

6.4.2: Born Haber Cycles

Calculating Lattice Enthalpy

It is impossible to measure the enthalpy change starting from a solid crystal and converting it into its scattered gaseous ions. It is even more difficult to imagine how you could do the reverse - start with scattered gaseous ions and measure the enthalpy change when these convert to a solid crystal. Instead, lattice enthalpies always have to be calculated, and there are two entirely different ways in which this can be done.

1. You can use a [Hess's Law](#) cycle (in this case called a Born-Haber cycle) involving enthalpy changes which can be measured. Lattice enthalpies calculated in this way are described as experimental values.
2. Or you can do physics-style calculations working out how much energy would be released, for example, when ions considered as point charges come together to make a lattice. These are described as theoretical values. In fact, in this case, what you are actually calculating are properly described as lattice energies.

Born-Haber Cycles

Standard Atomization Enthalpies

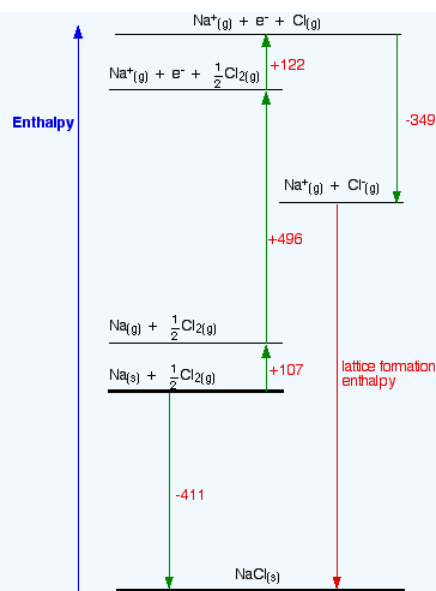
Before we start talking about Born-Haber cycles, we need to define the **atomization enthalpy**, ΔH_a° . The standard atomization enthalpy is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state. Enthalpy change of atomization is always positive. You are always going to have to supply energy to break an element into its separate gaseous atoms. All of the following equations represent changes involving atomization enthalpy:



Notice particularly that the "mol⁻¹" is per mole of atoms **formed** - NOT per mole of element that you start with. You will quite commonly have to write fractions into the left-hand side of the equation. Getting this wrong is a common mistake.

✓ Example 6.4.2.1: Born-Haber Cycle for NaCl

Consider a Born-Haber cycle for sodium chloride, and then talk it through carefully afterwards. You will see that I have arbitrarily decided to draw this for lattice formation enthalpy. If you wanted to draw it for lattice dissociation enthalpy, the red arrow would be reversed - pointing upwards.



Focus to start with on the higher of the two thicker horizontal lines. We are starting here with the elements sodium and chlorine in their standard states. Notice that we only need half a mole of chlorine gas in order to end up with 1 mole of NaCl. The arrow pointing down from this to the lower thick line represents the enthalpy change of formation of sodium chloride.

The Born-Haber cycle now imagines this formation of sodium chloride as happening in a whole set of small changes, most of which we know the enthalpy changes for - except, of course, for the lattice enthalpy that we want to calculate.

- The +107 is the atomization enthalpy of sodium. We have to produce gaseous atoms so that we can use the next stage in the cycle.
- The +496 is the first ionization energy of sodium. Remember that first ionization energies go from gaseous atoms to gaseous singly charged positive ions.
- The +122 is the atomization enthalpy of chlorine. Again, we have to produce gaseous atoms so that we can use the next stage in the cycle.
- The -349 is the first electron affinity of chlorine. Remember that first electron affinities go from gaseous atoms to gaseous singly charged negative ions.
- And finally, we have the positive and negative gaseous ions that we can convert into the solid sodium chloride using the lattice formation enthalpy.

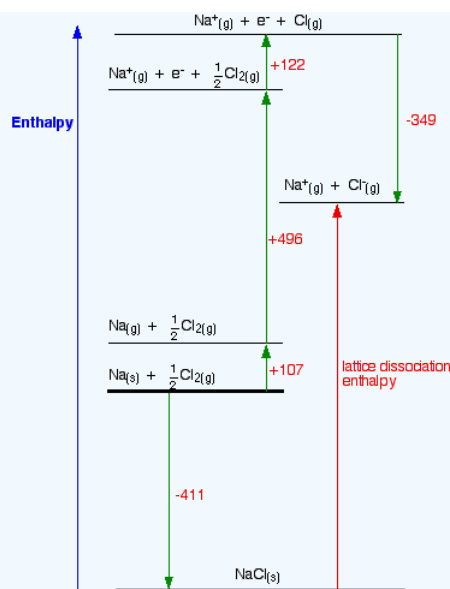
Now we can use Hess' Law and find two different routes around the diagram which we can equate. As drawn, the two routes are obvious. The diagram is set up to provide two different routes between the thick lines. So, from the cycle we get the calculations directly underneath it . . .

$$-411 = +107 + 496 + 122 - 349 + \text{LE}$$

$$\text{LE} = -411 - 107 - 496 - 122 + 349$$

$$\text{LE} = -787 \text{ kJ mol}^{-1}$$

How would this be different if you had drawn a lattice dissociation enthalpy in your diagram? Your diagram would now look like this:



The only difference in the diagram is the direction the lattice enthalpy arrow is pointing. It does, of course, mean that you have to find two new routes. You cannot use the original one, because that would go against the flow of the lattice enthalpy arrow. This time both routes would start from the elements in their standard states, and finish at the gaseous ions.

$$-411 + \text{LE} = +107 + 496 + 122 - 349$$

$$\text{LE} = +107 + 496 + 122 - 349 + 411$$

$$\text{LE} = +787 \text{ kJ mol}^{-1}$$

Once again, the cycle sorts out the sign of the lattice enthalpy.

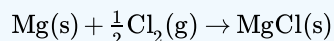
✓ Example 6.4.2.2: Born-Haber Cycle for MgCl_2

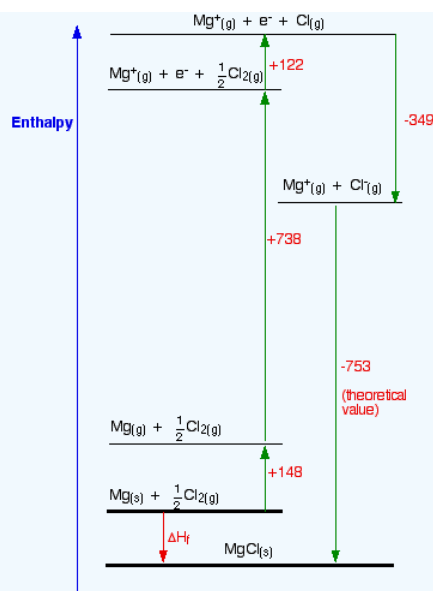
The question arises as to why, from an energetics point of view, magnesium chloride is MgCl_2 rather than MgCl or MgCl_3 (or any other formula you might like to choose). It turns out that MgCl_2 is the formula of the compound which has the most negative enthalpy change of formation - in other words, it is the most stable one relative to the elements magnesium and chlorine.

Let's look at this in terms of Born-Haber cycles of and contrast the enthalpy change of formation for the imaginary compounds MgCl and MgCl_3 . That means that we will have to use theoretical values of their lattice enthalpies. We cannot use experimental ones, because these compounds obviously do not exist! I'm taking theoretical values for lattice enthalpies for these compounds that I found on the web. I can't confirm these, but all the other values used by that source were accurate. The exact values do not matter too much anyway, because the results are so dramatically clear-cut.

1. The Born-Haber cycle for MgCl

We will start with the compound MgCl , because that cycle is just like the NaCl one we have already looked at.





Find two routes around this without going against the flow of any arrows. That's easy:

$$\Delta H_f = +148 + 738 + 122 - 349 - 753$$

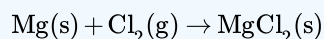
$$\Delta H_f = -94 \text{ kJ mol}^{-1}$$

So the compound MgCl is definitely energetically **more stable** than its elements. I have drawn this cycle very roughly to scale, but that is going to become more and more difficult as we look at the other two possible formulae. So I am going to rewrite it as a table. You can see from the diagram that the enthalpy change of formation can be found just by adding up all the other numbers in the cycle, and we can do this just as well in a table.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
atomization enthalpy of Cl	+122
electron affinity of Cl	-349
lattice enthalpy	-753
calculated ΔH_f	-94

2. The Born-Haber cycle for MgCl_2

The equation for the enthalpy change of formation this time is



So how does that change the numbers in the Born-Haber cycle?

- You need to add in the second ionization energy of magnesium, because you are making a 2+ ion.
- You need to multiply the atomization enthalpy of chlorine by 2, because you need 2 moles of gaseous chlorine atoms.
- You need to multiply the electron affinity of chlorine by 2, because you are making 2 moles of chloride ions.
- You obviously need a different value for lattice enthalpy.

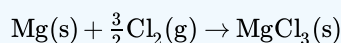
	kJ
atomization enthalpy of Mg	+148

	kJ
1st IE of Mg	+738
2nd IE of Mg	+1451
atomization enthalpy of Cl (x 2)	+244
electron affinity of Cl (x 2)	-698
lattice enthalpy	-2526
calculated ΔH_f	-643

You can see that much more energy is released when you make MgCl_2 than when you make MgCl . Why is that? You need to put in more energy to ionize the magnesium to give a $2+$ ion, but a lot more energy is released as lattice enthalpy. That is because there are stronger ionic attractions between $1-$ ions and $2+$ ions than between the $1-$ and $1+$ ions in MgCl . So what about MgCl_3 ? The lattice energy here would be even greater.

3. The Born-Haber cycle for MgCl_3

The equation for the enthalpy change of formation this time is



So how does that change the numbers in the Born-Haber cycle this time?

- You need to add in the third ionization energy of magnesium, because you are making a $3+$ ion.
- You need to multiply the atomization enthalpy of chlorine by 3, because you need 3 moles of gaseous chlorine atoms.
- You need to multiply the electron affinity of chlorine by 3, because you are making 3 moles of chloride ions.
- You again need a different value for lattice enthalpy.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
2nd IE of Mg	+1451
3rd IE of Mg	+7733
atomization enthalpy of Cl (x 3)	+366
electron affinity of Cl (x 3)	-1047
lattice enthalpy	-5440
calculated ΔH_f	+3949

This time, the compound is hugely energetically unstable, both with respect to its elements, and also to other compounds that could be formed. You would need to supply nearly 4000 kJ to get 1 mole of MgCl_3 to form!

Look carefully at the reason for this. The lattice enthalpy is the **highest** for all these possible compounds, but it is not high enough to make up for the very large third ionization energy of magnesium.

Why is the third ionization energy so big? The first two electrons to be removed from magnesium come from the 3s level. The third one comes from the 2p. That is closer to the nucleus, and lacks a layer of screening as well - and so much more energy is needed to remove it. The 3s electrons are screened from the nucleus by the 1 level and 2 level electrons. The 2p electrons are only screened by the 1 level (plus a bit of help from the 2s electrons).

Conclusion

Magnesium chloride is MgCl_2 because this is the combination of magnesium and chlorine which produces the most energetically stable compound - the one with the most negative enthalpy change of formation.

Contributors and Attributions

- Jim Clark ([Chemguide.co.uk](https://www.chemguide.co.uk))

This page titled [6.4.2: Born Haber Cycles](#) is shared under a [CC BY-NC 4.0](#) license and was authored, remixed, and/or curated by [Jim Clark](#).

- [Lattice Enthalpies and Born Haber Cycles](#) by [Jim Clark](#) is licensed [CC BY-NC 4.0](#).