

## Born-Haber Calculations

### Hess' law

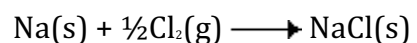
Hess' law is the fundamental basis behind the calculation of all thermodynamic quantities. The principle can be applied to ionic systems by considering the different energy changes required to get from one situation to another.

When Hess' law is applied to the standard enthalpy of formation of an ionic lattice, the different stages form a cycle, called a Born-Haber Cycle.

### Born-Haber Cycles

The enthalpy of formation of a compound is defined as the energy change when 1 mole of a compound is formed from its constituent elements in their states under standard conditions.

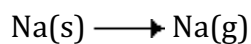
For an ionic compound it is the formation of 1 mole of an ionic lattice from its constituent elements in their standard states:



Notice the difference between the equation above and that of the lattice enthalpy, which forms the lattice from gaseous ions.

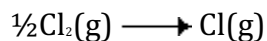
The Born Haber cycle must begin with the elements in their standard states and arrive finally at the ions in position within 1 mole of a lattice. For this, several theoretical energy transformations must take place. These processes are best considered while referring to a specific example, in this case sodium chloride.

**1** - The metal (sodium) must be turned into separate gaseous atoms - atomisation. This is an endothermic process as energy is required to overcome the metallic bonding forces. This is can also be referred to as vaporisation for elements that form atomic vapours (such as a metal)

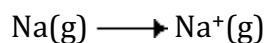


**2** - The non-metal must be turned into separate gaseous atoms - in the case of chlorine this means breaking half a mole of bonds to give one mole of

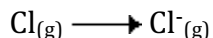
atoms. It is one half the bond enthalpy of chlorine. This can also be referred to as atomisation. However, it is important to note the difference between the definitions of atomisation enthalpy (energy quoted per mole of atoms formed) and the bond dissociation enthalpy (energy quoted per mole of bonds broken = 2 moles of atoms formed).



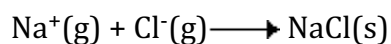
3 - The gaseous metal atoms must be ionised to form gaseous ions - this is the first ionisation energy of sodium. For atoms that have double charges there are two ionisations involved, the first ionisation energy and the second ionisation energy. You may be given the two values separately, or combined together.



4 - The chlorine atoms must be turned into ions. For a non-metal this involves adding an electron to the atom. This is an exothermic process called the electron affinity of chlorine. For negative ions with a double charge there are two electron affinities involved, the first electron affinity and the second electron affinity. The energies may be given to you separately, or combined into one value.



5 - The gaseous ions can then be brought together into the lattice. This is the *opposite* of the lattice enthalpy and is exothermic. Remember that the lattice enthalpy is defined by the IBO as the energy required to break the lattice. In the Born-Haber cycle the step is usually shown as forming the lattice. This should not be a problem providing you understand that breaking the lattice *must* be an endothermic process.



Hess' law tells us that the sum of the energies of all of these steps must equal the enthalpy of formation, as it also takes us from the same starting point to the same conclusion. Born-Haber presents this idea in a graphical form, with the endothermic steps on the left and the exothermic steps on the right.

To use a Born-Haber cycle your starting point and your destination are given by the question's requirements. You simply add up all of the quantities along the

alternative route, taking into account whether the energy change is negative or positive in the direction you are going.

### Born Haber Sodium Chloride

**Example:** Given the following information, calculate the lattice enthalpy of the sodium chloride lattice:

- $\Delta H(\text{atomisation Na}) = +107 \text{ kJmol}^{-1}$
- $\Delta H(\text{1st ionisation Na}) = +496 \text{ kJmol}^{-1}$
- $\Delta H(\text{bond dissociation Cl}_2) = +242 \text{ kJmol}^{-1}$
- $\Delta H(\text{1st electron affinity Cl}) = -349 \text{ kJmol}^{-1}$
- $\Delta H_f(\text{NaCl}) = -411 \text{ kJmol}^{-1}$

From the Born-Haber cycle, the enthalpy of formation equals the sum of all of the other steps involved. However, the bond dissociation enthalpy provides 2 moles of chlorine atoms and we only require 1 mole. Thus we use one half of this value.

$$\Delta H_f(\text{NaCl}) = \Delta H(\text{at. Na}) + \Delta H(\text{1st i.e. Na}) + \frac{1}{2}\Delta H(\text{b.d. Cl}_2) + \Delta H(\text{1st e.a. Cl}) + (-)\Delta H(\text{lattice NaCl})$$

Note that we are using the reverse of the lattice enthalpy, as we are forming the lattice from its ions.

Substitute the values:

$$-411 = 107 + 496 + \frac{1}{2}(242) + -349 + (-)\Delta H(\text{lattice NaCl})$$

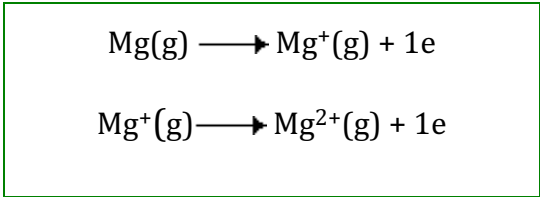
Rearrange:

$$\Delta H(\text{lattice NaCl}) = 411 + 107 + 496 + 121 - 349 = \boxed{786 \text{ kJmol}^{-1}}$$

### Doubly charged ions

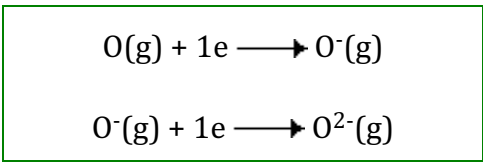
In compounds that involve doubly charged ions, such as magnesium or oxide, there are a couple more steps to take into account in the Born-Haber cycle.

The ionisation step of the metal atom, for example magnesium, must be performed twice to arrive at a double plus ion:



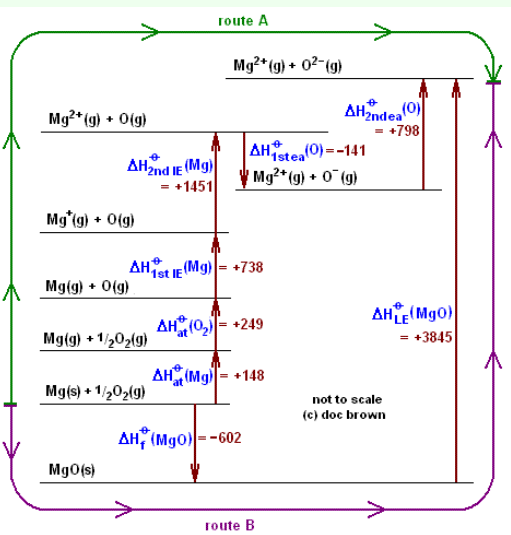
These are the first ionisation energy and the second ionisation energy of magnesium. They are both endothermic processes.

For the non-metal ion, eg oxide, there are two electron affinity steps to arrive at the double negative ion.



The first of these steps is exothermic, but the second electron affinity is always endothermic, as an electron is being added onto an already negatively charged species. This means that the Born-Haber cycle steps back upwards on the diagram. In terms of the calculations it makes no difference, as the values of the two electron affinity steps are simply included with the correct signs into the calculation. An alternative, easier, approach is to add the two electron affinities together before including them in the cycle.

Example: Born Haber cycle for magnesium oxide:



Although the cycle looks confusing it is just the same as that of sodium chloride with two extra steps (one extra ionisation energy and one extra electron affinity) added in. These extra steps could be combined with their corresponding similar steps (eg first and second ionisation energies combined) before constructing the cycle, providing you make it very clear that you have done this.

### Calculations


The actual calculations using a Born-Haber cycle are very simple. The only complication arises when the signs of the enthalpy change need to be reversed, or when the quantities of each component are not equivalent to the enthalpy change in question. We will deal with these complications as they arise.

As the enthalpy of formation equals the sum of all of the other steps, then if we are missing only 1 piece of data we can always work it out using the Born-Haber cycle. For example, in the case of sodium bromide, if we do not know the electron affinity of bromine, but all of the other quantities are known, then rearranging the equation:

$$\Delta H_f(\text{NaBr}) = \Delta H(\text{atomisation Na}) + \Delta H(\text{1st ionisation Na}) + \frac{1}{2}\Delta H(\text{bond dissociation Br}_2) + \Delta H(\text{electron affinity Br}) - \Delta H(\text{lattice enthalpy NaBr})$$

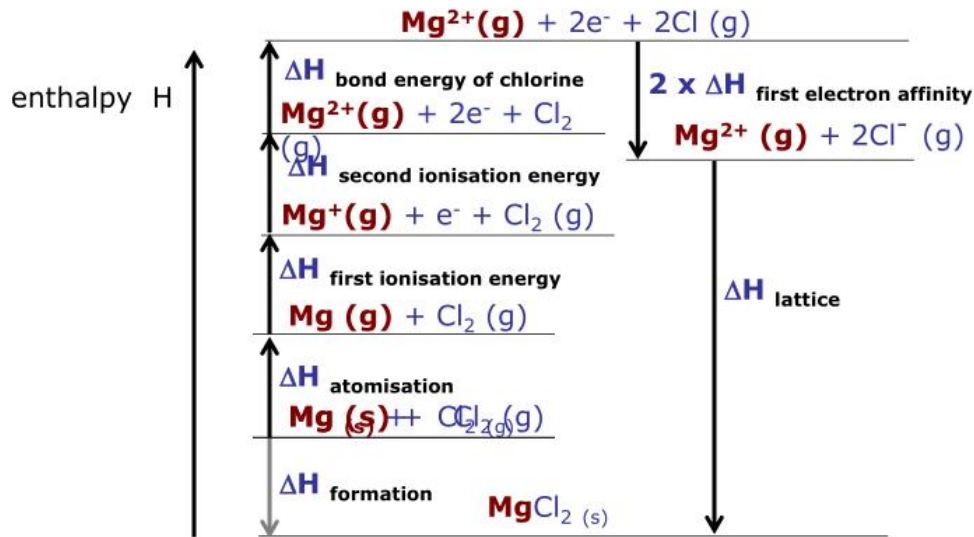
Gives:

$$\Delta H(\text{electron affinity Br}) = \Delta H_f(\text{NaBr}) + \Delta H(\text{lattice enthalpy NaBr}) - \Delta H(\text{atomisation Na}) - \Delta H(\text{1st ionisation Na}) - \frac{1}{2}\Delta H(\text{bond dissociation Br}_2)$$

 Note that the lattice enthalpy sign is reversed in the original equation, i.e. it is given a negative sign, as we are really dealing with the reverse of the lattice enthalpy, the energy released when the lattice is formed.

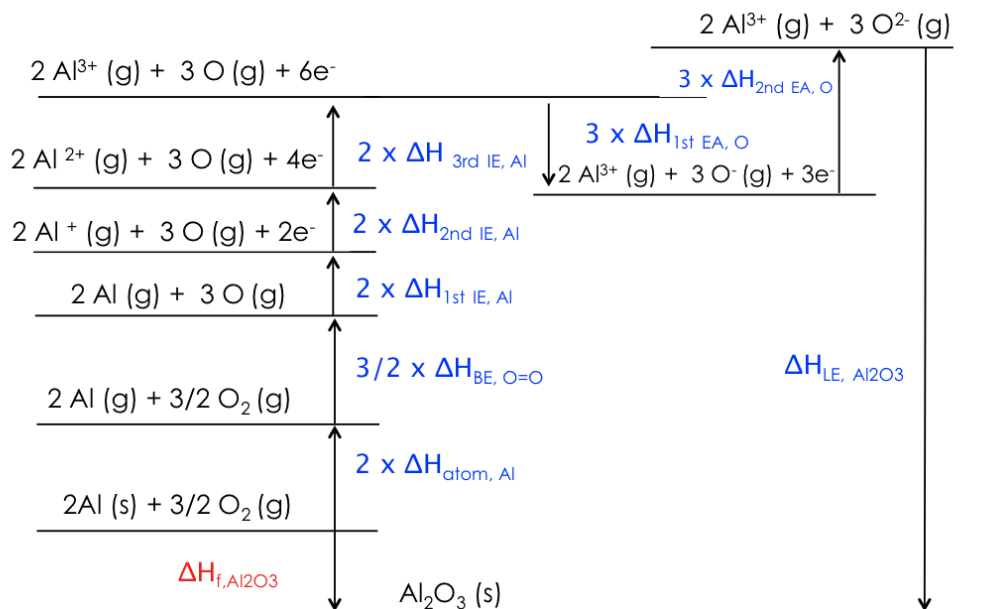
# Born-Haber Cycles

## magnesium chloride



1

Born-Haber cycle for  $\text{Al}_2\text{O}_3$



$$\Delta\text{H}_{\text{f, Al}_2\text{O}_3} = 2 \times \Delta\text{H}_{\text{atom, Al}} + 3/2 \times \Delta\text{H}_{\text{BE, O=O}} + 2 \times \Delta\text{H}_{1\text{st IE, Al}} + 2 \times \Delta\text{H}_{2\text{nd IE, Al}} + 2 \times \Delta\text{H}_{3\text{rd IE, Al}} + 3 \times \Delta\text{H}_{1\text{st EA, O}} + 3 \times \Delta\text{H}_{2\text{nd EA, O}} + \Delta\text{H}_{\text{LE, Al}_2\text{O}_3}$$