Chapter 14

Chemical equilibrium

The topic of chemical equilibrium is interesting, relevant and satisfying to study. In our study of equilibria we see that the position of equilibrium in a system corresponds to the maximum total entropy, learn how to manipulate systems which are at equilibrium and predict how they will respond to changes in conditions, work out the pH of acids and alkalis, and demonstrate how and why buffer solutions resist changes in pH.

14.1 Reversible reactions

Many reactions are reversible. This simply means that both the forward and back reactions can happen. In an equilibrium system both of these processes are occurring at the same time and at the same rate. We do not see an overall change in the composition of the reaction mixture, but the processes are still happening. We say that the system is *dynamic.*

Of course there are systems in which equilibrium is never reached. In industry, such as in the production of ammonia in the Haber process, equilibrium is seldom attained - the ammonia is removed as it is formed, this encourages the formation of more ammonia (think about it in terms of le Chatelier's principle).

$$\mathrm{N_{2(g)}} + 3\,\mathrm{H_{2(g)}} \rightleftharpoons 2\,\mathrm{NH_{3(g)}}$$

This is an example of the necessity of a system being **closed** for equilibrium to exist. A closed system is one which does not allow stuff in or out of the reaction mixture. (Don't get this confused with an isolated system, which allows neither stuff nor energy to get in or out.)

Equilibrium can be approached from either direction. In our ammonia example above we can imagine starting with a jar of ammonia and leaving it for a couple of days. Testing the end mixture we would find nitrogen, hydrogen and ammonia in there. Equally if we are making ammonia we know that we can do this by mixing some hydrogen and nitrogen gas together and leaving it for a bit.

Equilibria are sensitive - they respond to changes in a predictable manner. This makes it easy to work out how to improve the yield of a product or control the pH of a solution with a buffer.

14.2 The equilibrium law

This is an empirical law and, as an example from our ammonia example, an expression showing the relative proportions of the substances present at equilibrium:

$$K_\mathrm{c} = \frac{[\mathrm{NH}_{3(\mathrm{g})}]^2_\mathrm{eqm}}{[\mathrm{H}_{2(\mathrm{g})}]^3_\mathrm{eqm}[\mathrm{N}_{2(\mathrm{g})}]_\mathrm{eqm}} \tag{14.1}$$

We normally leave out the little 'eqm' because it gets tedious, although you should always put state symbols in. This can be rewritten in terms of partial pressures:

$$K_\mathrm{p} = \frac{p^2(\mathrm{NH}_3)}{p^3(\mathrm{H}_2)p(\mathrm{N}_2)} \tag{14.2}$$

K_c and K_p both have units and you should be able to work them out. What are they for the expressions in equations 14.1 and 14.2?

14.2.1 Equilibria with solids

Some equilibrium systems involve substances in different physical states (phases). In such cases we can still write meaningful expressions for K_c and K_p, although we *ignore solids*. This is because the idea of pressure or concentration of a solid is a bit vague. Which is to say really really vague. It is not a quantity that changes, as it is a function of the density of the substance. Be on the lookout for trick questions with solids in and remember that if you're writing $_{(\mathrm{s})}$ in your equilibrium constant expression you are doing something wrong.

14.2.2 Equilibria with gases

Equilibrium calculations with gases can be more complicated than those involving solutions because you could be asked to express your answers in terms of pressures rather than concentrations. The usual unit for pressure is the atmosphere, atm. The total pressure exerted by a mixture of gases is, intuitively, the sum of the individual, or *partial* pressures of the gases involved. We work out the partial pressure in the following way:

First we work out the *mole fraction.* This is the fraction of the total number of moles of substance that our gas of interest makes up. For instance, the mole fraction of nitrogen in air is about $\frac{4}{5}$.

$$\text{mole fraction} = \frac{\text{number of moles of a particular gas}}{\text{total number of moles of gas in the mixture}}$$

The partial pressure is then

$$\text{partial pressure} = \text{mole fraction} \times \text{total pressure}$$

So the partial pressure of nitrogen in a room is about 0.8 atm.

All of your knowledge of equilibrium constants is covered again and again by doing questions involving equilibria. You should be confident with this as you have had lots of practice.

14.3 Entropy and equilibrium

In topic 13 we met the idea that reactions only occur if there is an overall positive entropy change. In an equilibrium system two reactions are happening at once and in opposite directions. This is because there is a maximum entropy which lies somewhere in between completing either the forward or back reaction. The reason for this maximum is explained rather neatly in the book. I will try to paraphrase.

If we had a simple equilibrium such as $\mathrm{A} \rightleftharpoons \mathrm{B}$ we would, at first, imagine that as A turned into B the entropy increased - this is after all what we understand to be true from topic 13. You would expect, in fact, the increase in entropy to be linear and the reaction should go ‘to completion’. However, as your reaction proceeds you are producing some B. Your B mixes with the remaining A and *increases the entropy of your system* - you have a mixture of two things rather than either pure A or pure B. This means that in terms of the mixing of the A and B there is a maximum entropy - a sort of parabolic shape rather than a linear shape in our change in entropy which we expected. If we add the straight line and the parabola together we get an entropy profile for the extent of our reaction which has a maximum (turning point) in it somewhere.

You can further explain the fact that there is a maximum by considering how much the entropy of mixing changes. At first, as we make more B and use up A, the increase is large, but when we have a mixture of half A and half B the entropy of the mixture can only decrease (the entropy here is at its maximum).

In reality the position of the maximum can be governed by the detailed energetics of forward and back reactions, but the important part is that the mixing of the products with the reactants produces the maximum in the entropy profile of the reaction.

The upshot of all of this is that there is a relationship between the position of equilibrium (given by K_c) and the entropy change of the process:

$$\Delta S^{\ominus}_{\text{total}} = R \ln K_c \tag{14.3}$$

It's beautiful.

14.4 The response of equilibrium to change

The response of systems at equilibrium to changes in pressure or temperature can be summarised by le Chatelier's principle, which we've already met. In this topic we are invited to explain why lCp works. It is, of course, a result of changes in entropy driving our equilibrium reaction one way or another.

Consider, again (sorry), the familiar equilibrium established between nitrogen, hydrogen and ammonia in the Haber process.

14.4.1 Pressure change

If we increase the pressure on a gas we are, in effect, decreasing its volume. This will decrease the number of ways of arranging the gas particles in our system which is a decrease in the entropy of the gas. This corresponds to fewer gas particles - so increasing the pressure in the Haber process shifts the position of equilibrium to the right hand side.

You can also explain this mathematically, although it's a little more complicated. Our expression for K_p is

$$K_p = \frac{p^2(\text{NH}_3)}{p^3(\text{H}_2)p(\text{N}_2)} \tag{14.4}$$

Increasing the total pressure increases all of the partial pressures. The only way the right hand side of this K_p expression can remain constant in this case is if the top of the fraction increases more rapidly than the simple change in volume would allow (we have a pressure^4 term on the bottom but only a pressure^2 term on the top). Don't worry if this is nonsense to you, but feel warm inside if it makes a bit of sense.

14.4.2 Temperature change

Remember that we are talking about *total* entropy changes in this context. Remember also that the total entropy change is defined as (equation 13.5):

$$\Delta S^{\ominus}_{\text{total}} = \Delta S^{\ominus}_{\text{system}} + \Delta S^{\ominus}_{\text{surroundings}} \tag{14.5}$$

The entropy change of the system is pretty much temperature independent. The temperature of the surroundings is governed by whether or not the reaction is exo- or endothermic, and what the temperature is (equation 13.3):

$$\Delta S_{\text{surroundings}} = -\frac{\Delta H_{\text{reaction}}}{T} \tag{14.6}$$

This is the important bit. In any reaction we will reduce the effect of $\Delta S_{\text{surroundings}}$ if we increase the temperature (our value gets smaller).

If the reaction is exothermic then the $\Delta S_{\text{surroundings}}$ term becomes less positive - that is it provides less of a positive entropy change for the reaction, which means that the equilibrium position (the turning point in our entropy profile) moves towards the endothermic reaction.

14.5 Acid-base equilibria

You should know definitions for acids and bases, thanks to those Brönsted Lowry folks. Write them down.

You should know from this that the definition is a bit malleable - you should be able to describe reactions in which water acts as an acid and others in which it acts as a base (the correct term for this is **amphiprotic**, which not a lot people know and which you should therefore keep secret). We find it useful to describe acid base reactions as competitions for protons.

14.5.1 The pH of water

Water ionises. You can't stop it happening and you wouldn't want to anyway.

$$\mathrm{H_2O_{(l)}} \rightleftharpoons \mathrm{H^+{}_{(aq)}} + \mathrm{OH^-{}_{(aq)}} \tag{14.7}$$

It doesn't ionise very much however. In fact, we can say that the concentration of water is pretty much the same if it ionises or if it doesn't. This means that our expression for the equilibrium constant

$$K_\mathrm{c} = \frac{[\mathrm{H^+{}_{(aq)}}][\mathrm{OH^-{}_{(aq)}}]}{[\mathrm{H_2O_{(l)}}]}$$

can be rewritten as (and is equal to)

$$K_\mathrm{w} = [\mathrm{H^+{}_{(aq)}}][\mathrm{OH^-{}_{(aq)}}] = 1 \times 10^{-14}\ \mathrm{mol^2\ dm^{-6}}$$

In pure water the concentrations of $\mathrm{H^+}$ and $\mathrm{OH^-}$ are equal, so we eventually find out that $[\mathrm{H^+{}_{(aq)}}] = 1 \times 10^{-7}\ \mathrm{mol^2\ dm^{-6}}$. pH is defined as $-\log_{10}[\mathrm{H^+}]$, which means, when you put it into your calculator or magically work it out in your head, the pH of water is 7 (at 25 °C).

14.5.2 The pH of strong acids and alkalis

If our substance of interest ionises completely in water then we can easily work out the concentration of hydrogen or hydroxide ions in our solution - it'll be equal to the concentration of the species we're talking about.

For instance, the pH of 1.0 M hydrochloric acid is given by working out the concentration of hydrogen ions (1.0 M) and then converting this to pH, which gives us the answer of pH = 0.

The pH values of alkalis are a bit harder, but not much. If we have 1.0 M sodium hydroxide our concentration of hydroxide ions is 1.0 M. This means that our hydrogen ion concentration is 10^{-14} (from equation 14.5.1), so the pH is 14. Which is what we expected.

14.5.3 Acids and bases are not all strong

We know from our experience that some acids are 'weak'. This means that they don't completely dissociate into hydrogen ions and their conjugate base (the form of the acid that has lost $\mathrm{H^+}$. They are in equilibrium, which is why they're in this chapter. We can work out an equilibrium constant for their dissociation, which in this case is called K_a. K_a gives us a measure of how dissociated the acid is into its ions - it simply measures the extent of dissociation and hence the strength of the acid. Consider two weak acids which we have met - ethanoic and phenol. You know that ethanoic is a stronger acid than phenol and this is borne out by the $K_a$values which are 1.7×10^{-5} and 1.3×10^{-10} mol dm^{-3} respectively.

Note that these K_a values have units and that they are small. This enables us to assume that, as in the dissociation of water, the concentration of acid before and after dissociation is roughly the same and we can therefore use K_a expressions to work out pH values. This is something which comes from practice. Remember that you will need an equation and an expression for the acid dissocation constant. When you have this remember that for a general reaction

$$\mathrm{HA} \rightleftharpoons \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]}$$

$[\mathrm{H}^+] = [\mathrm{A}^-]$. It is then trivial to work out the pH.

14.6 Titrations and indicators

We are used to doing titrations. In fact, you're jolly good at it. We can expect jumps in pH in titrations when we go through the end point. Remember that the end point is defined as pH = 7, the point where neutralisation has occurred.

14.6.1 Strong acid - strong base

In such a titration we will expect the pH of the mixture to jump from quite acidic (pH = 3) to quite alkaline (pH = 11) with the addition of just 0.1 ml of alkali. The calculation behind this is in your notes. The end point (pH = 7) is a long way from either of these values and we find that most acid-base indicators change well within this range. This means that any such indicator is suitable to show us when our titration should finish.

14.6.2 Strong acid - weak base

In this instance we expect the pH to go from acidic (3) to mildly alkaline (8 or 9). The jump is smaller and most of it lies in the acidic range, so an indicator such as **methyl orange** which changes colour around pH 4 is suitable to show us where our end point is.

14.6.3 Weak acid - strong base

These systems show a titration curve like the previous one, but shifted up by a couple of pH units. This means that our indicator should change colour in a slightly alkaline pH, such as **phenolphthalein** does.

14.6.4 Weak acid - weak base

In this can there is no major jump, more a little bump, in the pH curve as the titration proceeds. In the absence of a sudden large change in pH it is suitable to find an indicator which changes colour over a sufficiently narrow and middling pH range (it would need to work in the 6.5 - 7.5 range).

14.6.5 Indicators

Indicators are weak acids in which either the acid and conjugate base forms are different colours. Addition (or removal) of hydrogen ions shifts the equilibrium according to le Chatelier's principle and therefore changes the colour.

$$\mathrm{HIn_{(aq)}} \rightleftharpoons \mathrm{H^+{}_{(aq)}} + \mathrm{In^-{}_{(aq)}}$$

14.7 Buffers

Buffer solutions resist changes in pH. They are not immune to changes in pH. They are very useful in real life. Fizzy drinks contain 'acidity regulators' which are usually salts of the conjugate base of citric acid. Your blood is very effective at resisting pH changes in order that the millions of enzyme-catalysed reactions which happen in you can take place.

If we add a soluble salt of our conjugate base (such as NaA) to a solution of an acid HA then we have two equilibria (leaving out state symbols for brevity):

$$\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-} \tag{14.8}$$

and

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-}$$

14.7.1 Addition of acid

The extra hydrogen ions introduced by adding acid can react with the A^- which is produced from the ionisation of our soluble salt. This will help shift the equilibrium of equation 14.8 to the left, removing the added H^+ and thus the pH won't change very much.

14.7.2 Addition of alkali

The extra hydroxide ions will react with H^+ in equation 14.7 to produce H_2O. This uses up the hydroxide ions, but also reduces the concentration of H^+, so the equilibrium in equation 14.8 moves to the right, pretty much restoring the pH to its original value.

14.7.3 The pH of buffer solutions

You may (and probably will) be asked to calculate the pH of a buffer solution. You should realise from the above argument that this will depend on the the *relative* concentrations of the acid and its conjugate base, and the extent of dissociation of the acid, K_a. This is expressed as

$$\mathrm{pH} = -\mathrm{logK_a} - \log\frac{[\mathrm{acid}]}{[\mathrm{base}]}$$

$-\mathrm{logK_a}$ is sometimes called $\mathrm{p}K_\mathrm{a}$. These calculations are simply a matter of plugging in the appropriate numbers.

Summary

Equilibrium is a good nutritious topic which finally gives you a chance to use all of the chemical knowledge you've built up so far, which is why we spend a lot of time doing it. Some of the ideas are complicated, but many of them are formulaic or straightforward and you should make sure that you are confident with the questions given at the end of the topic.