series of elementary processes starting with Na (s) and Cl_2 (g) and ending with formation of NaCl(s), $\Delta_{\text{Lattice}}H^{\ominus}$ can be calculated. Such a sequence of reactions for ionic compounds is called as *Born-Haber Cycle*. The concept is illustrated below by taking the formation of NaCl(s).

The heat of formation of sodium chloride can be calculated from bond energies very easily.

$$\text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) \longrightarrow \text{NaCl}(s) \qquad \Delta_f H^{\ominus} = -411 \text{ kJ mol}^{-1}$$

The following sequences can give the above equation :



1. Sublimation of one mole of Na(s) :

$$\text{Na}(s) \longrightarrow \text{Na}(g) \qquad \Delta_{\text{sub}}H^{\ominus} = +109 \text{ kJ mol}^{-1}$$

2. Dissociation of half mole of Cl_2 :

$$\frac{1}{2}\text{Cl}_2(g) \longrightarrow \text{Cl}(g) \qquad \frac{1}{2}\Delta_{\text{Bond}}H^{\ominus} = +122 \text{ kJ mol}^{-1}$$

(Bond energy of Cl_2 is $\Delta_{\text{Bond}}H^{\ominus} = 244$ kJ/mole)

3. Ionisation of one mole of Na atoms :

$$\text{Na}(g) \longrightarrow \text{Na}^{+}(g) + 1e^{-} \qquad \Delta_{\text{IE}}H^{\ominus} = +496 \text{ kJ mol}^{-1}$$

(First ionisation energy of Na atoms is 496 kJ/mole)

4. Addition of one mole of electrons to one mole of chlorine atoms:

$$\text{Cl}(g) + 1e^{-} \longrightarrow \text{Cl}^{-}(g) \qquad \Delta_{\text{EA}}H^{\ominus} = -348 \text{ kJ mol}^{-1}$$

(Electron affinity of chlorine is 348 kJ/mole)

(*Electron affinity is the energy released, so ΔH is negative*).

5. Condensation of gaseous ions to form one mole of solid NaCl :

This *can not* be calculated directly.

$$\text{Na}^{+}(g) + \text{Cl}^{-}(g) \longrightarrow \text{NaCl}(s) \qquad \Delta_r H^{\ominus} = -\Delta_{\text{Lattice}}H^{\ominus}$$

The summation of the above five reactions and their ΔH values allows us to calculate the value of $\Delta_{\text{Lattice}}H^{\ominus}$.

$$\Delta_f H^{\ominus}\ (-411) = \Delta_{\text{sub}}H^{\ominus}\ (+109\text{kJ}) + \frac{1}{2}\Delta_{\text{Bond}}H^{\ominus}\ (+122\text{kJ}) + \Delta_{\text{IE}}H^{\ominus}\ (+496\text{kJ}) + \Delta_{\text{EA}}H^{\ominus}\ (-348\text{kJ}) - \Delta_{\text{Lattice}}H^{\ominus}$$

$\Rightarrow \quad \Delta_{\text{Lattice}}H^{\ominus} = +790$ kJ/mol of solid NaCl.

Note : The crystal lattice is a measure of the stability of an ionic solid. The more negative its value, the more energy is released in the hypothetical reaction in which a mole of ionic solid is formed from its constituent ions in the gaseous state.

Illustration - 12 *Find the electron affinity of chlorine from the following data (in kcal/mol).*

Enthalpy of formation of LiCl is –97.5; Lattice energy of LiCl = 197.7 ; Dissociation energy of chlorine = 57.6

Sublimation enthalpy of Lithium = 38.3 ; Ionisation energy of Lithium = 123.8 ;

SOLUTION :

For a ionic compound of type LiCl :

$$\Delta_{\text{Lattice}}H^{\ominus}_{\text{LiCl}} = \Delta_{\text{EA}}H^{\ominus}_{\text{Cl}} - \Delta_{f}H^{\ominus}_{\text{LiCl}} + \frac{1}{2}\Delta_{\text{bond}}H^{\ominus}_{\text{Cl}_2} + \Delta_{\text{sub}}H^{\ominus}_{\text{Li}} + \Delta_{\text{IE}}H^{\ominus}_{\text{Li}}$$

$$197.7 = \Delta_{\text{EA}}H^{\ominus}_{\text{Cl}} - (-97.5) + \frac{1}{2}\times 57.6 + 38.3 + 123.8 \quad \Rightarrow \quad \Delta_{\text{EA}}H^{\ominus}_{\text{Cl}} = -90.7 \text{ kcal/mol}$$

Relation between Δ_rH and Δ_rU Section - 6

Enthalpy (H) and Internal Energy (U) are related as :

$$H = U + PV$$

$\Rightarrow$ $\Delta H = \Delta U + \Delta(PV)$

or $dH = dU + d(PV)$

Now, for a reaction, we can write : $\Delta_r H = \Delta_r U + P\Delta V$ [Chemical reactions occur at constant T and P]

or $\Delta_r H = \Delta_r U + \Delta n_g RT$ where $\Delta n_g = \sum (n_g)_{\text{products}} - \sum (n_g)_{\text{reactants}}$ = Change in the number of gaseous moles

Illustration - 13 *Find the sign of $\Delta_r H - \Delta_r U$ for the following reactions :*

(i) $H_2(g) + Cl_2(g) \longrightarrow HCl(g)$ **(ii)** $N_2(g) + O_2(g) \longrightarrow NO_2(g)$

(iii) $PH_3(g) \longrightarrow P_4(s) + H_2(g)$ **(iv)** $C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow CO_2(g) + H_2O(\ell)$

SOLUTION :

First, balance each reaction :

(i) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ **(ii)** $N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g)$

(iii) $4PH_3(g) \longrightarrow P_4(s) + 6H_2(g)$ **(iv)** $C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(\ell)$

Now, Use : $\Delta_r H - \Delta_r U = \Delta n_g RT$ and $\Delta n_g = \sum (n_g)_{\text{products}} - \sum (n_g)_{\text{reactants}}$

$\Rightarrow$ If $\Delta n_g > 0, \Delta_r H - \Delta_r U > 0$;

If $\Delta n_g < 0, \Delta_r H - \Delta_r U < 0$;

If $\Delta n_g = 0, \Delta_r H - \Delta_r U = 0$

(i) $\Delta n_g = 2 - (1 + 1) = 0$ **(ii)** $\Delta n_g = 2 - (1 + 2) = -1$ **(iii)** $\Delta n_g = (6 + 0) - 4 = 2$

(iv) $\Delta n_g = (2 + 0) - \left(1 + \frac{7}{2}\right) = -\frac{5}{2}$ [***Note :*** For $H_2O(\ell)$, $n_g = 0$]