Chapter 6

Energetics

Studying the energy changes which happen during reactions can tell us why things happen. If we can work out the likely energy changes then we can predict not just how much heat energy may be required for a process, but whether or not the process is likely to happen spontaneously. The posh name for this is *thermodynamics*.

6.1 Enthalpy

We start by considering enthalpy. Enthalpy is a new concept, but we can measure changes in enthalpy as they will normally be equal to a heat energy change (heat energy can be taken in or released by the system).

We measure changes in enthalpy by **calorimetry**. This involves measuring the temperature change accompanying a process. We then work out how much energy has been transferred to or from the system and finally scale up this value for a mole of whatever substance we are interested in.

6.1.1 Calorimetry with solids and solutions

Imagine you are asked to work out the enthalpy change accompanying the dissolving of 1 mole of iron (III) chloride. You are given the following data: 2 g of iron (III) chloride were used; 10 cm^3 of water were used; the temperature of the water increased by 8 °C.

Strategy: Work out how much energy was transferred to the water, then work out how many moles of solid caused this energy transfer, then work out what the enthalpy change would be for an entire mole of solid.

Working: We use the equation $Q = c\ m\ \Delta T$ to work out the energy transferred:

$$Q = 4.18 \times 10 \times 8 = 334.4 \text{ J}$$

4.18 is the specific heat capacity of water in joules per kelvin per gramme. 10 is the mass of the water in grammes. We ignore the mass of the solid because we are given the temperature rise of the solution and are thus ignoring anything other than that in our calculation. 8 is the temperature rise in kelvin.
We use $n = m/M_r$ to work out the number of moles of iron (III) chloride used:

$$n = 2/162.5 = 0.0123 \text{ moles}$$

We then decide on a sign for the enthalpy change. An exothermic change has a negative sign and an endothermic change has a positive sign. In this case the temperature of the water goes up, meaning that energy has been transferred from the stuff of interest to the surroundings, and so it is exothermic. To turn the energy change into an enthalpy change per mole of solid we divide by the number of moles of solid we used:

$$\Delta H = -Q/n = -334.4/0.0123 = -27170 \text{ J mol}^{-1}$$

We then need to tidy up a bit, this is far more significant figures than we're given in the question. It is probably appropriate to write $\Delta H = -27$ kJ mol^{-1}.

In these calculations it is important to work with the mass of the solution - that's what we measure the energy transfer to and then work with the mass of stuff we're interested in. If the reaction takes some time (like the first experiment we did with the reaction between metal and acid) it may be wise to plot a graph showing how the temperature varies with time and then extrapolating to assess the maximum temperature change.

6.1.2 Calorimetry with two solutions

We are sometimes asked to calculate the enthalpy change of neutralisation of some stuff. In this case it is often a case of mixing two solutions. These calculations are like the one above except now we use the total mass of the two solutions when working out the energy change, but again scale it up only for the stuff we're interested in.

6.1.3 Calorimetry problems

With calorimetry questions there are often parts asking why the value you get is different from the literature value. The normal reasons are

- Heat loss
- Using the heat capacity of water when technically it was something else
- Ignoring the mass of the solid (if relevant)

6.1.4 Hess's law

There are lots of different possible enthalpy changes. The useful upshot of this is that we can devise more than one way to get from one substance to another. This means that we can work out enthalpy changes which are difficult or even impossible to measure directly. This is a result of Hess's law, which can be stated something like this:

> The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.

The individual steps can be hypothetical, but we can still work them out!

6.1.5 Bond enthalpies

We can carry out a series of experiments to determine the energy required to break a certain type of bond. Of course, this will only be an *average* energy, so when you are asked why the literature and measured values disagree in a bond enthalpy calculation this is going to be one of your reasons why. Isn't it? Good. Average bond enthalpies are the energy required to break a mole of a particular type of bond in the substance of interest *in the gaseous state* to make atoms (or radicals) *in the gaseous state.*

6.1.6 Standard enthalpy changes

Standard conditions are defined in order that data are comparable between experiments and across continents. The standard conditions normally experienced are a temperature of 298 K (kelvin works in thermodynamics) and a pressure of 101.3

kPa. If solutions are involved in the measurement then we usually work with concentrations of 1 mol dm^{-3}. You need to know some definitions of standard changes. Standard quantities are often denoted with the symbol $^{\ominus}$.

> The **standard enthalpy of formation** $\Delta H_{\mathrm{f}}^{\ominus}$ of a substance is the enthalpy change accompanying the formation of one mole of the substance in its standard state from its elements in their standard states.

For instance $\Delta H_{\mathrm{f}}^{\ominus}$ for hydrogen chloride is:

$$\tfrac{1}{2}\mathrm{H}_{2\,(g)} + \tfrac{1}{2}\mathrm{Cl}_{2\,(g)} \longrightarrow \mathrm{HCl}_{\ (g)}$$

> The **standard enthalpy of combustion** $\Delta H_{\mathrm{c}}^{\ominus}$ of a substance is the enthalpy change accompanying the complete combustion of one mole of the substance in excess oxygen under standard conditions.

For instance $\Delta H_{\mathrm{c}}^{\ominus}$ for ethane is:

$$\mathrm{C_2H}_{6\,(g)} + \tfrac{7}{2}\mathrm{O}_{2\,(g)} \longrightarrow 2\,\mathrm{CO}_{2\,(g)} + 3\,\mathrm{H_2O}_{\ (l)}$$

> The **standard enthalpy of neutralisation** $\Delta H_{\mathrm{neut}}^{\ominus}$ is the enthalpy change accompanying the neutralisation of one mole of acid (or base) with a strong base (or acid).

This is really the enthalpy change for the reaction:

$$\mathrm{H}^{+}_{(aq)} + \mathrm{OH}^{-}_{(aq)} \longrightarrow \mathrm{H_2O}_{(l)}$$

> The **standard enthalpy of atomisation** $\Delta H_{\mathrm{at}}^{\ominus}$ is the enthalpy change associated with the formation of one mole of gaseous atoms of an elephant from the element in its standard state.

For a metal such as magnesium this is trivial:

$$\mathrm{Mg}_{(s)} \longrightarrow \mathrm{Mg}_{(g)}$$

For something like fluorine however it is a little more complicated:

$$\tfrac{1}{2}\mathrm{F}_{2\,(g)} \longrightarrow \mathrm{F}_{\ (g)}$$

which is actually just half of the bond enthalpy of fluorine ($\frac{1}{2}$ E(F-F)).

> The **electron affinity** $\Delta H^{\ominus}_{\mathrm{EA}}$ is the enthalpy change associated with adding a mole of electrons to a mole of gaseous atoms or ions.

For instance, the first electron affinity of sulfur is given by:

$$\mathrm{S_{(g)}} + \mathrm{e^-} \longrightarrow \mathrm{S^-_{(g)}}$$

The second electron affinity is:

$$\mathrm{S^-_{(g)}} + \mathrm{e^-} \longrightarrow \mathrm{S^{2-}_{(g)}}$$

The second is likely to be more endothermic than the first as we are trying to add a negative electron a negatively-charged ion.

> The **ionisation energy** E_j is the energy required to remove a mole of electrons from a gaseous substance.

E_2 for Mg is:

$$\mathrm{Mg^+_{(g)}} \longrightarrow \mathrm{Mg^{2+}_{(g)}} + \mathrm{e^-}$$

> The **lattice enthalpy** $\Delta H^{\ominus}_{\mathrm{latt}}$ is the energy released (or required) by the formation (or destruction) of a mole of an ionic crystal from its constituent ions in the gaseous state.

For the formation of a crystal $\Delta H^{\ominus}_{\mathrm{latt}}$ will be exothermic (negative).

$$\mathrm{Na^+_{(g)}} + \mathrm{Cl^-_{(g)}} \longrightarrow \mathrm{NaCl_{(s)}}$$

The lattice enthalpy is a measure of how strongly held together an ionic substance is. Obviously the lattice will be stronger if the ions have higher charges and if they are relatively smaller.

6.1.7 Born-Haber cycles

It is possible to combine $\Delta H^{\ominus}_{\mathrm{f}}$, $\Delta H^{\ominus}_{\mathrm{at}}$, $\Delta H^{\ominus}_{\mathrm{EA}}$, E_j and $\Delta H^{\ominus}_{\mathrm{latt}}$ values to form a fancy Hess cycle, called a Born-Haber cycle.

6.2 Entropy

We now meet a new thermodynamic idea - that of entropy. As chemists we are interested in whether or not a reaction will 'go', in other words whether or not a change will be **spontaneous**. Sometimes a spontaneous change needs a helping hand - heating or catalysing, but once it's up and running it happens. It seems somewhat fatuous to say that a reaction occurs when it is likely (overwhelmingly probable) that it will, however it is true. We are not considering blind chance here, rather we are thinking about something quantifiable and predictable. Experience and common sense suggest that if we see a reaction happen spontaneously 99 times, then it's likely that it will happen again. Processes which are not spontaneous require that some work is done to make the change happen. These notes are distinct from those in the book and which you have already been given, as an alternative look at the topic.

6.2.1 The direction of spontaneous change

We can't go very far without considering the first law of thermodynamics:

Energy is conserved in any process

You may meet lots of different statements of the first law, but this one is useful for now. Consider an *isolated* system, with a system and its surroundings. The first law tells us that if the energy of a system does decrease during a change, the energy of the surroundings ought to increase by the same amount and *vice versa.* Depending on your perspective this increase in energy of the surroundings is also spontaneous. When a change takes place the total energy of our isolated system is conserved, but is divided up in different ways. The suggestion of this is that it is the *distribution* of energy which controls the spontaneity of a change. *Spontaneous changes are always accompanied by a dispersal of energy into a more disordered form.*

Balls

Imagine a ball bouncing on the floor. The height of the bounce of the ball gets lower each time it bounces. The ball is our system, the floor is our surroundings. The direction of spontaneous change is one in which the ball is at rest on the floor. Where does the kinetic energy of the ball go? It is converted into thermal energy in the molecules of the ball and the floor. If we rested a ball on the floor on a warm day it wouldn't suddenly start bouncing higher and higher. But why not?

You can argue this yourself: For the ball to gain kinetic energy from the thermal energy of the floor molecules lots of things would have to happen. A lot of thermal energy would have to be localised over a small floor area. Not only that, but the thermal motion of the floor particles would have to be concerted - all the floor molecules would have to vibrate in the same direction. Common sense tells us that this is highly unlikely.

This is the key to spontaneous change - the direction of spontaneous change is that which leads to the greater chaotic dispersal of the total energy of the system. The bouncing ball stops bouncing because this spontaneous change results in the greater disorder. The ball at rest on the floor doesn't suddenly start bouncing because it is very improbably that the chaotic motion of the floor molecules will become organized and thrust the ball heavenwards.

6.2.2 S

The second law of thermodynamics uses the concept of entropy to help us spot spontaneous changes:

$$\Delta S_{\text{tot}} > 0 \tag{6.1}$$

Irreversible processes generate entropy (disorder). Reversible processes don't - they may transfer entropy from one part of an isolated system to another.

Eh?

Entropy is very tricky to define - you need to do statistical thermodynamics to apply the idea properly to atoms and molecules. I'm not very good at statistical thermodynamics so I'm not going to try - we don't need it anyway. Entropy can be viewed as a way of measuring the number of ways in which the energy of a system can be arranged among its atoms or molecules.

$$S = k \ln W \tag{6.2}$$

k is Boltzmann's constant, $k = 1.381 \times 10^{-23}\text{J K}^{-1}$. W is the number of different ways of arranging the energy. This starts to mean something if we think about a 'real' system. Before we start we should state that the entropy of a perfect crystal at absolute zero is zero (this is because $W = 1$ - there is only one way of ordering the parts of a perfect crystal at absolute zero - test this with equation 6.2 and your calculator).

If we think about a polar molecule like HCl at $T = 0$ we can imagine that if we have N HCl molecules then the lowest possible energy for this system is to have all the dipoles lined up neatly - there is only one way to arrange the molecules and so the entropy is zero. Carbon monoxide has almost no dipole and C and O are similar sizes. If we had N CO molecules instead there would be 2 ways in which we could arrange each molecule. The entropy is no longer zero because there are 2^N ways of arranging each CO. 1.00 mole of CO therefore has entropy

$$S = k \ln 2^N = Nk \ln 2 = (6.02 \times 10^{23}) \times (1.381 \times 10^{-23}) \times \ln 2 = 5.76 \text{ J K}^{-1}$$

Don't read this and think that HCl has no entropy! When we increase the temperature of the solid the molecules eventually get enough energy to move and overcome the forces which hold them in the particular arrangement described above. When the solid HCl melts the entropy will increase again and when it boils this value for S will increase again.

6.2.3 What can I use it for?

We are normally more interested in whether or not a reaction is likely to happen than how the molecules are arranged and how the energy of these molecules is distributed. Instead of absolute values of entropy the chemist finds *changes* in entropy useful. Changes in the entropy of the surrounding can be shown to obey the simple relationship

$$\Delta S_{\text{surroundings}} = -\frac{\Delta H_{\text{reaction}}}{T} \tag{6.3}$$

Remember that as this is thermodynamics we need to use the thermodynamic, absolute, temperature. This equation shows us that if a reaction is really exothermic ($\Delta H < 0$) then a lot of entropy is generated in the surroundings. This is intuitive - if a reaction yields a lot of heat energy it will increase the chaos of the air (or whatever) around it. An endothermic change will reduce the entropy of the surroundings, but endothermic changes can still occur spontaneously. Equation 6.3 gives important information about the direction of spontaneous change.

You will be given, where necessary, standard entropies of substances. These are fairly intuitive. Solids normally have lower entropies than liquids and gases as they are more ordered, for instance. These are all based on the assumption that at $T = 0$ $S = 0$ for a perfect crystal[1].

Following on directly from this is a demonstration of why entropy increases when something melts or boils (or *vice versa*). We call the temperature at which a solid and liquid phase of a substance are in equilibrium T_{t} (the transition temperature) - this is 273 K for ice / water and 373 K for water / steam. Our equation for the

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[1] The third law of thermodynamics, and one of my personal favourites

entropy change of the system (not the surroundings) is

$$\Delta S = \frac{\Delta_{\mathrm{t}} H}{T_{\mathrm{t}}} \tag{6.4}$$

Melting and boiling are both endothermic processes. The entropy change accompanying them must therefore be positive. For an exothermic transition, such as condensing and freezing which involve bond formation, the entropy change of the system will be negative. This backs up the idea we intuitively hold - that liquids and gases are more disordered than solids.

If we know the enthalpy (heat) change in a reaction and are given standard entropy (disorder) values then we can calculate the entropy change for a chemical reaction. Hurrah.

$$\Delta S^{\ominus}_{\mathrm{total}} = \Delta S^{\ominus}_{\mathrm{system}} + \Delta S^{\ominus}_{\mathrm{surroundings}} \tag{6.5}$$

A positive entropy change, an increase in disorder, suggest that a reaction will go spontaneously at a given temperature (for this equation at 298 K).

Positive entropy changes can inform us as to what the driving force may be in a spontaneous change, even one which is endothermic.

When answering questions involving entropy and entropy changes it is really important that you check your signs and units - do not confuse kJ and J for instance!

6.3 Spontaneity

The IB course treats entropy in a very grown up fashion. Chemists usually use the **Gibbs free energy** change ΔG to predict spontaneity.

$$\Delta G = -T\Delta S_{\mathrm{total}}$$

This equation tells us that if $\Delta S_{\mathrm{total}}$, the entropy change of the universe, is positive ΔGwill be negative. We can substitute this expression for ΔGinto equation 6.5 to give

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}_{\mathrm{system}} \tag{6.6}$$

As long as you get the units (joules, kilojoules, kelvin) correct then it is easy to evaluate equation 6.6 and decide whether or not a process 'goes'.

The expression in equation 6.6 is quite powerful. We can see that if a process is exothermic and gives more disordered products than reactants it will always be spontaneous. Conversely, a reaction which is endothermic and gives more ordered products than reactants will never be spontaneous. We can also see why some things happen which are endothermic (this is an idea which is quite alien the first time you see it happen) and why some things heating up an endothermic process makes it more likely to happen (the $\mathrm{T}\Delta S$ term gets bigger than the ΔH term). This is the real reason why things happen, and it is good that we meet it now.

The value of ΔG can be used in studies of equilibria. Remember that although it tells you whether or not a process will be spontaneous, it tells you nothing about how fast it will take place.

6.4 Some problems

The bombardier beetle, *Stenaptinus insignis* uses an explosive charge of quinone to defend itself. Hydroquinone is oxidised by hydrogen peroxide to produce quinone and water:

$$C_6H_4(OH)_{2\,(aq)} + H_2O_{2\,(aq)} \longrightarrow C_6H_4O_{2\,(aq)} + 2\,H_2O_{(l)}$$

It is possible to calculate the enthalpy change for this reaction, given that

Reaction	$\Delta H_f^{\ominus}$ kJ mol^{-1}
$C_6H_4(OH)_2(aq) \longrightarrow C_6H_4O_2(aq) + H_2(g)$	-177.4
$H_2(g) + O_2(g) \longrightarrow H_2O_2(aq)$	-191.2
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$	-241.8
$H_2O(g) \longrightarrow H_2O(l)$	-43.8

You should get something like -557.4 kJ mol^{-1}. Why do you think this is an effective defence strategy?

Calculate $\Delta H_\mathrm{f}^\ominus$ for glucose being produced in photosynthesis.

Species	$\Delta H_\mathrm{f}^\ominus$ kJ mol^{-1}
CO_2	-393.5
H_2O	-285.8
$C_6H_{12}O_6$	-1274.5
O_2	???

What is $\Delta H_\mathrm{f}^\ominus$ for the formation of oxygen?

Can you construct a Hess cycle to show $\Delta H_\mathrm{f}^\ominus = +2801.3$ kJ mol^{-1} for the production of glucose?