Physical Chemistry – crib sheet
Haber Cycles

What is a Haber Cycle?

A Haber cycle shows the energy changes between different stages of a reaction.

Energy changes

When bonds are made or broken, energy (in the form of heat) is either lost or gained.

In the study of anything to do with energy (known as thermodynamics), possibly the single most important rule is this

Energy cannot be made or destroyed, only ever changed.

For example, when sodium hydroxide (NaOH) reacts with hydrochloric acid (HCl), the amount of energy from the breaking of the bonds of the reactants is **more** than making of the bonds in the products.

The reaction between NaOH and HCl **gives out** heat and is known as an "exothermic" reaction ("exo" means outside, "thermic" means heat). This excess heat energy is absorbed by the surroundings (or to put it another way, the surroundings took in the extra energy). There has been no change in the overall amount of energy in the system.

When potassium nitrate dissolves in water, the energy from the **production** of the solution is **more** than the energy from the breaking of the bonds. The reaction mixture becomes cold and **takes heat** from the surroundings (which makes it feel cold). This is known as an "endothermic" reaction ("endo" means to take into). The amount of energy taken in from the surroundings equals the difference in energy between reactants and products.

This heat difference is given by ΔH and is known as enthalpy. There are many types of enthalpy.

Chemical reactions

All chemical reactions can be thought of like this

reactants → products

How the reactants get to the products is not always simple to understand.

Take the reaction of carbon with oxygen to form carbon dioxide. There are two routes which can be taken

1. $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$
2. $C_{(s)} + ½\ O_{2(g)} \rightarrow CO_{(g)}$
   $CO_{(g)} + ½\ O_{2(g)} \rightarrow CO_{2(g)}$

Note that the state of the compounds at 25ºC are given. These are known as the standard states and are given the symbol $^{\ominus}$.

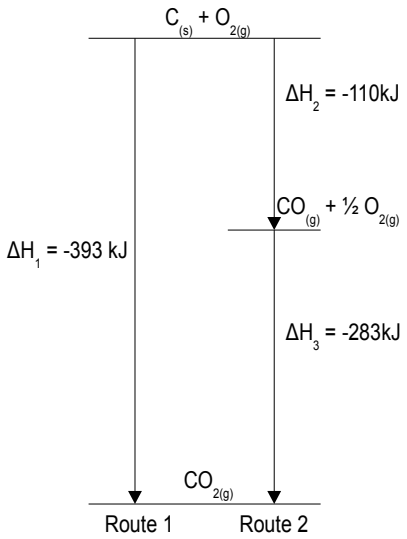
Route 1 will have an energy associated for it (in this case -393 kJ). Call this ΔH_1.
Route 2 has two parts. The first part is the heat of formation (ΔH_f) of CO = -110 kJ. Call this ΔH_2. The second part of route two is the heat of combustion of CO (ΔH_c – the CO is being burned in oxygen). Call this ΔH_3 and has a value of -283 kJ.

Looking at the numbers it can be seen that $\Delta H_1 = \Delta H_2 + \Delta H_3$. This is better known as Hess's Law of Constant Summation (*it doesn't matter which route is taken from reactants to product, the energy difference is always the same as long as the start and end conditions are the same*).

Drawing an energy diagram

There are two ways of drawing an energy diagram, both of which are equivalent to each other.

1. Energy level diagram

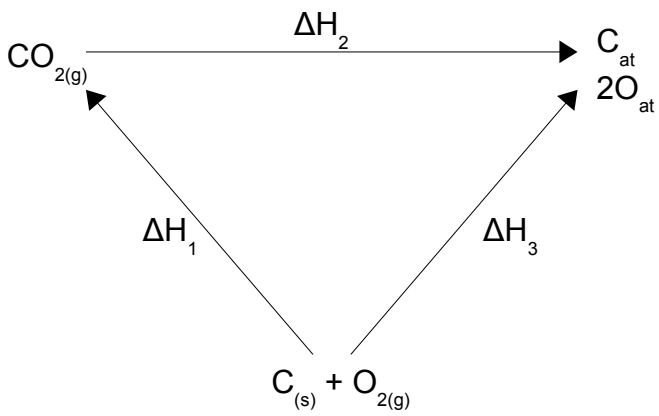


Energy level diagrams (*left*) are quite simple to understand as they show a relative energy difference between the different routes.

What they don't show though are the changes in state which can lead to errors in calculations with more difficult reactions

What is important though is that it is possible to see that Hess's Law does work.

2. Energy cycle diagram (*Haber cycle*)



Energy diagrams (*left*) are more common than energy level diagrams.

These diagrams are more useful as they can be used to show changes in state and are used for reactions harder than the one used so far.

Consider the reaction between carbon and hydrogen to form methane (CH_4 – $C + 2H_2$).

When these are reacted together, heat is given out. The CH_4 has formed from the elements. The enthalpy here is called the "enthalpy of formation" or ΔH_f. As heat is given out, it will have a negative (-) value.

Carbon and hydrogen start off as elements. Elements are very stable. If a piece of carbon was placed on a desk, it will do nothing – ever. Hydrogen, though explosive when an ignition source is placed near it, is stable. It exists as a diatomic molecule (the s^1 electrons are shared between the two atoms giving an effective full 1s shell) and is all around in the air.

For carbon and hydrogen to react, they must be turned into a reactive form – atoms. The process of producing atoms from the elements is called "atomisation" This requires an input of heat which has a positive (+) value and is called the heat of atomisation or ΔH_{at}.

The heat of formation is ΔH_1 and atomisation is ΔH_3.

The heat of atomisation is $C_{(s)} \rightarrow C_{(at)}$ and $2H_2 \rightarrow 4H_{(at)}$. These two values for the atomisation are added together.

This leaves ΔH_2.

Hess's Law states : $\Delta H_1 = \Delta H_2 + \Delta H_3$, therefore $\Delta H_1 - \Delta H_3 = \Delta H_2$. If the values for ΔH_1 & ΔH_3 are known, then ΔH_2 can be easily found.

<u>Additional energies.</u>

For energy cycles, all products need to be in the same state which is typically gas. If a product is not a gas, it needs to be changed to a gas which requires an additional energy input. This additional amount of energy has to be added.

For example

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(l)}$$

Here, H_2O is liquid and needs to be changed to a gas. This additional energy will be added to the product side. The additional energy requires is known as the heat of vaporization – ΔH_{vap}.

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

In this example, carbon needs to be changed from a solid to a gas (it has been atomised, known as heat of atomisation, ΔH_{at}). This additional energy would be added to the reactant side

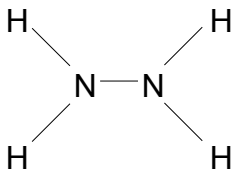
It is important to remember to add this energy!

Finding the energy difference

As has been seen before, the enthalpy of a reaction is the difference between the energy of bonds being broken and bonds being made (or products – reactants).

It is quite normal for tables of data giving enthalpies of formation to be used.

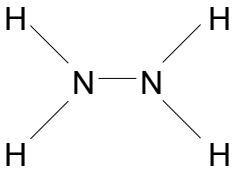
To find out how much of each enthalpy to use, first the number and types of bond in a compound have to be identified



Hydrazine (*left*) is a compound which is commonly used as a rocket fuel. When it breaks, a large amount of energy is released.

It has two different types of bond in this compound : 1 N-N bond and 4 N-H bonds. An N-N has an energy of 163 kJ mol^{-1}. Each N-H bond is 390 kJ mol^{-1}. The total for when a mole of N_2H_4 breaks is therefore (1 x 163) + (4 x 390) = 1723kJ mol^{-1}.

Consider the following reaction



+ 2 F-F → N≡N + 4H-F

Here, hydrazine is reacting with 2 moles fluorine to produce N_2 and 4 moles of hydrogen fluoride.

An F-F bond has an energy of 158 kJ mol^{-1}. As there are two moles of fluorine, this gives a total of 316 kJ mol^{-1}.

The total for the reactants is 1723 + 316 = 2039 kJ mol^{-1}

Next is to find the amount of energy from the bonds being made. There are 2 types of bond being made (in total) for the products – a N≡N and 4 moles of H-F.

N≡N has a value of 945 kJ mol^{-1}. H-F is 565 kJ mol^{-1}. As there are 4 moles of H-F, this gives a total of 2260 kJ mol^{-1} for HF. In total, the amount of energy for the products is 945 + 2260 = 3205 kJ mol^{-1}

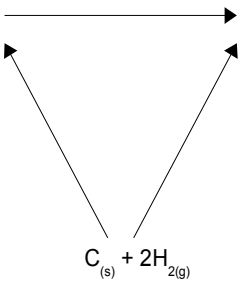
This will give a difference of -3205 + 2039 = $\Delta H_f^{\ominus}$ = -1166 kJ mol^{-1}

Worked examples

1. C-H bond energy in methane
2. $2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$

1.

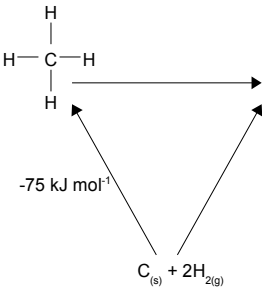
Methane starts off as C(s) and $2H_{2(g)}$ to produce $CH_{4(g)}$. The first step to solving this type of problem is to draw a Haber cycle diagram.



Remember, there are a number of important points here. First is that the bits at the bottom are the elemental state of the reactants and that their state at 25ºC is also given.

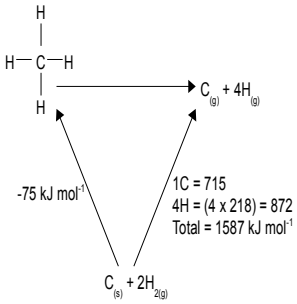
Make sure that the numbers balance. For every carbon, 4 hydrogens are required (sp^3 hybridised). As hydrogen exists as a diatomic molecule, 2 moles are required.

The heat of formation (ΔH_f^e) for methane is -75 kJ mol^{-1}. The heat of formation is the sum of the bonds broken and made. Put the structure (**not** the formula) at the top left of the diagram with ΔH_f^e in the middle of the line pointing to it.



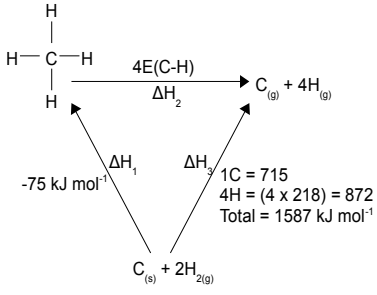
Next add in the enthalpies of atomisation (ΔH_{at}^e) and products. The products go at the top right of the triangle.

Remember with all enthalpies, multiply the number of atoms with the enthalpy and then add them all together. The ΔH_{at}^e for C is 715 kJ mol^{-1} and H is 218 kJ mol^{-1}.



Finally add in the number and types of bond. This is between the top left and top right (the molecule is being broken down to its gas form). There is only one type of bond here – C-H.

There are 4 of these bonds, so it is written as 4E(C-H) (E stands for energy)



The energy for the C-H bond is not known, but the others are. Hess's Law = $\Delta H_1 = \Delta H_2 + \Delta H_3$, therefore $-\Delta H_1 + \Delta H_3 = \Delta H_2$.

-(-75) + 1587 = 1662 kJ

As there are 4 C-H bonds, divide the answer by 4 to find 1 C-H bond = 1662 / 4 = 415.5 kJ mol^{-1}.

2

This is a different type of problem. Here a Haber cycle can be used, but it is simpler to just work out the bonds made and broken.

Additional information is available for this question :

Bond enthalpies : H-O = +464 kJ mol^{-1}, O-O = +144 kJ mol^{-1}, O=O = +498 kJ mol^{-1}.
Enthalpies of vaporization : $H_2O_{2(l)}$ = +43kJ mol^{-1}, $H_2O_{(l)}$ = +41 kJ mol^{-1}.

As with all reactions, a balanced equation is required. This has been given already.

$$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

2 moles of H_2O_2 produce 1 mole of O_2 and 2 moles of H_2O.

Next is to convert the liquids to gas form.

$2H_2O_2 = 2 \times \Delta H_{vap}\ H_2O_2 = 2 \times 43 = 86$ kJ
$2H_2O = 2 \times \Delta H_{vap}\ H_2O = 2 \times 41 = 82$ kJ

The reaction is now broken into reactants and products.

For the reactants, there are two types of bond. H_2O_2 has the structure H-O-O-H. There are two lots of O-H and one O-O. As there are 2 moles of H_2O_2, there are 4 lots of O-H and 2 lots of O-O

Reactants = 86 (from vaporization) + (4 x 464) + (2 x 144) = 2230 kJ mol^{-1}

The products are now looked at

Water has the structure H-O-H. This can be thought of as having a left OH and a right OH, so for every H_2O, it counts as being 2 lots of O-H.

There are 2 moles of water which is 4 lots of O-H. A mole of O=O is also formed

Products = 82 + (4 x 464) + (498) = 2436 kJ mol^{-1}

The energy difference is therefore 2230 – (+)2436 (reactants – products) = -206 kJ mol^{-1}

When performing any form of calculation, it is vitally important that every step is performed logically. It is very simple to rush this type of calculation and end up with an incorrect result.