7 Equilibria

Equilibria are introduced in this chapter for AS Level but are revisited in Chapter 25 for A Level.

Factors affecting chemical equilibria

In chemistry, **equilibrium** refers to chemical reactions that are in balance. The $\rightleftharpoons$ sign is used to represent a reaction in equilibrium. You need to know the following.

- *All* chemical reactions are reversible, given enough energy.
- In a reversible reaction at equilibrium, the rates of the forward and backward reactions are the same. In other words, the amount of reactants forming products in a given time is the same as the amount of products breaking down to give reactants in the same time. These are generally called **dynamic equilibria**.

An example of a dynamic equilibrium established in the gas phase is the reaction of nitrogen and hydrogen to form ammonia in the Haber process:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Dynamic equilibria can also happen in the liquid phase:

$$2H^+(aq) + 2CrO_4^{2-}(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

In a dynamic equilibrium:

- There is no net change in the concentration of each substance.
- The equilibrium compositions of the substances can be approached from either reactants or products.

Le Chatelier’s principle

The French chemist Henri le Chatelier studied many dynamic equilibria and suggested a general rule, **Le Chatelier's principle**, to help predict the changes in the position of equilibrium as different factors are changed.

KEY TERM

Le Chatelier's principle states that if a closed system at equilibrium is subject to a change, then the system will adjust in such a way so as to minimise the effect of the change.

STUDY TIP

Learn the rule but think carefully when you apply it in examinations.

The factors that can be changed easily are concentration, temperature and pressure. You might also have suggested using a catalyst – this possibility is looked at later (see page 51).

Consider a general reaction:

$$mA + nB \rightleftharpoons pC + qD \qquad \Delta H^{\ominus}\ -\text{ve (exothermic reaction)}$$

If you *increase* the concentration of *either* of the reactants A or B, more of the products C and D will be made.

The general reaction shown above is an exothermic reaction. If you *increase* the temperature, there will be less of the products made. The reverse would be true for an endothermic reaction.

The influence of pressure is relevant *only* for gas phase reactions. Think about the Haber process for making ammonia (see page 53):

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

There are fewer molecules on the right-hand side of the equation. This means that if you *increase* the pressure, the equilibrium will shift to produce more ammonia, reducing the total number of molecules in the system and therefore reducing the pressure.

NOW TEST YOURSELF

1 For each of the following reactions, use Le Chatelier's principle to decide what the effect will be on the position of equilibrium as a result of the changes stated:

a $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H^{\ominus}$ –ve

i increase the temperature

ii increase the pressure

b $C_2H_5OH(aq) + CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2C_2H_5(aq) + H_2O(l)$

i increase the concentration of CH_3CO_2H

ii remove H_2O from the system

In order to see what effect adding a catalyst might have, you have to think about the processes taking place. Look at Figure 7.1, which shows the energy profile of an equilibrium reaction with and without a catalyst present.

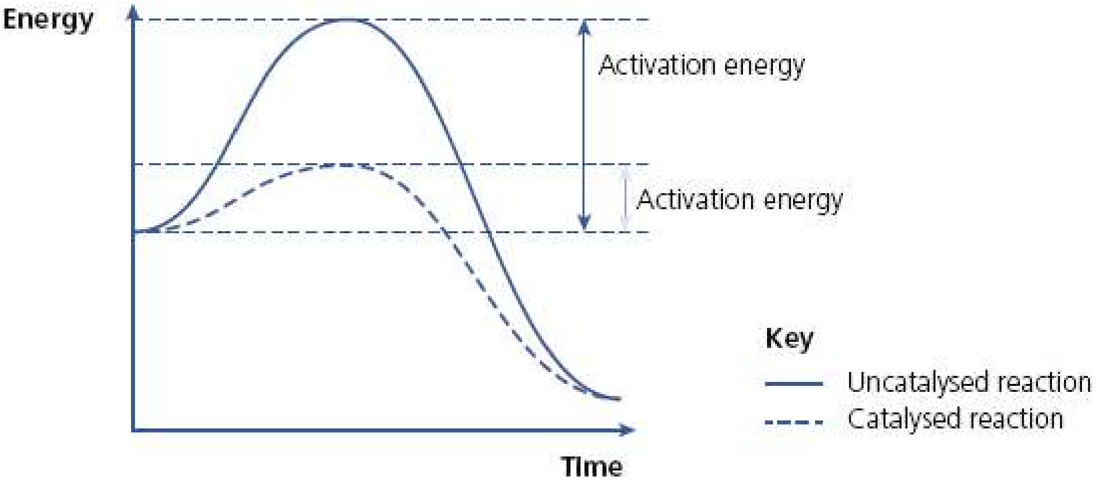

Figure 7.1 Reaction profile with and without a catalyst

Figure 7.1 shows that the catalyst has lowered the activation energy for the forward reaction. Consider the reverse reaction – the activation energy for this has also been lowered by the same amount. In other words, the presence of a catalyst does *not* change the position of equilibrium; it enables equilibrium to be established more quickly.

Equilibrium constants and calculations

Using K_c

For any equilibrium in the liquid state an equilibrium constant, K_c, can be defined in terms of concentration. For our general equation:

$$mA + nB \rightleftharpoons pC + qD$$

$$K_c = \frac{[C]^p[D]^q}{[A]^m[B]^n}$$

STUDY TIP

For equilibria involving liquids use K_c for the equilibrium constant, but for gas phase reactions use K_p.

The quantities in square brackets represent the concentrations of the different species at equilibrium. It is also important to remember that equilibrium constants depend on temperature.

For gas phase reactions, partial pressures (in atmospheres) of the species involved in the equilibrium are used. To distinguish this from reactions in solution, the symbol K_p is used for the equilibrium constant. So, for the reaction between hydrogen and iodine to form hydrogen iodide:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$K_p = \frac{p(HI) \times p(HI)}{p(H_2) \times p(I_2)} = \frac{p(HI)^2}{p(H_2) \times p(I_2)}$$

where p represents the partial pressure of each of the species.

Look at how these two constants are calculated.

WORKED EXAMPLE

Consider the reaction between ethanol and ethanoic acid:

$$C_2H_5OH(aq) + CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2C_2H_5(aq) + H_2O(l)$$

In an experiment, 0.100 mol of ethanol and 0.200 mol of ethanoic acid were mixed together and the mixture was allowed to reach equilibrium. The acid was then titrated with 1.00 mol dm^{-3} sodium hydroxide, and 115 cm^3 were needed to neutralise the acid. This volume of sodium hydroxide contains:

$$\frac{1.00 \times 115}{1000} = 0.115 \text{ mol of sodium hydroxide}$$

This means that there were 0.115 mol of ethanoic acid present in the equilibrium mixture.

Table 7.1 shows the other species present.

Table 7.1

	$C_2H_5OH(aq)$	$CH_3CO_2H(aq)$	$CH_3CO_2C_2H_5(aq)$	$H_2O(l)$
Start moles	$\frac{0.100}{V}$ mol	$\frac{0.200}{V}$ mol	$\frac{0.0}{V}$ mol	$\frac{0.0}{V}$ mol
Equilibrium moles	$\frac{?}{V}$ mol	$\frac{0.115}{V}$ mol	$\frac{?}{V}$ mol	$\frac{?}{V}$ mol

You have to divide by the total volume, *V*, because we are using concentrations.

You can deduce that (0.200 − 0.115) moles of ethanoic acid have been used. So the same amount of ethanol will have reacted. At equilibrium, the numbers of moles present are as shown in Table 7.2.

Table 7.2

	$C_2H_5OH(aq)$	$CH_3CO_2H(aq)$	$CH_3CO_2C_2H_5(aq)$	$H_2O(l)$
Equilibrium moles	$\frac{0.015}{V}$ mol	$\frac{0.115}{V}$ mol	$\frac{0.085}{V}$ mol	$\frac{0.085}{V}$ mol

Because there are the same numbers of molecules on each side of the equilibrium, the *V* terms cancel out. Substituting into the expression for K_c gives:

$$K_c = \frac{0.085 \times 0.085}{0.015 \times 0.115} = 4.19$$

Using K_p

You can use a similar process to calculate K_p for reactions taking place in the gas phase. To do this you need to understand what is meant by **partial pressure**.

KEY TERM

The **partial pressure** of a gas is its mole fraction multiplied by the total pressure.

Suppose we think of air as consisting of one-fifth oxygen and four-fifths nitrogen at a total pressure of 100 kPa:

$$\text{partial pressure of oxygen, } p(O_2) = \frac{1}{5} \times 100\,\text{kPa} = 20\,\text{kPa}$$

$$\text{partial pressure of nitrogen, } p(N_2) = \frac{4}{5} \times 100\,\text{kPa} = 80\,\text{kPa}$$

Together this gives the total pressure of 100 kPa.

WORKED EXAMPLE

Consider the dissociation of hydrogen iodide at 700 K:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

If the value of K_p under these conditions is 0.020, and the reaction started with pure hydrogen iodide at a pressure of 100 kPa, what will be the partial pressure of hydrogen at equilibrium?

Let x be the partial pressure of hydrogen. Table 7.3 shows a summary of the relevant data.

Table 7.3

	$2HI(g)$	$H_2(g)$	$I_2(g)$

Start partial pressure/kPa	100	0	0
Equilibrium partial pressure/kPa	$(100 - 2x)$	x	x

$$K_p = \frac{p(H_2) \times p(I_2)}{p(HI)^2}$$

Substituting gives:

$$0.020 = \frac{x^2}{(100 - 2x)^2}$$

Taking the square root of each side gives:

$$0.141 = \frac{x}{100 - 2x}$$

Rearranging gives:

$$14.1 - 0.282x = x$$

$$14.1 = 1.282x$$

$$x = 11.0\ \text{kPa (to 3 s.f.)}$$

NOW TEST YOURSELF

2 Write an expression for the equilibrium constant, K_c, for:

$$Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightleftharpoons Sn^{4+}(aq) + 2Fe^{2+}(aq)$$

3 Write an expression for the equilibrium constant, K_p, for:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

The Haber process

In the Haber (or Haber–Bosch) process, ammonia is produced on a massive scale using nitrogen from the air and hydrogen from the reaction of methane, CH_4, with steam:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^{\ominus} = -92\,\text{kJ}\,\text{mol}^{-1}$$

To make the process as economic as possible, the conditions needed are:

- a high equilibrium concentration of ammonia
- equilibrium to be reached in a short period of time

To understand the conditions chosen you need to know more about the reaction:

- At 298 K the equilibrium constant is very large, but only a tiny amount of ammonia is produced at this temperature because the rates of the forward and backward reactions are so low that equilibrium is never reached.
- Increasing the temperature increases the rates of both reactions but drastically reduces the equilibrium constant because the reaction is exothermic.
- Increasing the partial pressures of the reactants increases the equilibrium concentration of ammonia – for example, using 7500 kPa of hydrogen and 2500 kPa of nitrogen at 798 K gives a conversion with about 10% of ammonia at equilibrium.

The solution is to use an iron catalyst to increase the rate of attaining equilibrium, and then to use a compromise set of conditions – a relatively low temperature (around 750 K) and a moderately high pressure (20 000 kPa). The equilibrium mixture is then passed through a heat exchanger to cool and liquefy the ammonia, which is removed – the unreacted nitrogen and hydrogen are recycled.

The Contact process

The key stage in the production of sulfuric acid relies on an equilibrium reaction. In this process, sulfur dioxide is reacted with oxygen to form sulfur trioxide:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H^{\ominus} = -197\,kJ\,mol^{-1}$$

The forward reaction is exothermic. Therefore, Le Chatelier’s principle predicts that cooling the reaction mixture would give an increased yield. However, as you saw in the Haber process, this reduces the rate of attaining equilibrium.

Because there is an overall reduction in the number of molecules moving from left to right, Le Chatelier’s principle also predicts that increasing the pressure will drive the equilibrium to the right, increasing the yield of sulfur trioxide.

The conditions used mirror these principles. The gas mixture is passed over three catalyst beds and is cooled after each pass to try to force the equilibrium to the right. Although a higher pressure is predicted to push the equilibrium to the right, most chemical plants producing sulfuric acid operate at just above atmospheric pressure to reduce costs.

NOW TEST YOURSELF

4 Study the equations for the Haber and Contact processes given above, including the $\Delta H^\ominus$ values.

- a How do these help explain the best conditions for each reaction?
- b Give reason(s) why the industrial processes do not exactly reflect the best conditions.

Ionic equilibria

Brønsted–Lowry acids and bases

The Brønsted–Lowry theory is the most commonly used description of acidity. It describes an acid as a substance capable of donating protons (H^+) and a base as a substance capable of accepting them:

$$HCl + NH_3 \rightarrow Cl^- + NH_4^+$$

- In this reaction hydrogen chloride is acting as an acid by donating a proton to ammonia, which is acting as a base.
- In the reverse of this reaction, the chloride ion accepts a proton from the ammonium ion. This means that the ammonium ion would be acting as an acid in donating the proton to the chloride ion, which would be acting as a base.
- In this reaction, the chloride ion is known as the **conjugate base** of hydrogen chloride and the ammonium ion as the **conjugate acid** of

ammonia.

KEY TERM

Conjugate acid–base pairs In the Bronsted-Lowry theory an acid produces a conjugate base. For example, HCl forms a proton, H^+, and a chloride ion, Cl^-. The chloride ion is the conjugate base of HCl. In a similar way, bases form conjugate acids, e.g. $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

Here, NH_4^+ is the conjugate acid of NH_3.

It is also important to know how substances behave with water, the common solvent. Hydrogen chloride reacts with water:

$$HCl + H_2O \rightarrow Cl^- + H_3O^+$$

Here water is acting as a base, accepting a proton from hydrogen chloride; the H_3O^+ ion is its conjugate acid.

Water also reacts with ammonia:

$$H_2O + NH_3 \rightarrow OH^- + NH_4^+$$

Water is acting as an acid, donating a proton to ammonia; the OH^- ion is its conjugate base.

NOW TEST YOURSELF

5 Look at this equation and label the conjugate acid–base pairs.

$$H_2CO_3 + H_2O \rightarrow HCO_3^- + H_3O^+$$

Strong and weak acids and bases

It is important to understand the difference between *dilute* and *weak*, and *concentrated* and *strong* when you are writing about acids and bases:

- A **strong acid** or **strong base** is *completely* ionised in solution. We often refer to the compound as being completely dissociated.

- A **weak acid** or **weak base** is only *partially* ionised in solution. We often refer to the compound as being partly dissociated.
- A **concentrated acid** or **concentrated base** has a *large* number of moles per unit volume of the acid or base.
- A **dilute** solution has a *small* number of moles relative to the solvent.

Examples of strong and weak acids and bases are shown in Table 7.4.

Table 7.4

Acids				Bases			
Strong	**pH**	**Weak**	**pH**	**Strong**	**pH**	**Weak**	**pH**
HCl	1	CH_3CO_2H	3	$NaOH$	14	NH_3	11
HNO_3	1	H_2CO_3	4	KOH	14	CH_3NH_2	12
H_2SO_4	1	H_2O	7	$Ca(OH)_2$	12	H_2O	7

The pH values in Table 7.4 are given to the nearest whole number for 0.1 mol dm^{-3} solutions.

The categories ‘strong’ and ‘weak’ are qualitative. To be accurate you need to be able to make quantitative comparisons using dissociation constants or the pH values of solutions of the compounds.

When an acid, HA, dissolves in water, the equilibrium established is:

$$\mathrm{HA(aq) + H_2O(l) \rightleftharpoons H^+(aq) + A^-(aq)}$$

The position of the equilibrium depends the strength of the acid. For a strong acid, the equilibrium favours the products, and the reaction goes almost to completion. For a weak acid, the equilibrium favours the reactants, with relatively few H$^+$(aq) ions being produced.

A more precise indication of the position of equilibrium can be obtained by working out an equilibrium constant:

$$K = \frac{[\mathrm{H^+(aq)}][\mathrm{A^-(aq)}]}{[\mathrm{HA(aq)}][\mathrm{H_2O(l)}]}$$

$[H_2O(l)]$ is in excess and is almost constant, so you use a new equilibrium constant called the **acid dissociation constant**, K_a, which includes this and has units mol dm^{-3}.

$$K_a = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]}$$

Values of K_a are small (especially for weak acids and bases) and it is usual to convert them to a logarithm (to base 10) of their value (pK_a), as with $[H^+(aq)]$ and pH.

Consider water at 298 K. The concentration of $H^+(aq)$ ions is 10^{-7} mol dm^{-3}:

$$pH = -\log[H^+(aq)]$$

$$pH = -\log(10^{-7}) = 7$$

The numbers are not always this simple. Suppose that in a given solution $[H^+(aq)] = 8.6 \times 10^{-9}$ mol dm^{-3}.

To calculate the pH of this solution you need to understand how to work out the logarithm of this sort of number:

$$\begin{aligned} pH &= -\log[H^+(aq)] \\ &= -\log(8.6 \times 10^{-9}) \\ &= -((\log 8.6) - 9) \\ &= -(0.9345 - 9) \\ &= 8.0655 \text{ or } 8.07 \text{ to 3 s.f.} \end{aligned}$$

You can also calculate $[H^+(aq)]$ given the pH of a solution. A solution with a pH of 2.73 has its hydrogen ion concentration worked out like this:

$$\begin{aligned} pH = 2.73 &= -\log[H^+(aq)] \\ \log[H^+(aq)] &= -2.73 \\ [H^+(aq)] &= 10^{-2.73} \\ &= 1.862 \times 10^{-3} \\ &= 1.86 \times 10^{-3} \text{ mol dm}^3 \text{ to 3 s.f.} \end{aligned}$$

Another piece of information that is useful is the **ionic product** of water, K_w. This is the product of $[H^+(aq)]$ and $[OH^-(aq)]$ and at 298 K is equal to 10^{-14} $mol^2\ dm^{-6}$. This enables us to calculate $[OH^-(aq)]$ as well as $[H^+(aq)]$ in any aqueous solution.

NOW TEST YOURSELF

6 What is the pH of:

- **a** a solution containing 10^{-5} mol dm^{-3} $H^+(aq)$
- **b** a solution containing $10^{-3.5}$ mol dm^{-3} $H^+(aq)$
- **c** a solution containing $10^{-5.5}$ mol dm^{-3} $OH^-(aq)$?

Choosing indicators for titrations

When carrying out a titration, it is the pH of the solution at the end point that is critical when choosing a suitable indicator. Two main factors need to be considered:

- The colour change should be sharp – no more than one drop of acid or alkali should give a distinct colour change.
- The end point should occur when the solution contains the same number of hydrogen ions as hydroxide ions.

Plotting graphs of the change in pH with the addition of the titrating solution produces different curves for combinations of weak and strong acids with weak and strong bases, as Figure 7.2 shows.

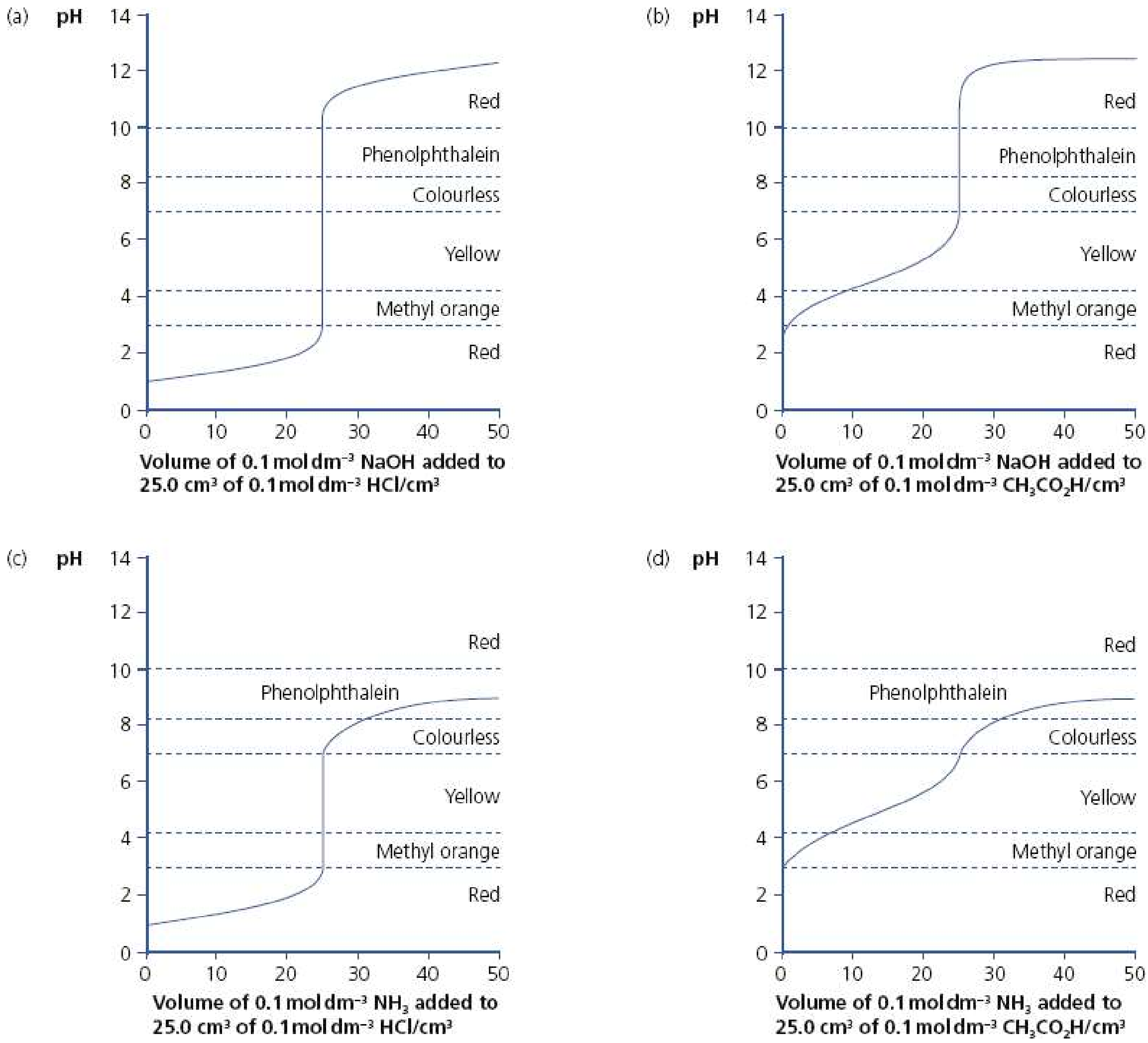

Figure 7.2 Titration curves for (a) a strong acid with a strong base, (b) a weak acid with a strong base, (c) a strong acid with a weak base, (d) a weak acid with a weak base

- Figure 7.2(a) shows the change in pH during the titration of a 25 cm^3 sample of 0.1 mol dm^{-3} strong acid when adding strong base. Notice that there is a long vertical portion at 25 cm^3 showing a large change in pH.
- Figure 7.2(b) shows the change in pH during the titration of a 25 cm^3 sample of 0.1 mol dm^{-3} weak acid when adding strong base. Notice that, although the vertical portion occurs at 25 cm^3, it is shorter and it starts at a higher pH than in (a).
- Figure 7.2(c) shows the change in pH during the titration of a 25 cm^3 sample of 0.1 mol dm^{-3} strong acid when adding weak base. Notice that, although the vertical portion occurs at 25 cm^3, it is shorter and it starts at a lower pH than (a).

- Figure 7.2(d) shows the change in pH during the titration of a 25 cm^3 sample of 0.1 mol dm^{-3} weak acid when adding weak base. Notice that now the vertical portion has practically disappeared, but it is closer to pH 7.

STUDY TIP

The vertical portion of the pH versus volume graph has to be in the pH range of the indicator to give a colour change.

The diagrams also show the effective ranges of two common indicators – phenolphthalein and methyl orange. Table 7.5 shows the choice of indicator for the four titrations shown in Figure 7.2. Study the diagrams and try to decide on the reasons for the choices.

Table 7.5

Acid/base combination	Indicator used
Strong acid/strong base	Either would do
Weak acid/strong base	Phenolphthalein
Strong acid/weak base	Methyl orange
Weak acid/weak base	Neither is suitable; a different method is needed

REVISION ACTIVITY

a Consider the reaction:

$$2X(aq) + Y(aq) \rightleftharpoons X_2Y(aq);\ \Delta H \text{ is +ve}$$

i Write an expression for K_c for this reaction.

ii What will be the effect on K_c of increasing the temperature of the reaction mixture?

iii What will be the effect on K_c of increasing the concentration of Y(aq)?

iv What will be the effect on K_c of adding a catalyst to the reaction mixture?

b Consider the reaction of $N_2(g)$ with $H_2(g)$ to form ammonia, $NH_3(g)$. At 800 K, K_p for the reaction is 1.45×10^{-5}. In an equilibrium mixture of the three gases, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3?

c **i** Sort these compounds into acids and bases:

H_3PO_4 PH_3 HCO_2H NH_3 NH_3 H_2S

ii Indicate whether each of the acids and bases is strong or weak.

END OF CHAPTER CHECK

By now you should be able to:

- understand reversible reactions and dynamic equilibria
- define and use Le Chatelier's principle
- deduce and use expressions for K_c and K_p in calculations
- describe and explain conditions used in the Haber and Contact processes
- describe the Brønsted–Lowry theory of acids and bases and the nature of strong and weak acids and bases
- understand and use the terms conjugate acids and bases, define conjugate acid–base pairs and identify these pairs in reactions
- understand neutralisation and pH titration curves, including the selection of indicators