Born Haber

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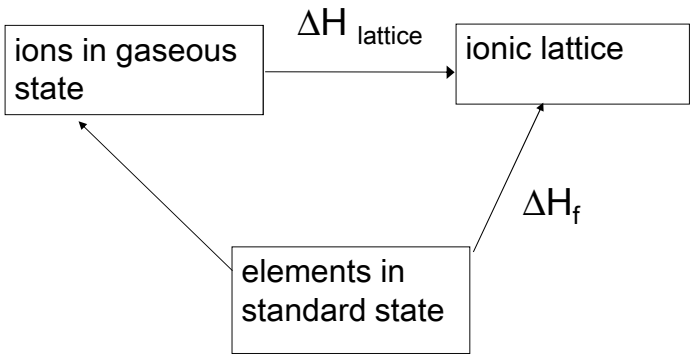
BORN HABER CYCLES

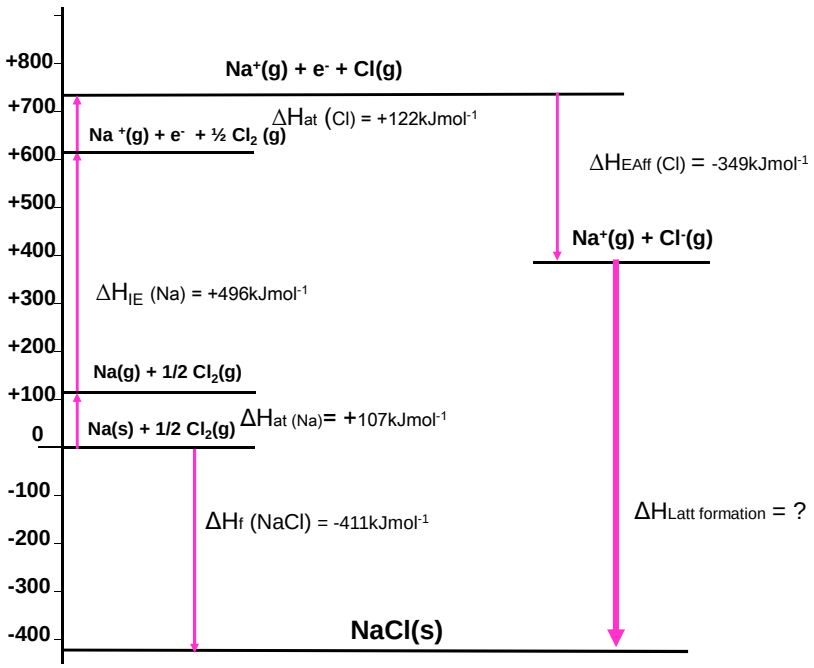
For an ionic compound the **lattice enthalpy** is the heat energy released when one mole of solid in its standard state is formed from its ions in the gaseous state.

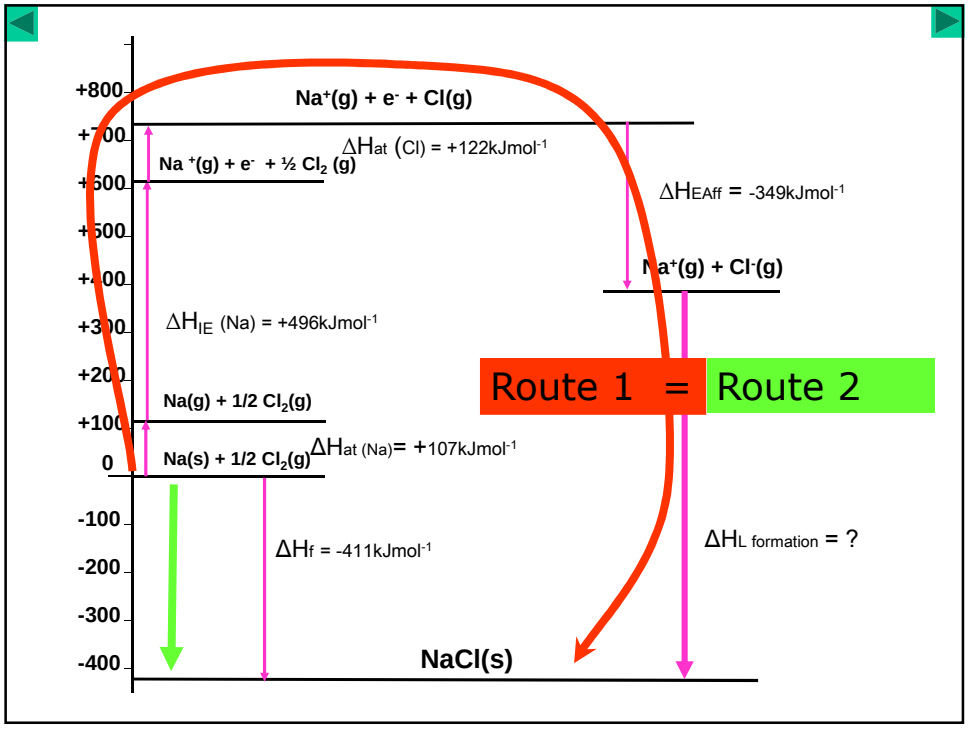
This value cannot be determined directly and so we make use of changes for which data are available and link them together with an enthalpy cycle.

This enthalpy cycle is based on the formation of the compound from its elements in their standard states.

The Born Haber cycle links all these enthalpy changes in an enlarged version of a Hess's law cycle.







Born-Haber Cycles: applying Hess's Law

$\Delta H_{formation}$ = $\Delta H_{atm}Na + \Delta H_{IE}Na + \Delta H_{atm}Cl + \Delta H_{Ea}Cl + \Delta H_{lattice}$

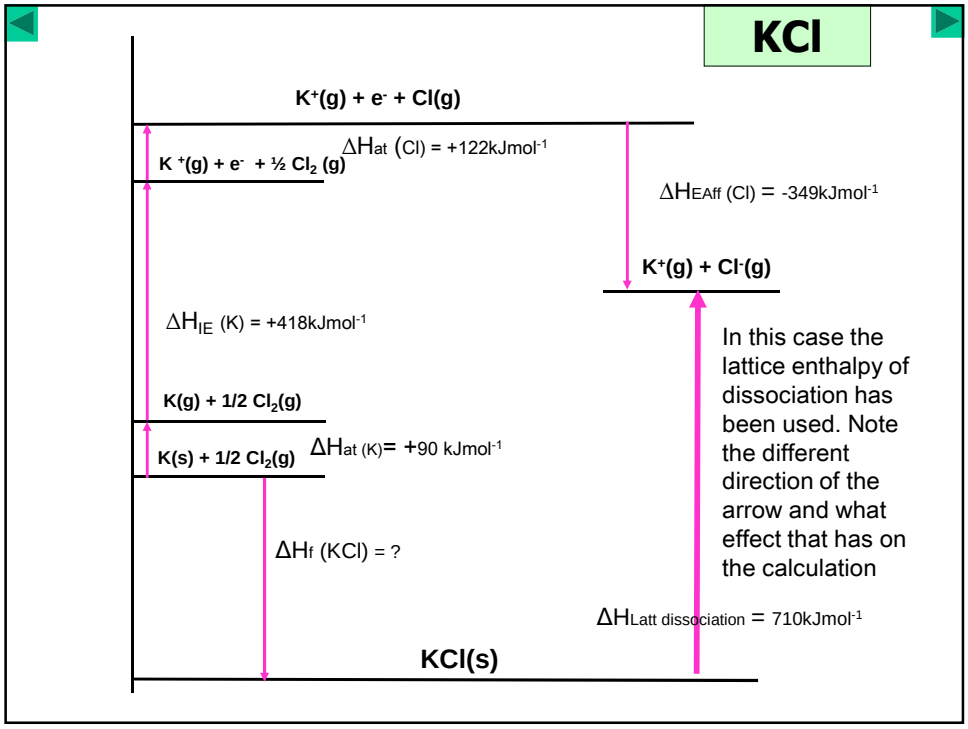
Rearrange to find the lattice energy:

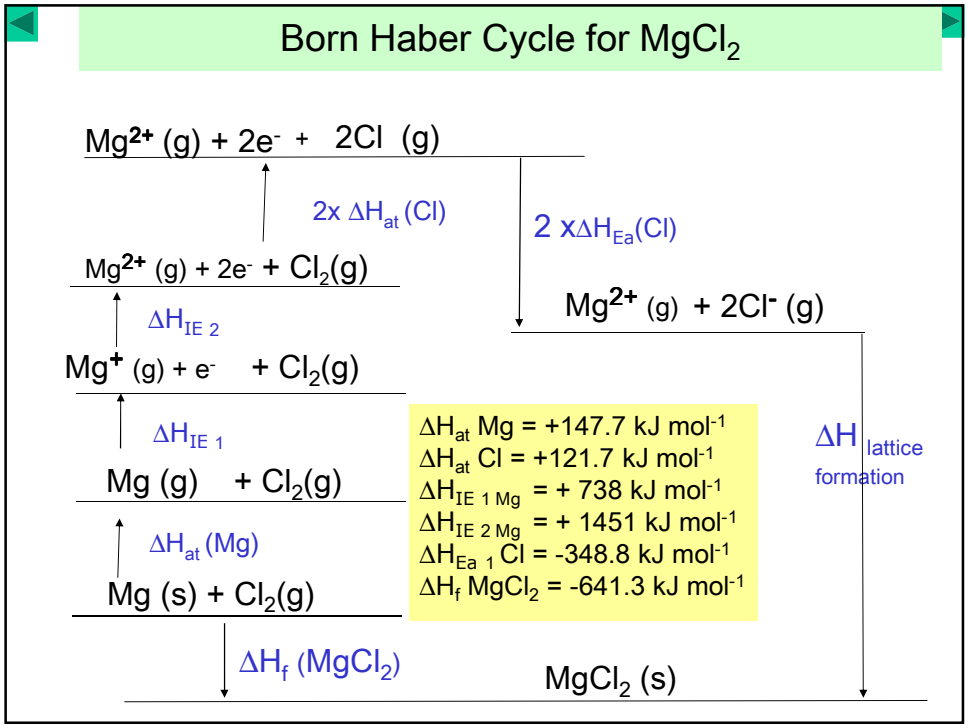
$\Delta H_{lattice} = \Delta H_{formation} - (\Delta H_{atm}Na + \Delta H_{IE}Na + \Delta H_{atm}Cl + \Delta H_{Ea}Cl)$

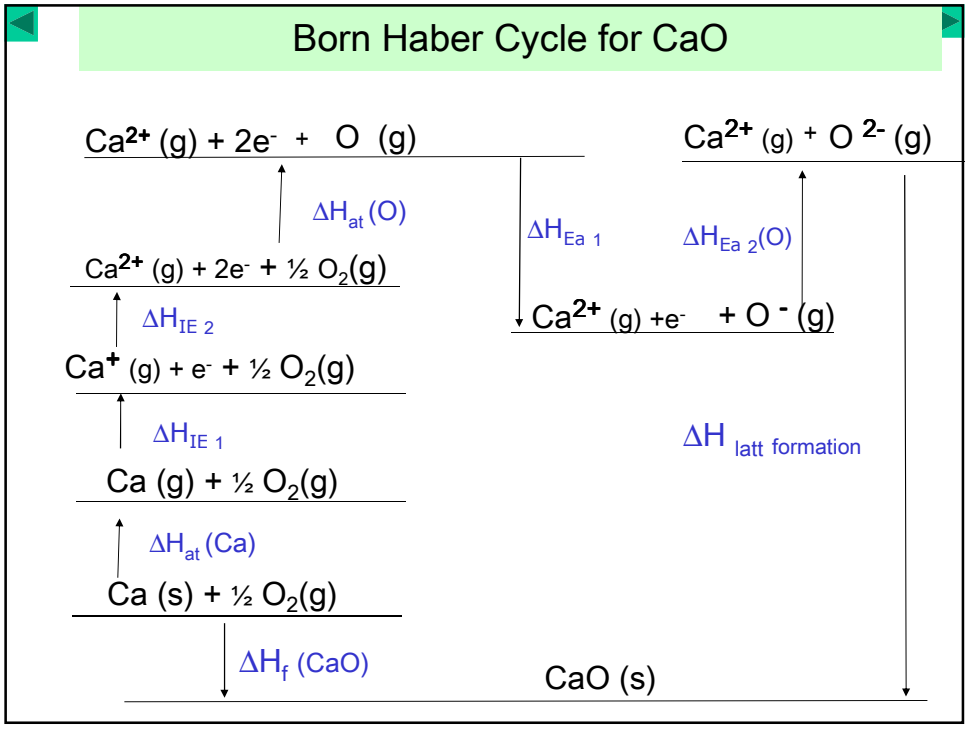
$\Delta H_{lattice}$ =-411 – (+107 + 496 + 122 + -349)

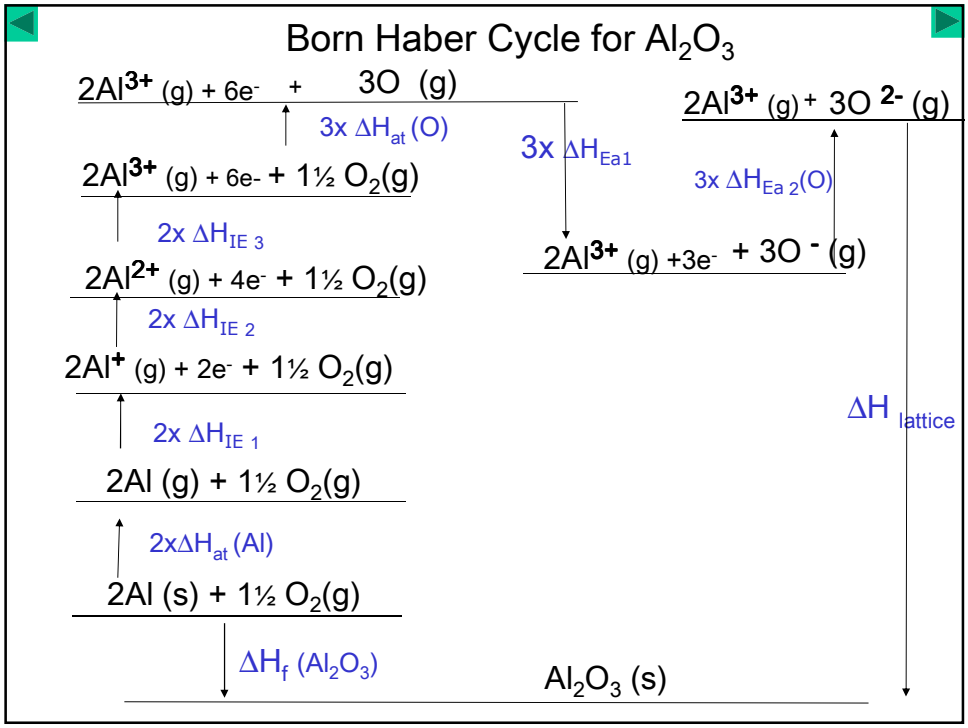
$\Delta H_{lattice}$ = -787 kJmol^{-1}

So Born-Haber cycles can be used to calculate a measure of ionic bond strength based on experimental data.


KCl
K+(g) + e- + Cl(g)
ΔHat (Cl) = +122kJmol-1
K +(g) + e- + ½ Cl2 (g)
ΔHEAff (Cl) = -349kJmol-1
K+(g) + Cl-(g)
ΔHIE (K) = +418kJmol-1
In this case the lattice enthalpy of dissociation has been used. Note the different direction of the arrow and what effect that has on the calculation
K(g) + 1/2 Cl2(g)
K(s) + 1/2 Cl2(g)
ΔHat (K)= +90 kJmol-1
ΔHf (KCl) = ?
ΔHLatt dissociation = 710kJmol-1
KCl(s)


Born Haber Cycle for MgCl2
Mg2+ (g) + 2e- + 2Cl (g)
2x ΔHat (Cl)
2 xΔHEa(Cl)
Mg2+ (g) + 2e- + Cl2(g)
Mg2+ (g) + 2Cl- (g)
ΔHIE 2
Mg+ (g) + e- + Cl2(g)
ΔHIE 1
Mg (g) + Cl2(g)
ΔHat Mg = +147.7 kJ mol-1
ΔHat Cl = +121.7 kJ mol-1
ΔHIE 1 Mg = + 738 kJ mol-1
ΔHIE 2 Mg = + 1451 kJ mol-1
ΔHEa 1 Cl = -348.8 kJ mol-1
ΔHf MgCl2 = -641.3 kJ mol-1
ΔH lattice formation
ΔHat (Mg)
Mg (s) + Cl2(g)
ΔHf (MgCl2)
MgCl2 (s)


Born Haber Cycle for CaO
Ca2+ (g) + 2e- + O (g)
Ca2+ (g) + O 2- (g)
ΔHat (O)
ΔHEa 1
ΔHEa 2(O)
Ca2+ (g) + 2e- + ½ O2(g)
ΔHIE 2
Ca2+ (g) +e- + O - (g)
Ca+ (g) + e- + ½ O2(g)
ΔHIE 1
ΔH latt formation
Ca (g) + ½ O2(g)
ΔHat (Ca)
Ca (s) + ½ O2(g)
ΔHf (CaO)
CaO (s)


Born Haber Cycle for Al2O3
2Al3+ (g) + 6e- + 3O (g)
2Al3+ (g) + 3O 2- (g)
3x ΔHat (O)
3x ΔHEa1
3x ΔHEa 2(O)
2Al3+ (g) + 6e- + 1½ O2(g)
2x ΔHIE 3
2Al3+ (g) +3e- + 3O - (g)
2Al2+ (g) + 4e- + 1½ O2(g)
2x ΔHIE 2
2Al+ (g) + 2e- + 1½ O2(g)
ΔH lattice
2x ΔHIE 1
2Al (g) + 1½ O2(g)
2xΔHat (Al)
2Al (s) + 1½ O2(g)
ΔHf (Al2O3)
Al2O3 (s)

Trends in Lattice Enthalpies

The strength of a lattice enthalpy depends on the following factors

1. The sizes of the ions:

The larger the ions, the less negative the lattice enthalpy (i.e. a weaker lattice). As the ions are larger the charges become further apart and so have a weaker attractive force between them.

The lattice enthalpies become less negative down any group. e.g. LiCl, NaCl, KCl, RbCl

less negative →

LiF, LiCl, LiBr, LiI

2. The charges on the ion:

The **larger the charge** of the ion, the greater the attraction between the ions so the stronger the lattice enthalpy (more negative values).

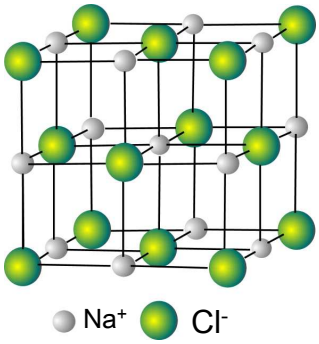
e.g group 1 halides (eg NaF KI) have lattice enthalpies of around –700 to -1000

group 2 halides (eg $MgCl_2$) have lattice enthalpies of around –2000 to –3500

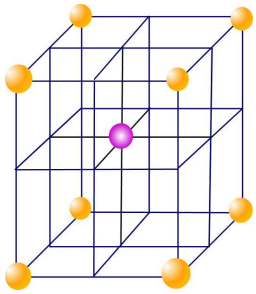
group 2 oxides eg MgO have lattice enthalpies of around –3000 to –4500 $kJmol^{-1}$

3. The structure of the solid.

There are several different arrangements of lattices. Some lattices will have the ions closer together than others



NaCl



CsCl