

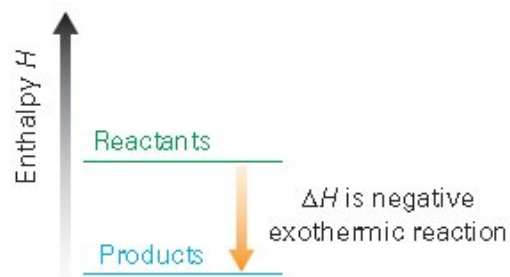
Thermodynamics

Standard enthalpy change, ΔH

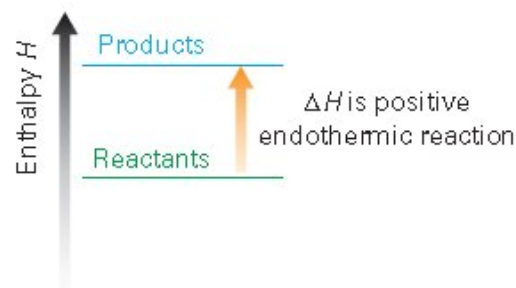
Enthalpy change, ΔH , is defined as the heat energy change measured under conditions of constant pressure. The value of the enthalpy change for a particular reaction depends on the pressure, the temperature, and the amount of substance used. So enthalpy changes are quoted for standard conditions of temperature and pressure. Standard enthalpy changes have the symbol ΔH and are measured in units of kJ mol^{-1} . The symbol shows the substances are in their standard states and the conditions used are:

A pressure of 100 kPa and a temperature of 298 K

and the enthalpy change is measured per mole of the specified substance. Exothermic and endothermic reactions Reactions can be exothermic or endothermic, depending on whether there is an overall transfer of energy to the surroundings or from them.



In an exothermic reaction, more energy is released when new bonds form in the products than is needed to break existing bonds in the reactants.



In an endothermic reaction, more energy is needed to break existing bonds in the reactants than is released when new bonds form in the products.

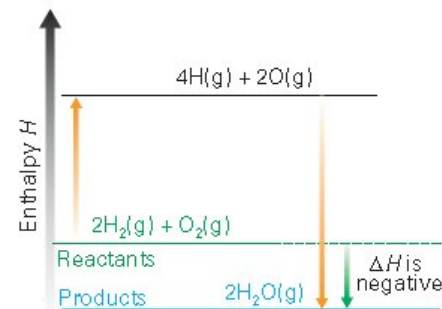
Standard enthalpy of formation, ΔH_f^\ominus

The standard enthalpy of formation, ΔH_f^\ominus the enthalpy change when one mole of a compound is formed from its elements in their standard states under standard conditions. By definition, this is equal to zero for an element in its standard state.

For example, the standard enthalpy of formation for water is:



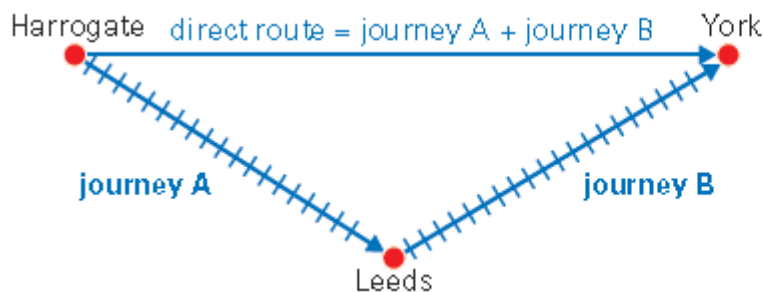
The negative sign for ΔH_f^\ominus shows that the reaction is exothermic.



The energy level diagram for the formation of water.

Hess's Law

Hess's Law states that if a reaction can happen by more than one route, the overall enthalpy change is the same whichever route is taken. This lets you calculate the enthalpy change for reactions that are difficult to achieve in practice.



If you want to travel from Harrogate to York by train you can take the direct route. Or you can take the indirect route via Leeds. Whichever way you do it, the end result is the same.

The standard enthalpy of formation of methane is the enthalpy of the Reaction

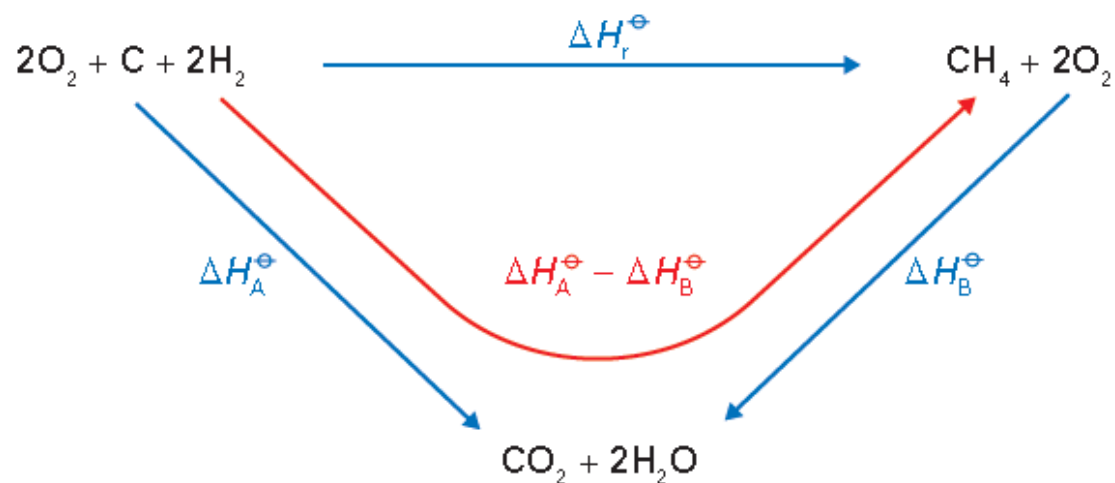


If it could be carried out under standard conditions. It can be calculated using an enthalpy cycle diagram and the data in the table.

quantity	reaction	ΔH^\ominus (kJ mol ⁻¹)
$\Delta H_f^\ominus(\text{CO}_2(\text{g}))$	$\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	-393.5
$\Delta H_f^\ominus(\text{H}_2\text{O(l)})$	$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)}$	-285.8
$\Delta H_c^\ominus(\text{CH}_4(\text{g}))$	$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O(l)}$	-890.3

ΔH_c^\ominus represents the standard enthalpy of combustion, the enthalpy change when one mole of a substance is completely burned in oxygen under standard conditions.

When you draw an enthalpy cycle diagram, it is easiest to put the reaction for the enthalpy change you are trying to calculate across the top.



The enthalpy cycle for the formation of methane.

From the enthalpy cycle diagram, $\Delta H_f^\ominus = \Delta H_A^\ominus - \Delta H_B^\ominus$ (remember you reverse the sign if you go against the arrow).

$$\Delta H_A^\ominus = \Delta H_f^\ominus(\text{CO}_2(\text{g})) + 2\Delta H_f^\ominus(\text{H}_2\text{O}(\text{l}))$$

$$\Delta H_A^\ominus = -393.5 + 2(-285.8) = -393.5 - 571.6 = \mathbf{-965.1 \text{ kJ mol}^{-1}}$$

$$\Delta H_B^\ominus = \Delta H_c^\ominus(\text{CH}_4(\text{g})) = \mathbf{-890.3 \text{ kJ mol}^{-1}}$$

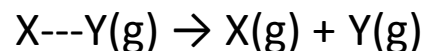
So $\Delta H_f^\ominus = -965.1 - (-890.3) = \mathbf{-74.8 \text{ kJ mol}^{-1}}$
(an exothermic reaction)

Mean bond enthalpies

When a reaction happens, heat energy is absorbed from the surroundings to break bonds in the reactants, and heat energy is transferred to the surroundings when new bonds are formed in the products. The enthalpy change for the reaction is the difference between the energy absorbed and the energy released.

Standard bond dissociation enthalpy $\Delta H_{\text{diss}}^{\ominus}$

The standard bond dissociation enthalpy, $\Delta H_{\text{diss}}^{\ominus}$, is the enthalpy change when one mole of bonds of the same type in gaseous molecules is broken under standard conditions, producing gaseous fragments:



For example, the standard bond dissociation enthalpy of the H---Cl bond is the enthalpy change when one mole of gaseous HCl molecules forms gaseous H and Cl atoms:



Bond dissociation enthalpy values are always positive, because energy must be absorbed to break bonds. The enthalpy change for making the same bond is the same amount but with the opposite sign. So the enthalpy change when one mole of H---Cl bonds forms is -432 kJ mol^{-1} .

Mean bond enthalpies

Some bonds only occur in one substance. For example, H---H bonds only occur in hydrogen molecules, H₂, and Cl---Cl bonds only occur in chlorine molecules, Cl₂. But most bonds can occur in more than one substance. For example, the C---H bond can occur in almost every organic compound. The strength of the C---H bond varies, depending on its chemical environment. It will differ from one compound to the next, and even within the same compound if it occurs at different positions.

The idea of mean bond enthalpies gets around this problem. The mean bond enthalpy is the enthalpy change when one mole of a specified type of bond is broken, averaged over different compounds. Mean bond enthalpies can be used to calculate an approximate value of ΔH for reactions.

bond	mean bond enthalpy (kJ mol ⁻¹)
H—H	436
O—H	463
O=O	498
C—H	413
C—C	348
C=C	612
C=O	743

Mean bond enthalpy values vary slightly from one source to another, depending on the range of compounds included.

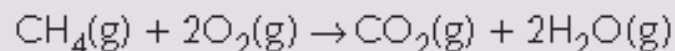
Mean bond enthalpies and ΔH

The approximate value of ΔH for a reaction is calculated like this:

- Add the mean bond enthalpies together for the bonds in the reactants.
- Add the mean bond enthalpies together for the bonds in the products.
- Then subtract the second answer from the first one.

Worked example

Calculate the enthalpy change for the combustion of methane using mean bond enthalpy values.



Step 1 Add together the mean bond enthalpies for all the bonds in the reactants.

$$\begin{aligned} & [4 \times \text{C—H}] + [2 \times \text{O=O}] \\ & (4 \times 413) + (2 \times 498) = 2648 \text{ kJ mol}^{-1} \end{aligned}$$

Step 2 Add together the mean bond enthalpies for all the bonds in the products.

$$\begin{aligned} & [2 \times \text{C=O}] + [4 \times \text{O—H}] \\ & (2 \times 743) + (4 \times 463) = 3338 \text{ kJ mol}^{-1} \end{aligned}$$

Step 3 $\Delta H = \text{energy in} - \text{energy out}$
 $\Delta H = 2648 - 3338 = -690 \text{ kJ mol}^{-1}$ (an exothermic reaction)

Calculations like these give an approximate value for the enthalpy change. They are not as accurate as ones using enthalpy cycles. This is because mean bond enthalpies are average values from a range of compounds, and may not be the exact values for the substances in the reaction.

Combustion of Methane is exothermic. Promise.



The combustion of methane can be very dangerous. This building was wrecked by a gas explosion.

Dissolving

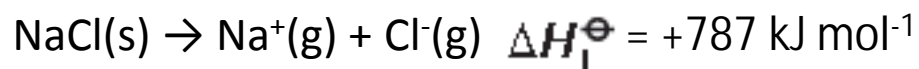
Two processes happen when an ionic solid such as sodium chloride dissolves in water. The ions in the crystal lattice are separated from each other, and the separate ions become surrounded by water molecules. The first process is endothermic and the second one is exothermic. The overall enthalpy change when an ionic solid dissolves is the difference between the enthalpy changes for these two processes. So dissolving can be an exothermic process or an endothermic one.

Lattice enthalpy, ΔH_L^\ominus

There are two conflicting definitions for lattice enthalpy. It is important that you realize this and take care when answering questions involving lattice enthalpy, so always look at the defining equation.

Lattice dissociation enthalpy

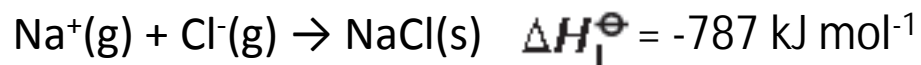
The lattice dissociation enthalpy, ΔH_L^\ominus is the enthalpy change when one mole of an ionic solid is separated into its gaseous ions. For example:



Energy must be absorbed to overcome the strong ionic bonds in the ionic solid. So lattice dissociation is an endothermic process, and lattice dissociation enthalpies have positive values. We will tend to use lattice dissociation enthalpies.

Lattice formation enthalpy

The lattice formation enthalpy is the enthalpy change when one mole of an ionic solid is formed from its gaseous ions. For example:



Energy is released when ionic bonds form. So lattice formation is an exothermic process, and lattice formation enthalpies have negative values. Notice that the enthalpy change is the same amount as the lattice dissociation enthalpy but with the opposite sign.

Factors affecting ΔH_L^\ominus

The table below shows some values for lattice dissociation enthalpies. Two main factors influence the size of the lattice dissociation enthalpy: 1. the distance between the ions in the crystal and 2. the charges on the ions.

Distance between the ions

The halide ions increase in size in the order $F^- < Cl^- < Br^-$. Notice that the lattice dissociation enthalpies for the sodium halides NaF, NaCl, and NaBr decrease in the same order. The larger the distance between the oppositely charged ions in a crystal lattice, the weaker the force of attraction between them.

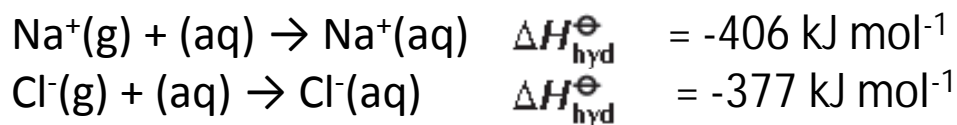
The charges on the ions

The greater the charges on the ions in a crystal lattice the greater the force of attraction between them. Sodium fluoride and magnesium oxide have similar structures, but the lattice dissociation enthalpy of magnesium oxide is around four times larger. This is because the product of the charges in $Mg^{2+}O^{2-}$ is four times larger than the product of charges in Na^+F^- .

compound	ΔH_L^\ominus (kJ mol ⁻¹)
NaF	918
NaCl	780
NaBr	742
KCl	711
RbCl	685
CsCl	661
MgO	3791

Enthalpy of hydration, $\Delta H_{\text{hyd}}^{\ominus}$

The enthalpy of hydration $\Delta H_{\text{hyd}}^{\ominus}$ is the enthalpy change when one mole of separated gaseous ions is dissolved completely in water to form one mole of aqueous ions. For example:



Energy is released when bonds form between the ions and water molecules. So hydration is an exothermic process, and enthalpies of hydration have negative values.

Enthalpy of solution $\Delta H_{\text{soln}}^{\ominus}$

The enthalpy of solution, $\Delta H_{\text{soln}}^{\ominus}$, is the enthalpy change when one mole of an ionic substance is dissolved in a volume of water large enough to ensure that the ions are separated and do not interact with each other. For example:

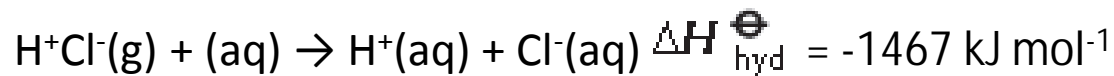


An enthalpy of solution can be positive or negative, depending on the values for lattice dissociation enthalpy and enthalpies of hydration.

Determining $\Delta H_{\text{hyd}}^{\ominus}$

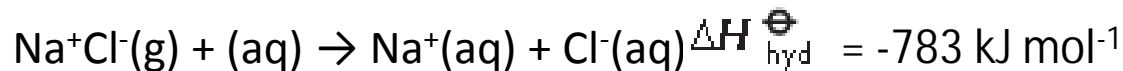
The enthalpy of hydration of a single ion cannot be determined directly because the ion will always be accompanied by an oppositely charged ion. Instead, the enthalpies of hydration for pairs of ions are determined. For example, this is how you could determine the values of $\Delta H_{\text{hyd}}^{\ominus}$ for Na^+ and Cl^- .

The enthalpy change for the hydration of HCl can be measured:



The enthalpy of hydration of the hydrogen ion has an accepted value of $-1090 \text{ kJ mol}^{-1}$. So for the chloride ion, $\Delta H_{\text{hyd}}^{\ominus} = -1467 - (-1090) = -377 \text{ kJ mol}^{-1}$

The enthalpy change for the hydration of NaCl can be measured, too:



So for the sodium ion, $\Delta H_{\text{hyd}}^{\ominus} = -783 - (-377) = -406 \text{ kJ mol}^{-1}$

Enthalpy of Solution

When an ionic substance dissolves in water, its enthalpy of solution depends on the difference between its lattice enthalpy and the enthalpies of hydration of its ions. The enthalpy of solution can be calculated with the help of an enthalpy cycle diagram.

Calculating the enthalpy of solution, $\Delta H_{\text{soln}}^{\ominus}$
Remember that the enthalpy of solution, $\Delta H_{\text{soln}}^{\ominus}$, is the enthalpy change when one mole of an ionic substance is dissolved in a volume of water large enough to ensure that the ions are separated and do not interact with each other. Here is the equation for sodium chloride dissolving in water:



Two processes can be identified when sodium chloride dissolves.

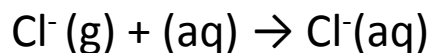
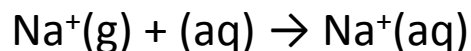
1. Breaking the bonds in the sodium chloride crystal lattice to produce gaseous ions:



The enthalpy change that accompanies this process is the lattice dissociation enthalpy,



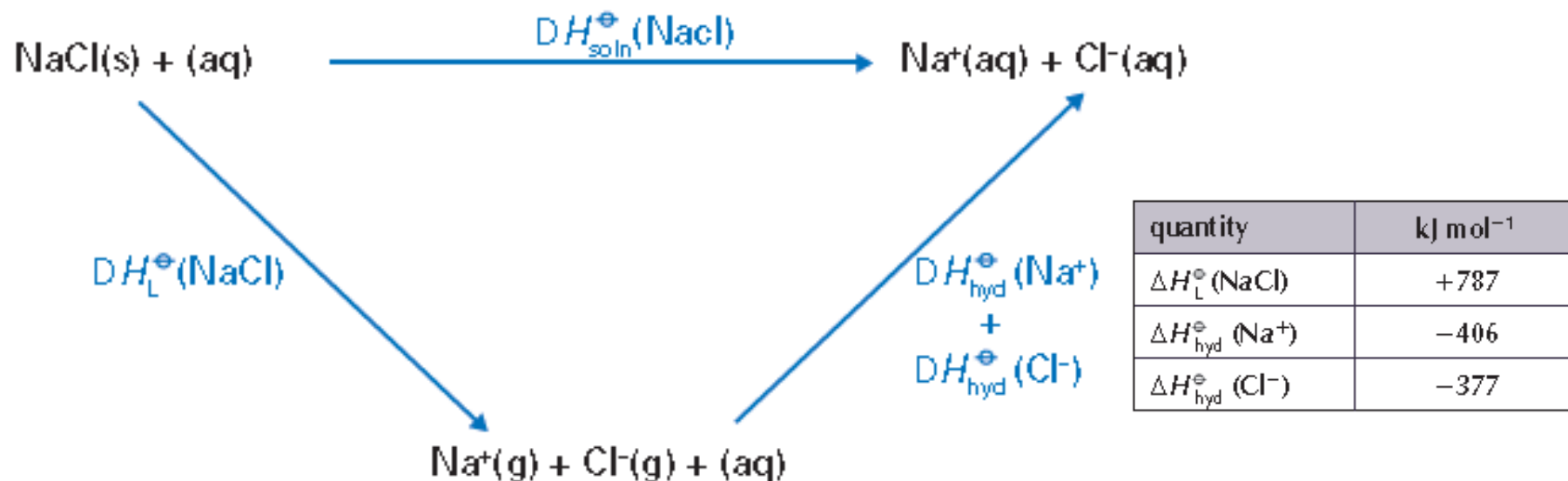
2. The separated gaseous ions become surrounded by water molecules:



The enthalpy changes that accompany this process are the enthalpies of hydration,



These equations can be combined to produce an enthalpy cycle diagram.



An enthalpy cycle diagram for the dissolving of sodium chloride in water.

From the enthalpy cycle diagram:

$$\Delta H_{\text{soln}}^{\ominus}(\text{NaCl}) = \Delta H_{\text{L}}^{\ominus}(\text{NaCl}) + \Delta H_{\text{hyd}}^{\ominus}(\text{Na}^{\oplus}) + \Delta H_{\text{hyd}}^{\ominus}(\text{Cl}^{\ominus})$$

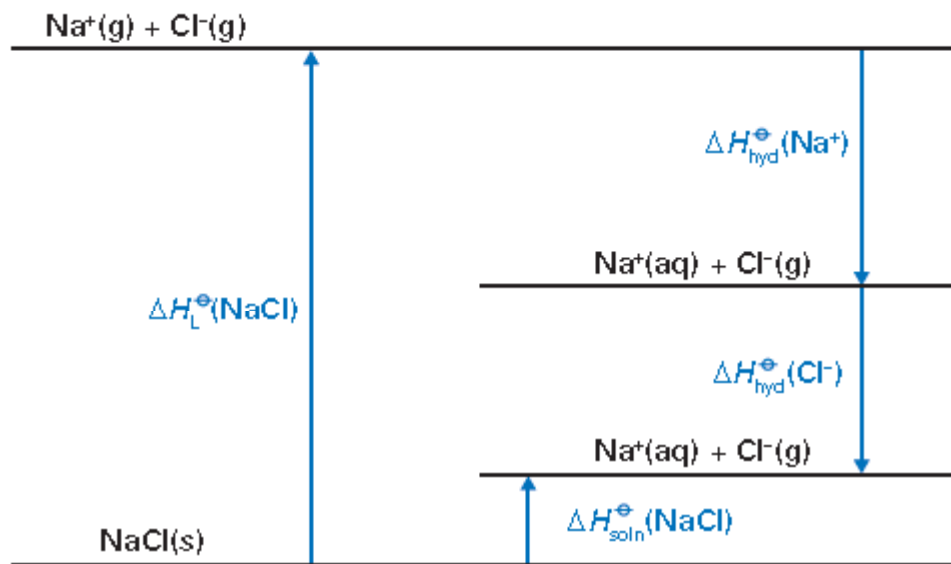
The enthalpy of solution can be calculated using the values in the table.

$$\begin{aligned} \Delta H_{\text{soln}}^{\ominus}(\text{NaCl}) &= +787 + (-406) + (-377) \text{ kJ mol}^{-1} \\ &= +787 - 406 - 377 \text{ kJ mol}^{-1} \\ &= \mathbf{+4 \text{ kJ mol}^{-1}} \end{aligned}$$

Dissolving sodium chloride in water is an endothermic process. The solution will become colder as the sodium chloride dissolves. Energy is transferred from the surroundings if the process is carried out at constant temperature.

Enthalpy level diagrams for dissolving

Enthalpy level diagrams are another way to represent the processes involved in dissolving. These are charts in which exothermic processes are shown with downwards pointing arrows, and endothermic processes are shown with upwards pointing arrows. They may be shown drawn to scale, where the length of each arrow is proportional to the enthalpy change it represents.



An enthalpy level diagram for the dissolving of sodium chloride in water.

You should be prepared to interpret data shown in either way. This includes naming the enthalpy change represented by each arrow, and writing the equation that defines it. You may also be asked to calculate any of the quantities if you are given information about the other two. For example, the lattice dissociation enthalpy can be calculated from the enthalpy of solution and the enthalpies of hydration.

Instant cold

Cold packs are used to treat sports injuries. Instant cold packs use endothermic reactions such as the dissolving of ammonium nitrate to achieve a low temperature quickly. Water and ammonium nitrate are held in two separate compartments in the pack. The pack is activated by breaking one of the compartments so that the contents mix together. The amounts of water and ammonium nitrate are calculated to achieve the maximum cooling effect, and the packs can stay cold for around 20 minutes.



Instant cold packs rely on a highly endothermic dissolving process to bring relief from injuries such as ankle sprains.

Born - Haber Cycle

You have used enthalpy cycles to calculate enthalpy changes involved in dissolving ionic compounds, and to calculate enthalpy changes involved in the formation of simple covalent compounds. A Born–Haber cycle is an enthalpy level diagram that lets you calculate enthalpy changes involved in the formation of ionic compounds. You will need to know a few more definitions first however.

Ionization enthalpy, ΔH_i^\ominus

Ionization enthalpy, ΔH_i^\ominus , is the enthalpy change when cations are formed. It is the enthalpy change when an electron is removed from a mole of gaseous atoms, ions, or molecules to form a gaseous cation. Ionization enthalpies have positive values.

First ionization enthalpy

The first ionization enthalpy is the enthalpy change when the highest energy electrons are removed from a mole of gaseous atoms or molecules to form a mole of gaseous ions, each with a single positive charge. For example for sodium atoms:



Second ionization enthalpy

The second ionization enthalpy is the enthalpy change when the highest energy electrons are removed from a mole of gaseous ions with single positive charges to form a mole of gaseous ions, each with two positive charges. For example for sodium ions:



Electron affinity, $\Delta H_{\text{ea}}^{\ominus}$

Electron affinity, $\Delta H_{\text{ea}}^{\ominus}$, is the enthalpy change when anions are formed. It is the enthalpy change when an electron is gained by a mole of gaseous atoms, ions, or molecules to form a gaseous anion. Electron affinities can have positive or negative values.

First electron affinity

The first electron affinity is the enthalpy change when electrons are gained by a mole of gaseous atoms or molecules to form a mole of gaseous ions, each with a single negative charge. For example for chlorine atoms:



Second electron affinity

The second electron affinity is the enthalpy change when electrons are gained by a mole of gaseous ions with single negative charges to form a mole of gaseous ions, each with two negative charges. For example for O_2 ions:



Enthalpy of atomization, $\Delta H_{\text{at}}^{\ominus}$

The enthalpy of atomization, $\Delta H_{\text{at}}^{\ominus}$, is the enthalpy change when one mole of gaseous atoms is formed from an element or compound. Enthalpies of atomization have positive values because they represent processes in which energy must be absorbed to break bonds. Enthalpies of atomization can appear in several different ways. The key to success here is to identify the equation that describes the process. For example, enthalpies of atomization can also appear as bond dissociation enthalpies. Consider atomizing chlorine molecules, Cl_2 . Here are the equations that describe the enthalpy of atomization of chlorine and the bond dissociation enthalpy of chlorine:



Notice that the enthalpy of atomization of chlorine is half its bond dissociation enthalpy. You could be supplied data describing either process, so make sure you know the definitions for the various enthalpy changes and the equations that go with them. For example, the enthalpy of atomization of a metal might be shown as an enthalpy of sublimation. Sublimation is the process where a solid turns directly into a gas without passing through the liquid state.

Born Haber Cycles

Your previous examples show enthalpy level diagrams for dissolving ionic compounds. These are charts in which exothermic processes are shown with downwards pointing arrows, and endothermic processes are shown with upwards pointing arrows. A Born–Haber cycle is an enthalpy level diagram that lets you calculate enthalpy changes involved in the formation of ionic compounds. You must be able to draw Born–Haber cycles and use them to calculate lattice enthalpies.

Drawing a Born–Haber cycle

We will look at the Born–Haber cycle for sodium chloride. The lattice dissociation enthalpy of sodium chloride is represented by this process:



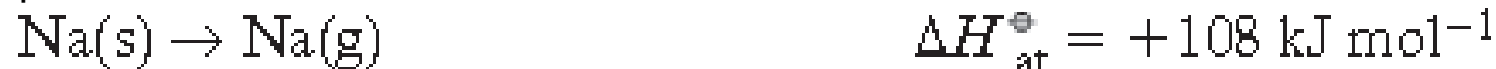
The description

In the Born–Haber cycle there are several steps in the indirect route for dissociated the sodium chloride crystal lattice.

Step 1 The reverse of the enthalpy of formation



Step 2 Atomize solid sodium



Step 3 Atomize gaseous chlorine



Step 4 Form gaseous sodium ions



Step 5 Form gaseous chloride ions

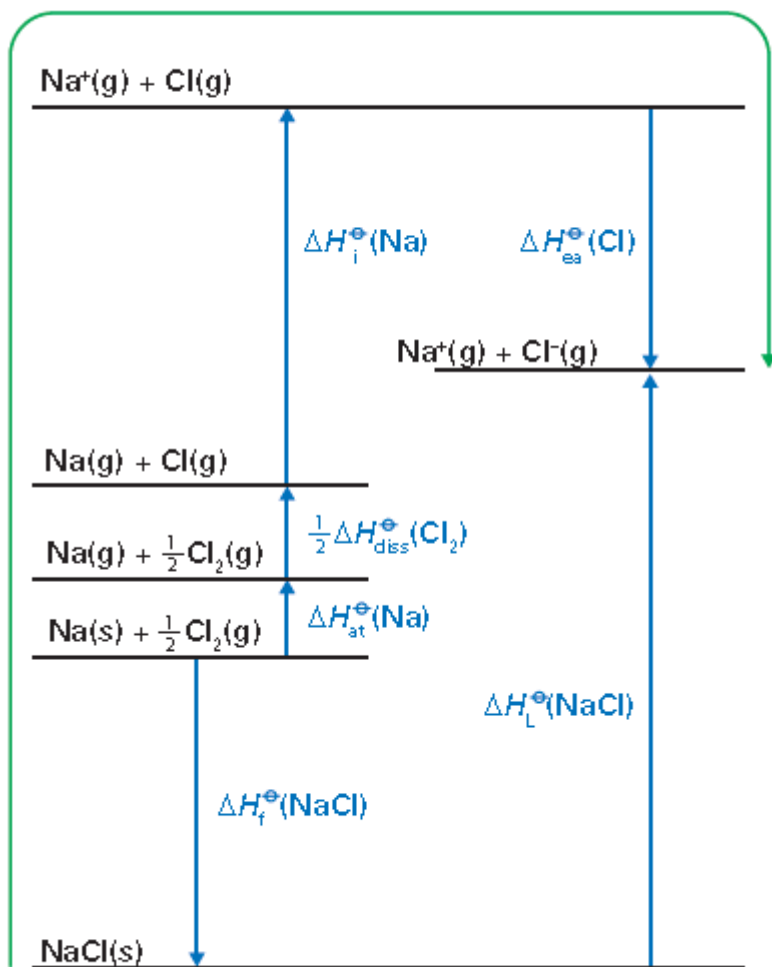


If all these enthalpy changes are added together, they equal the lattice dissociation enthalpy of sodium chloride:

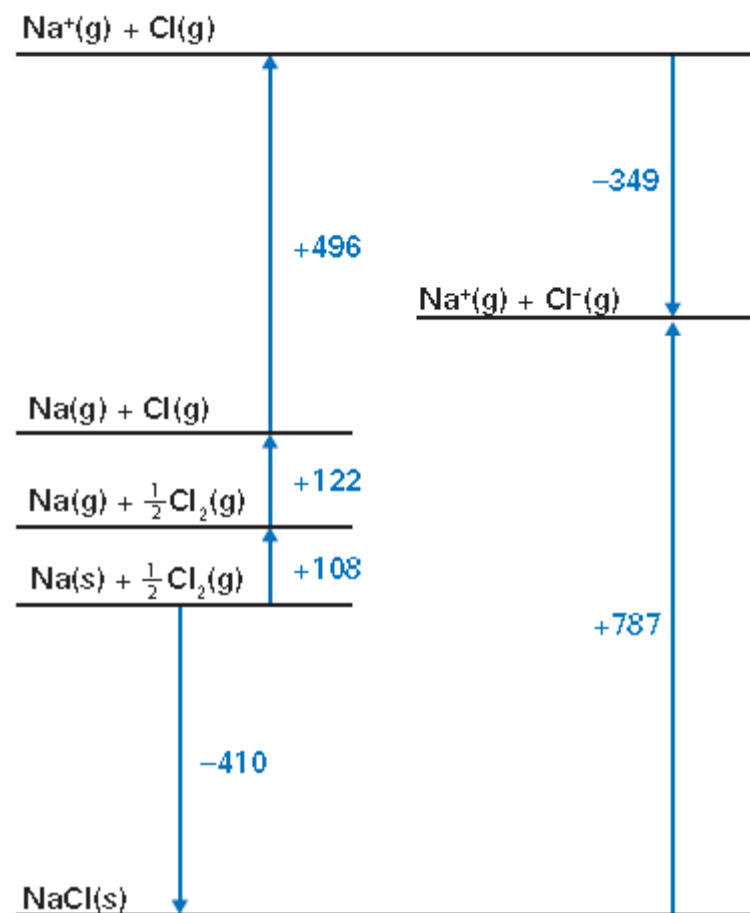
$$\begin{aligned} \Delta H_{\text{L}}^\ominus(\text{NaCl}) &= -\Delta H_f^\ominus(\text{NaCl}) + \Delta H_{\text{at}}^\ominus(\text{Na}) + \frac{1}{2} \Delta H_{\text{diss}}^\ominus(\text{Cl}_2) + \Delta H_{\text{i}}^\ominus(\text{Na}) \\ &\quad + \Delta H_{\text{ea}}^\ominus(\text{Cl}) \\ &= +410 + 108 + 122 + 496 + (-349) \text{ kJ mol}^{-1} \\ &= \mathbf{+787 \text{ kJ mol}^{-1}} \end{aligned}$$

The enthalpy cycle diagram

Remember to represent endothermic processes with upwards pointing arrows and exothermic processes with downwards pointing arrows. Make sure you can identify each step in the cycle. The Born–Haber cycle can be drawn to scale with the length of each arrow proportional to the enthalpy change, but it does not have to be.



The Born–Haber cycle for the formation of sodium chloride with each enthalpy change identified. The large green arrow represents the five steps described above.

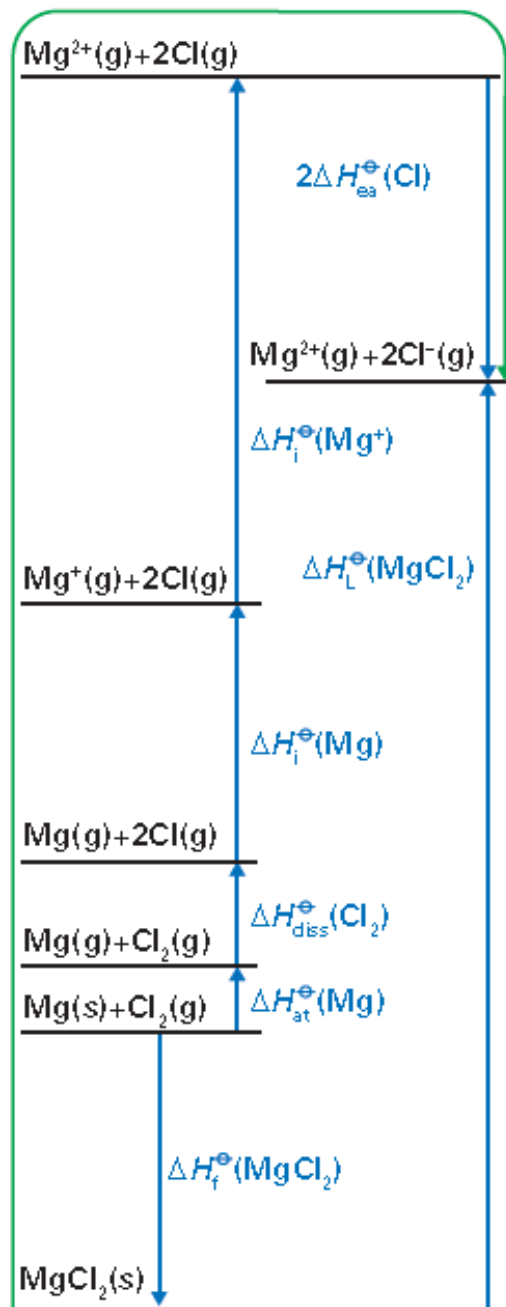


The Born–Haber cycle for the formation of sodium chloride with the value in kJ mol^{-1} for each enthalpy change. You have to go in the opposite direction to the arrow in the enthalpy of formation step, so in the calculation the sign is reversed to give $+410 \text{ kJ mol}^{-1}$ rather than -410 kJ mol^{-1} .

The Born–Haber cycles for sodium chloride and potassium chloride are relatively simple to draw. The cycles for compounds such as magnesium chloride and sodium oxide are more complex. They have more steps because ions with two charges are involved. The table shows the data needed to draw the Born–Haber cycle for magnesium chloride MgCl_2 .

standard enthalpy changes		kJ mol^{-1}
ΔH_f^\ominus	Enthalpy of formation of magnesium chloride	-641
$\Delta H_{\text{at}}^\ominus$	Enthalpy of atomization of magnesium	+148
$\Delta H_{\text{diss}}^\ominus$	Bond dissociation enthalpy of chlorine	+244
ΔH_i^\ominus	First ionization enthalpy of magnesium	+738
ΔH_i^\ominus	Second ionization enthalpy of magnesium	+1451
$\Delta H_{\text{ea}}^\ominus$	First electron affinity of chlorine	-349

Notice that there is an extra ionization enthalpy step compared to the data for sodium chloride and potassium chloride. This is because magnesium atoms ionize to form Mg^{2+} ions:



first ionization enthalpy



second ionization enthalpy

Here is the calculation for the lattice dissociation enthalpy:

$$\begin{aligned} \Delta H_{\text{L}}^{\ominus}(\text{MgCl}_2) &= -\Delta H_{\text{f}}^{\ominus}(\text{MgCl}_2) + \Delta H_{\text{at}}^{\ominus}(\text{Mg}) + \Delta H_{\text{diss}}^{\ominus}(\text{Cl}_2) + \Delta H_{\text{f}}^{\ominus}(\text{Mg}) \\ &\quad + \Delta H_{\text{f}}^{\ominus}(\text{Mg}^+) + 2\Delta H_{\text{ea}}^{\ominus}(\text{Cl}) \\ &= -(-641) + 148 + 244 + 738 + 1451 + 2(-349) \text{ kJ mol}^{-1} \\ &= +2524 \text{ kJ mol}^{-1} \end{aligned}$$

The Born-Haber cycle for the formation of magnesium chloride with each enthalpy change identified.

Sodium oxide

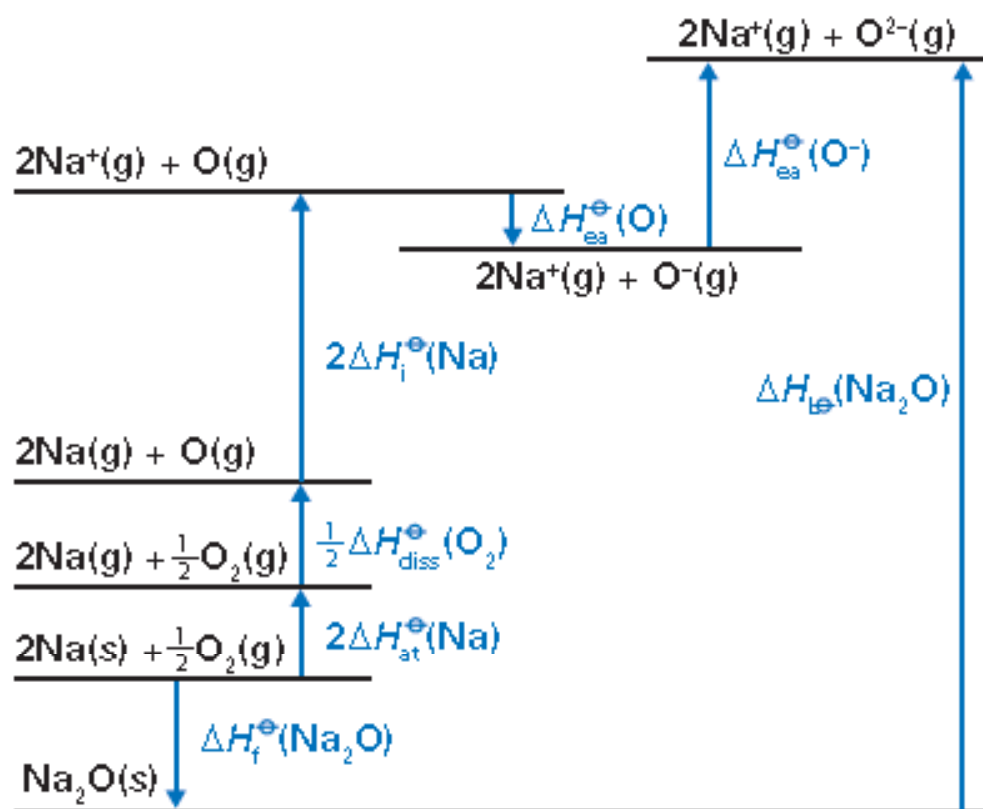
The table shows the data needed to draw the Born–Haber cycle for sodium oxide, Na₂O.

standard enthalpy changes		kJ mol ⁻¹
ΔH_f^\ominus	Enthalpy of formation of sodium oxide	-414
$\Delta H_{\text{at}}^\ominus$	Enthalpy of atomization of sodium	+108
$\Delta H_{\text{diss}}^\ominus$	Bond dissociation enthalpy of oxygen	+498
ΔH_i^\ominus	First ionization enthalpy of sodium	+496
$\Delta H_{\text{ea}}^\ominus$	First electron affinity of oxygen	-141
$\Delta H_{\text{ea}}^\ominus$	Second electron affinity of oxygen	+798

Notice that there is an extra electron affinity step. This is because oxygen atoms ionize to form O²⁻ ions:



Notice too that the second electron affinity of oxygen has a positive value. It represents an endothermic process, so it is shown in the Born–Haber cycle by an upwards pointing arrow.



The Born-Haber cycle for the formation of sodium oxide with each enthalpy change identified.

Here is the calculation for the lattice dissociation enthalpy:

$$\begin{aligned}
 \Delta H_{\text{L}}^{\ominus}(\text{Na}_2\text{O}) &= -\Delta H_{\text{f}}^{\ominus}(\text{Na}_2\text{O}) + 2\Delta H_{\text{at}}^{\ominus}(\text{Na}) \\
 &\quad + \frac{1}{2} \Delta H_{\text{diss}}^{\ominus}(\text{O}_2) + 2\Delta H_{\text{i}}^{\ominus}(\text{Na}) \\
 &\quad + \Delta H_{\text{ea}}^{\ominus}(\text{O}) + \Delta H_{\text{ea}}^{\ominus}(\text{O}^-) \\
 &= -(-414) + 2(108) + \frac{1}{2}(498) + \\
 &\quad 2(496) + (-141) + 798 \text{ kJ mol}^{-1} \\
 &= +2528 \text{ kJ mol}^{-1}
 \end{aligned}$$

It is very easy to forget to multiply or divide by two where necessary in these calculations, so take care.

Sneaky bromine

Take care in a question involving bromine, which is a liquid in its standard state. Unless you are given the enthalpy of atomization of bromine, you might need two steps to produce gaseous bromine atoms:

- vaporization of bromine: $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$
- bond dissociation enthalpy: $\text{Br}_2(\text{g}) \rightarrow 2\text{Br}(\text{g})$

You will be given the data you need.

Why is it MgCl_2 , and not MgCl or MgCl_3 ? Born–Haber cycles can be used to calculate other enthalpy changes, not just lattice dissociation enthalpies. For example, the enthalpy of formation can be calculated if the other enthalpy changes are known. This is useful for calculating the enthalpies of formation of hypothetical compounds such as MgCl . The table shows the data needed.

standard enthalpy changes		kJ mol^{-1}
$\Delta H_{\text{at}}^{\ominus}$	Enthalpy of atomization of magnesium	+148
$\Delta H_{\text{diss}}^{\ominus}$	Bond dissociation enthalpy of chlorine	+244
$\Delta H_{\text{i}}^{\ominus}$	First ionization enthalpy of magnesium	+738
$\Delta H_{\text{ea}}^{\ominus}$	First electron affinity of chlorine	-349
$\Delta H_{\text{L}}^{\ominus}$	Lattice dissociation enthalpy of MgCl	+753

Here is the calculation for the enthalpy of formation of MgCl :

$$\begin{aligned}
 \Delta H_{\text{f}}^{\ominus}(\text{MgCl}) &= \Delta H_{\text{at}}^{\ominus}(\text{Mg}) + \frac{1}{2} \Delta H_{\text{diss}}^{\ominus}(\text{Cl}_2) \\
 &\quad + \Delta H_{\text{i}}^{\ominus}(\text{Mg}) + \Delta H_{\text{ea}}^{\ominus}(\text{Cl}) \\
 &\quad - \Delta H_{\text{L}}^{\ominus}(\text{MgCl}) \\
 &= 148 + \frac{1}{2}(244) + 738 + (-349) - 753 \text{ kJ mol}^{-1} \\
 &= -94 \text{ kJ mol}^{-1}
 \end{aligned}$$

The formation of MgCl is just exothermic, whereas the formation of MgCl_2 is much more exothermic. Similarly, the calculated enthalpy of formation of MgCl_3 is $13949 \text{ kJ mol}^{-1}$, which is very endothermic. So MgCl_2 is formed in preference to MgCl or MgCl_3 because this transfers the most energy to the surroundings.