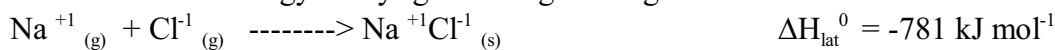


## Lattice Energies: The Born –Haber Cycle

The Born – Haber cycle is a technique for applying Hess's Law to the standard enthalpy changes which occur when an ionic compound is formed.

**Lattice Energy** of ionic compounds is a thermodynamic quantity defined as the enthalpy change, which occurs when one mol of an ionic solid is formed, as a crystal lattice, from its constituent gaseous ions.

This definition of lattice energy always gives a negative sign:



If we were considering the energy required to separate sodium chloride into its constituent ions, then the enthalpy change must have a positive sign:



Lattices energies vary with:

- (i) interionic distances in the crystal, i.e. when the ions are closer together the forces of attraction between them are stronger; example: NaCl: - 771, KCl: - 707, NaF: -918, CsF: - 747
- (ii) the charge on the ions, example: NaCl: - 771, MgO: - 3791

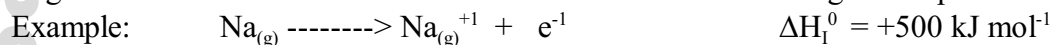
Thus, **the closer together the ions and the larger their charges, the greater the lattice energy.**

Since it is impossible to determine lattice energies directly by experiment we use an indirect method where we construct an energy diagram called a Born- Haber cycle. The Born-Haber cycle is yet another application of Hess' Law but the alternative routes involve more steps.

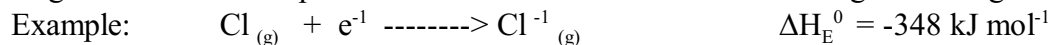
(This cycle was introduced by M. Born, K.Fajans, and F, Haber in 1919. For reason unknown, the cycle is commonly called the “Born- Haber” cycle rather than, more correctly, the Born-Fajans-Haber cycle).

To construct a Born- Haber cycle, we need two enthalpy changes not previously encountered: ionisation energy and electron affinity.

**$\Delta H_{\text{I}}^0$  The ionisation energy of an element** is the enthalpy change, which occurs when one mol of gaseous atoms loses one mol of electrons to form one mol of gaseous positive ions:



**$\Delta H_{\text{E}}^0$  The electron affinity of an element** is the enthalpy change which occurs when one mol of its gaseous atoms accepts one mol of electron to form one mol of gaseous negative ions.



The reactions in the cycle for the formation of a metal halide of formula MX represent (i) the vaporisation of the metal to gaseous atoms and the conversion of the solid metal to cations in the gas phase (step 1 and 2 in the diagram below), (ii) the dissociation of the halogen molecules to halogen atoms and the subsequent conversion of the halogen atoms to anions in the gas phase (step 3 and 4), and (iii) the combination of the gaseous ions to give the solid compound (step 5). The enthalpy change for the last step (step 5) is the lattice energy.

Energies of atomisation (step 1), ionisation energies(step 2 ), and bond dissociation energies (step 3) are generally known from experimental measurements. *Electron affinities (step 4) and lattice energies (step 5), are difficult to measure experimentally, are often determined by Born-Haber cycle calculations.*

## Constructing a Born-Haber Cycle: Formation of $\text{MX}_{(s)}$ from $\text{M}_{(s)}$ and $\frac{1}{2} \text{X}_{2(g)}$



$\Delta H_1$  = energy of atomisation,  $\Delta H^0_s$ , measured by direct calorimetry

$\Delta H_2$  = ionisation energy,  $\Delta H^0_i$ , measured from spectroscopy

$\Delta H_3$  =  $\frac{1}{2}$  bond dissociation energy,  $\frac{1}{2} \Delta H^0_D$ , measured directly from enthalpy of reaction

$\Delta H_4$  = electron affinity,  $\Delta H^0_E$ , difficult to measure directly

$\Delta H_L^0$  = standard Lattice enthalpy, difficult to measure directly

$$\text{Standard Enthalpy of Formation, } \Delta H_f^0 (\text{MX}) = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_L$$

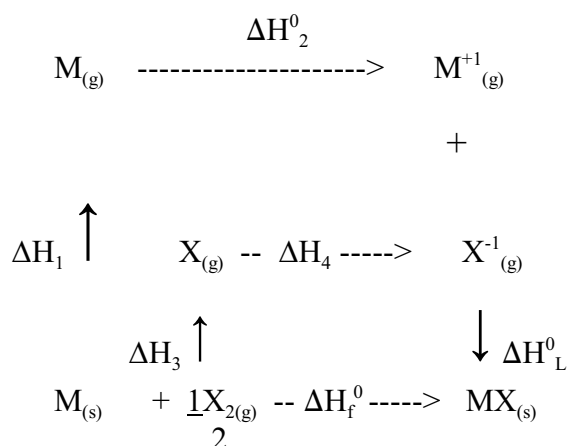
Step (1), (2), and (3) all require the input of energy and have positive  $\Delta H$  values.

Electron affinity( step 4) is negative for the halogens.

Lattice energy,  $\Delta H^0_L$ , values are always negative.

When the lattice energy and electron affinity combined provide the energy required by steps (1) to (3), the formation of the ionic compound in question is exothermic and therefore is more favourable than if it were endothermic.

An easier way to represent the Born-Haber cycle for the compound MX is:



$$\begin{aligned}
 \text{Standard Enthalpy of Formation, } \Delta H_f^0 (\text{MX}) &= \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_L \\
 \Delta H_f^0 (\text{MX}) &= \Delta H^0_s + \Delta H^0_i + \frac{1}{2} \Delta H^0_D + \Delta H^0_E + \Delta H^0_L
 \end{aligned}$$

From the Born-Haber cycle, it can be seen that the greatest contribution in a Born-Haber cycle is made by the ionisation energy (i.e. the energy required), and the lattice energy (i.e. the energy released); these are always opposite in sign ---- i.e. they compete with each other. If ionisation energy is greater than lattice energy, i.e. the overall formation of the compound is an endothermic process, then the compound formed will be unstable, hence not likely to exist.

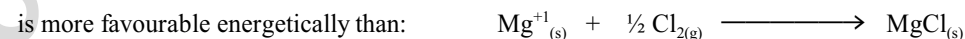
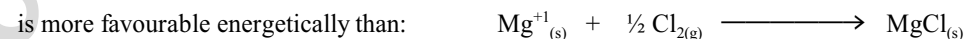
When there is good agreement between the calculated and the experimental lattice energy, then good evidence for the ionic nature of the compound is indicated, otherwise some degree of covalent character is indicated, i.e. to say the bonding is not purely ionic. In all cases discrepancy between the theoretical and the calculated value arises either when the anion is large – due to "polarisation", example  $I^{-1}$ . Deviation in lattice energy values also arise due to "partial covalent character" when the cation ion is small with a multiple charge, example:  $Be^{+2}$ ,  $Mg^{+2}$ ,  $Al^{+3}$ .

In practice, it is easier to measure standard enthalpies of formation than to measure some of the other steps. The electron affinity is the hardest term to measure experimentally: Born-Haber cycles are often used to calculate electron affinities.

Born-Haber cycle may also be used to *calculate  $\Delta H_f^0$  of a hypothetical compound* to see if it exists or why not, if both lattice energy and electron affinity are known.

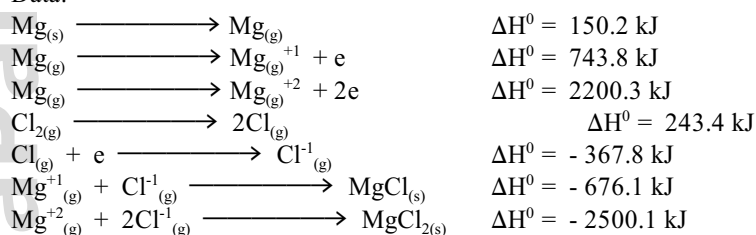
### Example 1

Even though much less energy is required to remove one valence electron from a magnesium atom than both electrons the element from compounds containing  $Mg^{+2}$  ions rather than  $Mg^{+1}$ . With the use of thermo-chemical data provided (at 25°C) show that the reaction:



is more favourable energetically than: Discuss the relative stability of  $MgCl$  and  $MgCl_2$ . Does this explain why  $MgCl$  is not known?

Data:



(Answer: LE  $MgCl_{(s)} = -28.2 \text{ kJ}$ , LE  $MgCl_{2(s)} = -641.8 \text{ kJ}$ .)

The major factor in stability is: Lattice energy of  $MgCl_2 \gggg$  lattice energy of  $MgCl$ . The smaller size and greater charge of  $Mg^{+2}$  compared to  $Mg^{+1}$  contribute to greater lattice energy of  $MgCl_2$

### Example 2

The heat of formation of  $KF_{(s)}$  at 25°C is  $-562.58 \text{ kJ mol}^{-1}$ . Use the following thermodynamic data at 25°C to calculate the lattice energy of  $KF_{(s)}$



(Answer:  $-806.8 \text{ kJ/mol}$ )

### Example 3

a) Sketch the Born - Haber cycle for the formation of  $MO_{(s)}$ , from  $M_{(s)}$  and  $O_{2(g)}$ . Write the expression for  $\Delta H_f^0$  in terms of various enthalpy changes involved.

b) Sketch the Born – Haber cycle for the formation of  $MgS_{(s)}$

### Example 4

Calcium chloride,  $CaCl_2$  is a stable compound. Neither  $CaCl$  nor  $CaCl_3$  exists. according to calculations:

a)  $CaCl_3$  would have a large positive standard enthalpy of formation, and

b)  $CaCl$  would have a small negative value.

Explain (a) and (b) in terms of Born-Haber cycle.

(Answer: (a) The third ionisation energy for Ca is very high,  $\therefore CaCl_3$  is not formed.

(b) To form  $Ca^{+2}$  is more endothermic than the formation of  $Ca^{+1}$ . However, the formation of  $CaCl_2$  includes the term (2x electron affinity of Cl) which is highly exothermic. The sum of the terms makes the formation of  $CaCl_2$  more exothermic than that of  $CaCl$  and  $\therefore$  preferred.