Chapter 13

Entropy

In topic 13 we 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.

13.1 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.*

13.1.1 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.

13.2 Entropy

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

$$\Delta S_{\mathrm{tot}} > 0 \tag{13.1}$$

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

13.2.1 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.

$$S = k \ln W \tag{13.2}$$

k is Boltzmann's constant, $k = 1.381 \times 10^{-23}$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 13.2 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.

13.3 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

$$\Delta S_{\text{surroundings}} = -\frac{\Delta H_{\text{reaction}}}{T} \tag{13.3}$$

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 13.3 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 entropy change of the system (not the surroundings) is

$$\Delta S = \frac{\Delta_\mathrm{t} H}{T_\mathrm{t}} \tag{13.4}$$

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.

$$\Delta S^\ominus_\mathrm{total} = \Delta S^\ominus_\mathrm{system} + \Delta S^\ominus_\mathrm{surroundings} \tag{13.5}$$

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!

---

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