

22 Quantitative equilibria

In this topic we use equilibrium constants to provide a quantitative measure of the acidity of acids and bases. The relationship between the pH scale and the hydrogen ion concentration in a solution is described. This scale covers the whole range of acidity found in the laboratory. We also look at the concepts of solubility product and partition coefficients.

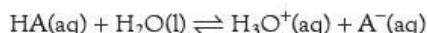
Learning outcomes

By the end of this topic you should be able to:

- 7.2c) explain the terms pH, K_a , pK_a , K_w and use them in calculations
- 7.2d) calculate $[H^+(aq)]$ and pH values for strong and weak acids and strong bases
- 7.2e) explain the choice of suitable indicators for acid–base titrations, given appropriate data
- 7.2f) describe the changes in pH during acid–base titrations and explain these changes in terms of the strengths of the acids and bases
- 7.2g) explain how buffer solutions control pH, and describe and explain their uses, including the role of HCO_3^- in controlling pH in blood
- 7.2h) calculate the pH of buffer solutions, given appropriate data
- 7.2i) show understanding of, and use, the concept of solubility product, K_{sp}
- 7.2j) calculate K_{sp} from concentrations and vice versa
- 7.2k) show understanding of the common ion effect
- 7.3a) state what is meant by partition coefficient; calculate and use a partition coefficient for a system in which the solute is in the same molecular state in the two solvents.

22.1 The dissociation of weak acids

An acid, HA, dissociates in water as follows:



HA and H_3O^+ are Brønsted–Lowry acids (see section 6.2) – they can donate a proton. H_2O and A^- are their conjugate bases – they can accept a proton. If the equilibrium lies over to the left, H_3O^+ is a stronger acid than HA, and HA is said to be a **weak acid**.

We may write the equilibrium expression (see section 9.7) for this reaction as follows:

$$K_c = \frac{[H_3O^+(aq)][A^-(aq)]}{[H_2O(l)][HA(aq)]}$$

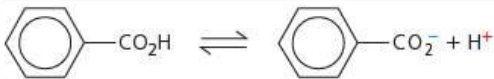
Pure water has a molar mass of 18.0 g mol^{-1} and a density of 1.00 g cm^{-3} . Because 1 dm^3 of water has a mass of 1000 g,

$$[H_2O(l)] = \frac{1000}{18.0 \times 1} = 55.5 \text{ mol dm}^{-3}$$

In any dilute aqueous solution, $[H_2O(l)]$ is very little different from this value and so may be taken as a constant. The value of 55.5 mol dm^{-3} can be combined with the equilibrium constant, K_c , and a new constant can be defined, called the **acid dissociation constant**, K_a , as follows:

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

Table 22.1 Acid dissociation constants for some weak acidsTable 22.1 lists the K_a values for some common weak acids.

Name of acid	Equilibrium	$K_a/\text{mol dm}^{-3}$
sulfurous acid	$\text{H}_2\text{SO}_3 \rightleftharpoons \text{HSO}_3^- + \text{H}^+$	1.3×10^{-2}
nitrous acid	$\text{HNO}_2 \rightleftharpoons \text{NO}_2^- + \text{H}^+$	5.6×10^{-4}
carbonic acid	$\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	2.0×10^{-4}
methanoic acid	$\text{HCO}_2\text{H} \rightleftharpoons \text{HCO}_2^- + \text{H}^+$	1.6×10^{-4}
ethanoic acid	$\text{CH}_3\text{CO}_2\text{H} \rightleftharpoons \text{CH}_3\text{CO}_2^- + \text{H}^+$	1.7×10^{-5}
benzoic acid		6.3×10^{-5}
hydrocyanic acid	$\text{HCN} \rightleftharpoons \text{CN}^- + \text{H}^+$	4.9×10^{-10}

K_a values can be used to calculate the concentration of hydrogen ions in solutions of weak acids. For example, if a solution of $0.020 \text{ mol dm}^{-3}$ ethanoic acid is made up, some of it will dissociate to produce $x \text{ mol dm}^{-3}$ of both $\text{H}^+(\text{aq})$ and $\text{A}^-(\text{aq})$:

	$[\text{HA}(\text{aq})]$	$[\text{H}^+(\text{aq})]$	$[\text{A}^-(\text{aq})]$
initial/ mol dm^{-3}	0.020	0	0
equilibrium/ mol dm^{-3}	$(0.020 - x)$	x	x

$$K_a = \frac{x^2}{(0.020 - x)} = 1.7 \times 10^{-5} \text{ mol dm}^{-3}$$

To avoid having to solve a quadratic equation, the solution to this equation can be simplified by assuming that x is small, so that $(0.020 - x) \approx 0.020$. This is usually justified because the degree of ionisation of a weak acid is very small. Hence:

$$x^2 = 0.020 \times 1.7 \times 10^{-5}$$

$$x = \sqrt{(0.020 \times 1.7 \times 10^{-5})} = 5.8 \times 10^{-4} \text{ mol dm}^{-3}$$

(Without the approximation, the answer would have been $5.75 \times 10^{-4} \text{ mol dm}^{-3}$. The difference is insignificant because it is within the limits of the accuracy to which the data is given.)

For an acid whose dissociation constant is K_a and whose initial concentration is $c \text{ mol dm}^{-3}$, we may use the formula $[\text{H}^+] = \sqrt{(K_a \times c)}$. Notice that this equation can only be used if there are no added $\text{H}^+(\text{aq})$ ions or $\text{A}^-(\text{aq})$ ions: it *cannot* be used for calculations involving buffer solutions (see section 22.3).

For a weak acid:

$$[\text{H}^+] = \sqrt{(K_a \times c)}$$

Now try this

Using K_a values from Table 22.1, calculate the hydrogen ion concentration in each of the following aqueous solutions.

- 0.0036 mol dm^{-3} methanoic acid
- 1.3 mol dm^{-3} hydrocyanic acid

Worked example

Calculate the hydrogen ion concentration in aqueous $0.0050 \text{ mol dm}^{-3}$ hydrofluoric acid, for which $K_a = 5.6 \times 10^{-4} \text{ mol dm}^{-3}$.

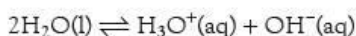
Answer

$$[\text{H}^+] = \sqrt{(K_a \times c)} = \sqrt{(5.6 \times 10^{-4} \times 5.0 \times 10^{-3})} = 1.7 \times 10^{-3} \text{ mol dm}^{-3}$$

22.2 The ionic product of water (K_w) and the pH scale

The ionic product of water

Pure water conducts electricity slightly, so it must be ionised to a small extent:



For this equilibrium:

$$K_c = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{H}_2\text{O}(\text{l})]^2}$$

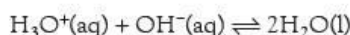
Because $[\text{H}_2\text{O}(\text{l})]$ is a constant, we can define a new constant called the **ionic product of water**, K_w , such that $K_w = [\text{H}_3\text{O}^+(\text{aq})][\text{OH}^-(\text{aq})]$. Because $[\text{H}_3\text{O}^+] = [\text{H}^+(\text{aq})]$ (hydrogen ions in water are all hydrated), this expression is often simplified to $K_w = [\text{H}^+][\text{OH}^-]$.

Experimentally, K_w is found to have a value of $1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 25°C .

The ionic product of water, K_w :

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 25^\circ\text{C}$$

This expression shows that in an acidic solution there will be a few hydroxide ions, and that in an alkaline solution there will be a few hydrogen ions. Even in a concentrated solution of sodium hydroxide, there are still some hydrogen ions – the equilibrium of the reaction:



is displaced to the right by the hydroxide ions added, but a few $\text{H}_3\text{O}^+(\text{aq})$ ions remain.

Worked example

Calculate the hydrogen ion concentration, $[\text{H}_3\text{O}^+]$, in a 2.0 mol dm^{-3} solution of sodium hydroxide.

Answer

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{2.0} = 5 \times 10^{-15} \text{ mol dm}^{-3}$$

In a **neutral solution**, the concentrations of H_3O^+ and OH^- are equal:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-]$$

Therefore:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}_3\text{O}^+]^2$$

and

$$\begin{aligned} [\text{H}_3\text{O}^+]^2 &= 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \\ [\text{H}_3\text{O}^+] &= \sqrt{(1.0 \times 10^{-14})} = 1.0 \times 10^{-7} \text{ mol dm}^{-3} \end{aligned}$$

The pH scale

The hydrogen ion concentration is a measure of the acidity of a solution. In different solutions, the hydrogen ion concentration, $[\text{H}^+]$, can have a wide range of values (from about 1 mol dm^{-3} to $1.0 \times 10^{-14} \text{ mol dm}^{-3}$). To make the numbers representing acidity easier to deal with, the **pH scale** was introduced. This scale is defined by the expression:

$$\text{pH} = -\log_{10} [\text{H}^+]$$

(or, more precisely, as $\text{pH} = -\log_{10} ([\text{H}^+]/\text{mol dm}^{-3})$, because logarithms can only be taken of a quantity without units).

So in a **neutral solution**, in which $[\text{H}^+] = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$,

$$\begin{aligned} \log_{10} [\text{H}^+] &= -7.0 \\ \text{pH} &= 7.0 \end{aligned}$$

We can calculate the pH of an **acidic solution**, for example one in which $[\text{H}^+] = 3.0 \times 10^{-2} \text{ mol dm}^{-3}$, as follows:

$$\begin{aligned} [\text{H}^+] &= 3.0 \times 10^{-2} \text{ mol dm}^{-3} \\ \log_{10} [\text{H}^+] &= -1.52 && \text{(taking } \log_{10}) \\ \text{pH} &= 1.52 && \text{(changing sign)} \end{aligned}$$

Now try this

Calculate the pH of each of the following solutions:

- 1 a $0.002 \text{ mol dm}^{-3}$ solution of $\text{HCl}(\text{aq})$
- 2 concentrated $\text{HCl}(\text{aq})$, in which $[\text{HCl}] = 18 \text{ mol dm}^{-3}$.

To find the pH of an **alkaline solution**, for example one in which $[\text{OH}^-] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$, we must first work out $[\text{H}^+]$ using K_w :

$$[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-3}} = 4.0 \times 10^{-12} \text{ mol dm}^{-3}$$

$$\log_{10}[\text{H}^+] = -11.40$$

$$\text{pH} = 11.40$$

The pH of strong acids and bases

We can calculate the pH of a solution of a strong acid or a strong base if we assume it to be completely ionised. For a monoprotic acid, that is, one that releases only one H^+ ion per molecule of acid, $[\text{H}^+] = [\text{acid}]$. For a monoprotic base, that is, one that reacts with only one H^+ ion, $[\text{OH}^-] = [\text{base}]$.

For a strong diprotic acid such as sulfuric acid, the situation is complicated by the fact that although the first ionisation is that of a strong acid, the second is not:



As an approximation, we can ignore the second ionisation and treat sulfuric acid as a strong monoprotic acid.

For strong diprotic bases such as barium hydroxide, $\text{Ba}(\text{OH})_2$, we may assume complete ionisation and so $[\text{OH}^-] = 2 \times [\text{base}]$.

pH and $\text{p}K_a$

The symbol 'p' means $-\log_{10}$. It can also be used with K_a and other similar equilibrium constants:

$$\text{p}K_a = -\log_{10} K_a \quad (\text{or, more strictly, } \text{p}K_a = -\log_{10}(K_a/\text{mol dm}^{-3}))$$

For ethanoic acid, $K_a = 1.7 \times 10^{-5} \text{ mol dm}^{-3}$ and $\text{p}K_a = 4.76$. Sometimes 'pOH' is used to represent $-\log_{10}[\text{OH}^-]$. Notice that $\text{pH} + \text{pOH} = 14$.

Worked example

Calculate the pH of each of the following solutions.

- a a $0.050 \text{ mol dm}^{-3}$ solution of hydriodic acid, HI (a strong acid)
- b a 0.30 mol dm^{-3} solution of hydrofluoric acid, HF ($K_a = 5.6 \times 10^{-4} \text{ mol dm}^{-3}$)
- c a 0.40 mol dm^{-3} solution of sodium hydroxide

Answer

- a Because HI is a strong acid,
 $[\text{HI}] = [\text{H}^+] = 0.050 \text{ mol dm}^{-3}$
 $\log_{10}[\text{H}^+] = -1.3$ and $\text{pH} = \mathbf{1.3}$
- b $[\text{H}^+] = \sqrt{(K_a \times c)} = \sqrt{(5.6 \times 10^{-4} \times 0.30)} = 1.30 \times 10^{-2} \text{ mol dm}^{-3}$
 $\log_{10}[\text{H}^+] = -1.9$ and $\text{pH} = \mathbf{1.9}$
- c Because $[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$,

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{0.4} = 2.5 \times 10^{-14} \text{ mol dm}^{-3}$$

 $\log_{10}[\text{H}^+] = -13.6$ and $\text{pH} = \mathbf{13.6}$

Now try this

Calculate the pH of each of the following solutions.

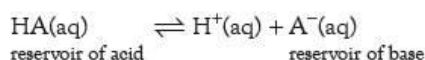
- 1 0.5 mol dm^{-3} HCl
- 2 2.5 mol dm^{-3} KOH(aq)
- 3 0.5 mol dm^{-3} benzoic acid (Use the K_a value from Table 22.1.)

22.3 Buffer solutions

What is a buffer?

Many experiments, particularly in biochemistry, need to be carried out in solutions of constant pH. Although it is impossible to make a solution whose pH is totally unaffected by the addition of small quantities of acid or alkali, it is possible to make a solution, called a **buffer solution**, whose pH remains *almost* unchanged. A moderately concentrated solution of a strong acid or alkali behaves in this way, and can be used to provide solutions of nearly constant pH in the 0–2 or 12–14 ranges. Dilute solutions of strong acids and bases are useless as buffers between pH 2 and pH 12, because the addition of small quantities of acid or alkali changes their pH considerably. This intermediate range of pH is very useful, particularly for biochemical experiments, and so other means of making buffer solutions in this range have been devised.

A weak acid, by itself, acts as a poor buffer solution because its pH drops sharply when a small quantity of acid is added. A mixture of a weak acid and one of its salts, however, behaves as a good buffer solution. In such a mixture, there is a high concentration of $A^-(aq)$ from the salt, as well as the undissociated acid. So the equilibrium:



is well over to the left, which increases the pH of the solution. When a small amount of strong acid is added, most of the extra $H^+(aq)$ ions react with the reservoir of $A^-(aq)$, and so the equilibrium moves to the left to remove the added H^+ . This tends to minimise the decrease in pH. When a small amount of strong base is added, most of the extra $OH^-(aq)$ ions react with the reservoir of $HA(aq)$, and this tends to minimise the increase in pH.

Worked example

Write equations to show how the buffer solution described above removes:

a added H^+ ions **b** added OH^- ions.

Answer

a $A^-(aq) + H^+(aq) \rightarrow HA(aq)$ **b** $HA(aq) + OH^-(aq) \rightarrow A^-(aq) + H_2O(l)$

Finding the pH of a buffer solution

To calculate the pH of a buffer solution of known composition, we start with the equation:

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

Because the presence of excess $A^-(aq)$ suppresses the ionisation of HA , the equilibrium concentrations of $A^-(aq)$ and $HA(aq)$, $[A^-(aq)]_{eq}$ and $[HA(aq)]_{eq}$, are almost identical to their initial concentrations, $[A^-(aq)]_{in}$ and $[HA(aq)]_{in}$, which were added to make the buffer solution. Therefore:

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

and

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

This is the equation used for buffer solution calculations: notice that the equation $[H^+] = \sqrt{K_a \times c}$ *must not* be used in this case, because $[H^+] \neq [A^-]$.

A **buffer solution** is one whose pH remains nearly constant on the addition of small quantities of acid or base. For a buffer solution:

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

For a buffer solution, note that:

$$[H^+(aq)] \neq \sqrt{K_a \times c}$$

Worked example

Calculate the pH of a solution made by mixing 100 cm^3 of 0.10 mol dm^{-3} ethanoic acid ($K_a = 1.76 \times 10^{-5}\text{ mol dm}^{-3}$) with 100 cm^3 of 0.20 mol dm^{-3} sodium ethanoate.

Answer

After mixing, the volume is 200 cm^3 and so the solution contains 0.050 mol dm^{-3} ethanoic acid and 0.10 mol dm^{-3} sodium ethanoate.

$$[\text{H}^+(\text{aq})] = \frac{K_a[\text{HA}(\text{aq})]_{\text{in}}}{[\text{A}^-(\text{aq})]_{\text{in}}} = \frac{1.76 \times 10^{-5} \times 0.050}{0.10} = 8.5 \times 10^{-6}\text{ mol dm}^{-3}$$

$$\text{pH} = 5.1$$

Now try this

- 1 Calculate the pH of the buffer solution formed by adding 0.003 mol of NaOH to 100 cm^3 of 0.1 mol dm^{-3} methanoic acid ($K_a = 1.6 \times 10^{-4}\text{ mol dm}^{-3}$).
- 2 A buffer solution is made by mixing 100 cm^3 of 0.20 mol dm^{-3} Na_2HPO_4 with 500 cm^3 of 0.30 mol dm^{-3} NaH_2PO_4 . For the equilibrium:

$$\text{H}_2\text{PO}_4^-(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$$
 $K_a = 6.3 \times 10^{-7}\text{ mol dm}^{-3}$. Calculate the pH of the solution.
- 3 (Harder) Calculate the change in pH when 0.050 cm^3 of 1.00 mol dm^{-3} hydrochloric acid is added to:
 - a 100 cm^3 of a solution of $0.00010\text{ mol dm}^{-3}$ hydrochloric acid
 - b 100 cm^3 of a solution that contains 0.10 mol dm^{-3} ethanoic acid and 0.10 mol dm^{-3} sodium ethanoate.
 K_a for ethanoic acid is $1.7 \times 10^{-5}\text{ mol dm}^{-3}$.
 (Hint: assume that all the hydrochloric acid reacts with ethanoate ions.)

Using buffer solutions

There are many situations where it is essential to control the pH. In the following examples, just the addition of an acid or an alkali is sufficient to keep the pH in the required range without buffering.

- In swimming pools, sterilisation is usually carried out using chlorine. This makes the water acidic (see section 11.4). Solid calcium hydroxide is added to bring the pH to just above 7.
- Acidic soils are treated with calcium carbonate or calcium hydroxide.
- For acid-loving plants, ammonium sulfate may be added to the soil. This acts as a weak acid and can bring the pH of the soil to pH 4, which is suitable for many azaleas and rhododendrons.

In other cases, more accurate control of pH is essential. In the human body, the production of carbon dioxide by respiration lowers the pH of the blood from about pH 7.5 to pH 7.3. The pH of blood does not fall below this value because blood acts as an efficient buffer. There are several ways in which this buffering is accomplished, of which the following are the most important.

- Proteins are made up of amino acids (see Topic 27). These contain both acidic and basic groups and can therefore act as buffers, removing H_3O^+ or OH^- :

$$\text{R}-\text{NH}_2 + \text{H}^+ \rightarrow \text{R}-\text{NH}_3^+$$

$$\text{R}-\text{CO}_2\text{H} + \text{OH}^- \rightarrow \text{R}-\text{CO}_2^- + \text{H}_2\text{O}$$
- The acid H_2CO_3 , derived from dissolved carbon dioxide, is buffered by the presence of the hydrogencarbonate ion, HCO_3^- .

Many other processes, including the use of shampoos and other hair treatments, developing photographs, medical injections and fermentation, all require strict pH control. This is achieved by the use of an appropriate buffer solution.

Now try this

Write equations to show how the $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ buffer system reacts with:

- a added H^+ ions
- b added OH^- ions.

22.4 Titration curves and indicators

Titration curves for different acids and alkalis

During a titration, acid is usually put into the burette and run into alkali in the presence of an indicator. This indicator suddenly changes colour at the **end-point**, which is the point at which the number of moles of acid is exactly balanced by the same amount of alkali. As we shall see, this does not always mean that the solution at this point has a pH of 7.

Figure 22.1 In this experimental set-up to record titration curves, the reaction mixture is stirred magnetically and the change in pH is recorded on the meter.



Figure 22.2 The graphs show the pH changes as 1.0 mol dm^{-3} acid is run into 100 cm^3 of 0.10 mol dm^{-3} alkali. The end-point comes after 10 cm^3 of acid have been added. The purpose of making the acid ten times as concentrated as the alkali is to ensure there is very little pH change due to dilution.

Either the acid or the alkali, or both, may be strong or weak, so that there are four possible combinations. If an acid is run into an alkali, the pH changes as shown in Figure 22.2.

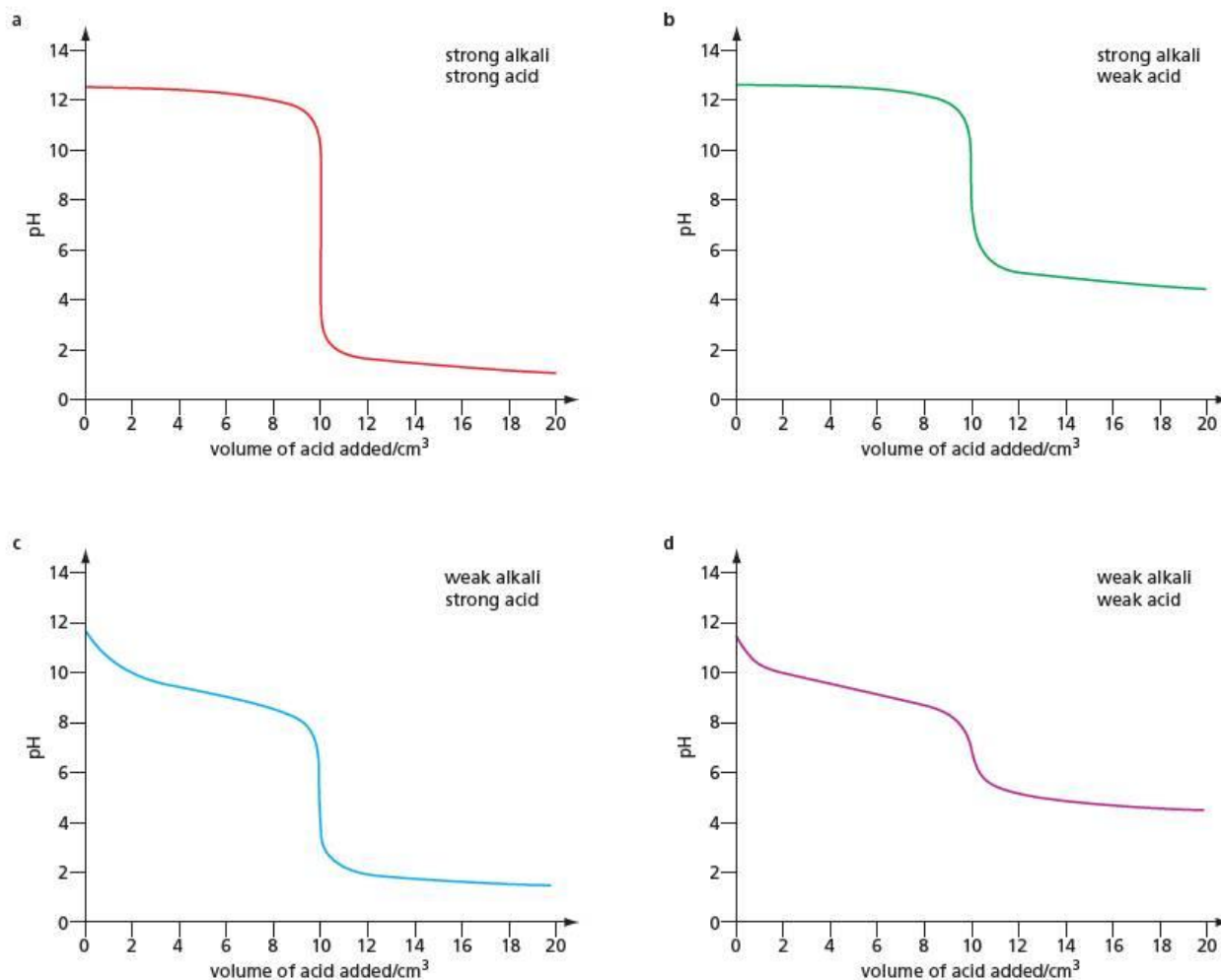


Table 22.2 The suitability of methyl orange and phenolphthalein as indicators for titrations between strong and weak acids and alkalis

Alkali	Add	Indicator
strong	strong	methyl orange or phenolphthalein
strong	weak	phenolphthalein
weak	strong	methyl orange
weak	weak	neither

With a strong alkali, such as sodium hydroxide, the pH starts at 13 and then decreases slowly until 10 cm^3 of acid have been added. At this point, the **equivalence point**, there is a sharp drop in pH – to about pH3 with a strong acid or to about pH5 with a weak acid.

With a weak alkali, such as ammonia, the pH starts at about 11 and falls with an S-shaped curve to about pH7 until 10 cm^3 of acid have been added. At this point there is a drop – sharply with a strong acid to about pH2 and slowly with a weak acid to about pH5.

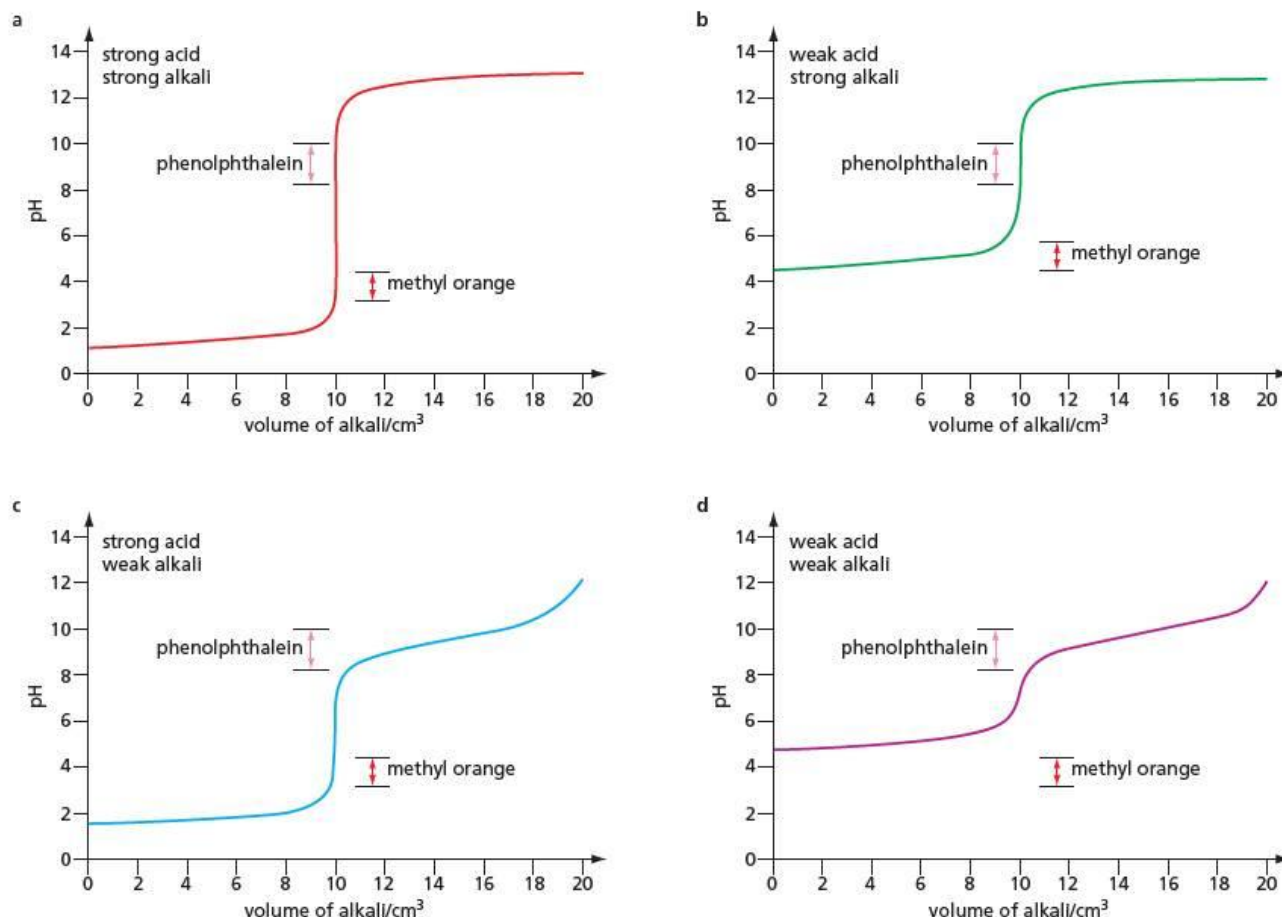
To find the equivalence point accurately, an indicator must be chosen which changes colour when the curve is steepest. The colour will then change when only one further drop of acid is added. Two common indicators are methyl orange and phenolphthalein. Methyl orange changes colour over the pH range 3.2 to 4.4 and phenolphthalein over the pH range 8.2 to 10.0. The titration curves show us that methyl orange is suitable for titrations between a strong or weak alkali and a strong acid, and phenolphthalein is suitable for titrations between a strong alkali and a strong or weak acid. Neither indicator gives a clear end-point with a distinct colour change in a titration between a weak alkali and a weak acid. This is summarised in Table 22.2.

Figure 22.3 shows the titration curves when alkali is added to acid, rather than the other way around. The pH ranges over which methyl orange and phenolphthalein change colour are also shown.

The steep portions of Figures 22.2 and Figure 22.3 are the parts where the pH changes most rapidly with added alkali or acid. It is at these points that an indicator will change colour most rapidly. The pH range over which an indicator changes colour is usually about 2 pH units, so it is important to choose an indicator whose colour-change range is covered by the steep portion of the titration curve.

Conversely, the flat portions of the graphs show where the pH changes most slowly on addition of acid or alkali. These flat portions are, therefore, where the best buffering action occurs.

Figure 22.3 Titration curves starting with 100 cm^3 of 0.10 mol dm^{-3} acid and adding 1.0 mol dm^{-3} alkali. The curves are a reflection of those in Figure 22.2. The ranges of the indicators are shown beside the steep portions of the curves.



Worked example

Some 0.10 mol dm^{-3} sodium hydroxide is added to 25.0 cm^3 of 0.10 mol dm^{-3} hydrochloric acid. Calculate the pH of the resulting solution after the addition of:

- a** 24.9 cm^3 of alkali **b** 50.0 cm^3 of alkali.

Answer

$$\text{a Amount of HCl remaining} = c = \frac{v}{1000} = 0.10 \times \frac{(25.0 - 24.9)}{1000} = 1.0 \times 10^{-5} \text{ mol}$$

$$\text{Volume of solution} = 25.0 + 24.9 = 49.9 \text{ cm}^3$$

$$[\text{H}^+] = \frac{n}{v} = \frac{1.0 \times 10^{-5}}{49.9 \times 10^{-3}} = 2.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ and pH} = 3.7$$

- b** The acid has now all reacted, so we need to calculate the pH from the concentration of hydroxide ions in the solution.

$$\text{Amount of NaOH remaining} = c \times \frac{v}{1000} = 0.10 \times \frac{(50.0 - 25.0)}{1000} = 2.5 \times 10^{-3} \text{ mol}$$

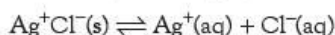
$$\text{Volume of solution} = 25.0 + 50.0 = 75.0 \text{ cm}^3$$

$$[\text{OH}^-] = \frac{n}{v} = \frac{2.5 \times 10^{-3}}{75.0 \times 10^{-3}} = 0.033 \text{ mol dm}^{-3}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{0.033} = 3.0 \times 10^{-13} \text{ mol dm}^{-3} \text{ and pH} = 12.5$$

22.5 Solubility of salts

An important example of heterogeneous equilibrium is dissolving an ionic substance in water. Take, for example, solid silver chloride in contact with a saturated solution:



We can write:

$$K_c = \frac{[\text{Ag}^+(\text{aq})][\text{Cl}^-(\text{aq})]}{[\text{Ag}^+\text{Cl}^-(\text{s})]}$$

At a given temperature, the $[\text{Ag}^+\text{Cl}^-(\text{s})]$ term is a constant, irrespective of the amount of silver chloride present. We can absorb this $[\text{Ag}^+\text{Cl}^-(\text{s})]$ term into the equilibrium constant and define a new equilibrium constant:

$$K_{sp} = [\text{Ag}^+(\text{aq})][\text{Cl}^-(\text{aq})]$$

where K_{sp} is called the **solubility product**. For $\text{AgCl}(\text{s})$, the value of K_{sp} is $1 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$. In a saturated solution of silver chloride in water, $[\text{Ag}^+(\text{aq})] = [\text{Cl}^-(\text{aq})]$; since their product is $1 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$, each of them must equal $\sqrt{(1 \times 10^{-10})} = 1 \times 10^{-5} \text{ mol dm}^{-3}$.

Worked example

Calculate the solubility of SrSO_4 , for which $K_{sp} = 5.0 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$.

Answer

$$K_{sp} = [\text{Sr}^{2+}][\text{SO}_4^{2-}] = 5.0 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$$

So in a saturated solution

$$\begin{aligned} [\text{Sr}^{2+}] &= [\text{SO}_4^{2-}] = \sqrt{(5.0 \times 10^{-7})} \\ &= 7.1 \times 10^{-4} \text{ mol dm}^{-3} \end{aligned}$$

One mole of SrSO_4 dissolves to give one mole of Sr^{2+} ions, so the solubility of SrSO_4 is **$7.1 \times 10^{-4} \text{ mol dm}^{-3}$** .

The situation is more complex if the salt has ions with different charges, for example calcium hydroxide. The solubility of $\text{Ca}(\text{OH})_2$ is $1.5 \times 10^{-2} \text{ mol dm}^{-3}$. But here one mole of $\text{Ca}(\text{OH})_2$ dissolves to give one mole of Ca^{2+} ions and two moles of OH^- ions.

Let $[\text{Ca}(\text{OH})_2]$ in the saturated solution be x . Then $[\text{Ca}^{2+}] = x$ and $[\text{OH}^-] = 2x$. The solubility product is given by:

$$\begin{aligned} K_{\text{sp}} &= [\text{Ca}^{2+}][\text{OH}^-]^2 \\ &= x \times (2x)^2 \\ &= 4x^3 \\ &= 4 \times (1.5 \times 10^{-2})^3 = 1.35 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9} \end{aligned}$$

The connection between solubility and solubility product is summarised in Table 22.3.

Table 22.3 The relationship between the solubility ($x \text{ mol dm}^{-3}$) and solubility product for salts with different ionic types

Charge on cation	Charge on anion	Example	Expression for K_{sp}
1	1	AgBr	$x^2 \text{ mol}^2 \text{ dm}^{-6}$
2	2	MgCO_3	$x^2 \text{ mol}^2 \text{ dm}^{-6}$
1	2	Ag_2CrO_4	$4x^3 \text{ mol}^3 \text{ dm}^{-9}$
2	1	PbI_2	$4x^3 \text{ mol}^3 \text{ dm}^{-9}$
3	1	$\text{Fe}(\text{OH})_3$	$27x^4 \text{ mol}^4 \text{ dm}^{-12}$

Now try this

- 1 The solubility of nickel hydroxide is $1.0 \times 10^{-4} \text{ mol dm}^{-3}$. What is its solubility product?
- 2 The solubility product of silver sulfate is $1.6 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$. What is its solubility?

These connections between solubility and solubility product can only be used if no other ions have been added which would disturb the equilibrium. If, for example, we have a saturated solution of silver chloride, its solubility will be decreased if we increase either the $[\text{Ag}^+(\text{aq})]$ or the $[\text{Cl}^-(\text{aq})]$ term, for example, by adding silver nitrate or sodium chloride. This would cause silver chloride to precipitate out of the solution, by what is known as the **common ion effect**.

Now try this

Aqueous sodium hydroxide is added to aqueous calcium chloride to precipitate calcium hydroxide. The final concentration of hydroxide ions is 0.50 mol dm^{-3} . What is the solubility of the calcium hydroxide remaining in solution? $[K_{\text{sp}} \text{ Ca}(\text{OH})_2 = 1.4 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}]$

Worked example

If sodium chloride is added to a saturated solution of silver chloride, so that $[\text{Cl}^-(\text{aq})] = 0.10 \text{ mol dm}^{-3}$, what is the maximum value for $[\text{Ag}^+(\text{aq})]$ in the solution? $[K_{\text{sp}}(\text{AgCl}) = 1.0 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}]$

Answer

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] \text{ so } [\text{Ag}^+] = \frac{K_{\text{sp}}}{[\text{Cl}^-]} = \frac{1.0 \times 10^{-10}}{0.10} = 1.0 \times 10^{-9} \text{ mol dm}^{-3}$$

22.6 The partition coefficient

A special case of equilibrium is how a solute divides between two immiscible liquid phases. If we take a solute such as iodine, which is soluble in a variety of solvents, it is not surprising to find that it is not equally soluble in all the solvents. Taking the two immiscible solvents water and hexane, we find that iodine is much more soluble in hexane than it is in water. Methanol, on the other hand, is much more soluble in water than it is in hexane.

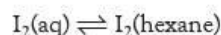
Now try this

Considering the various intermolecular forces that might operate, explain why iodine is more soluble in hexane than it is in water, whereas methanol is more soluble in water.

Figure 22.4 Iodine partitioned between water and hexane



When some iodine crystals are shaken with a mixture of hexane and water until no further change takes place, and the two layers allowed to separate (see Figure 22.4), we find that the ratio of the concentrations of iodine in each layer is a constant. This is true if we use only a small amount of iodine, or a much larger amount. This constant is the equilibrium constant for the change:



$$K = \frac{[\text{I}_2(\text{hexane})]}{[\text{I}_2(\text{aq})]}$$

K is the **partition coefficient** of iodine between hexane and water. An alternative phrase is **distribution coefficient**. Like all equilibrium constants, the value of a partition coefficient changes with temperature.

It is important always to write an equation alongside a value of a partition coefficient. Following the usual equilibrium constant expression:

$$K = \frac{[\text{products}]}{[\text{reactants}]}$$

we need to know which solution is the 'product' and which is the 'reactant'. There is no universally accepted convention, but usually the organic solution is the 'product' on the right-hand side.

The equilibrium is a dynamic one: iodine molecules are constantly crossing the interface between the two solvents. Equilibrium is established when the rates of these two processes are equal:

$$\text{rate of leaving aqueous layer} = k_1[\text{I}_2(\text{aq})]$$

$$\text{rate of leaving hexane} = k_2[\text{I}_2(\text{hexane})]$$

(k_1 and k_2 are rate constants).

At equilibrium,

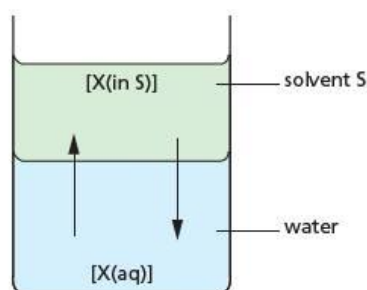
$$k_1[\text{I}_2(\text{aq})] = k_2[\text{I}_2(\text{hexane})]$$

$$\frac{[\text{I}_2(\text{hexane})]}{[\text{I}_2(\text{aq})]} = \frac{k_1}{k_2} = K$$

Notice that partition coefficients do not usually have units.

The technique of **solvent extraction** depends on partition. This is used when an organic compound is extracted from an aqueous solution by an organic solvent, which is immiscible with water. Examples would be if the aqueous solution contained a perfume component or a pharmaceutical extracted from a plant, or contained the

Figure 22.5 At equilibrium, the rates at which I_2 leaves each layer are equal.

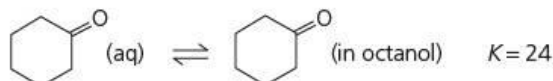


product formed during a synthetic reaction carried out in a laboratory. If we know the value of the partition coefficient for the compound, we can calculate how much would be extracted into the organic layer.

Industrially, octan-1-ol is often used as the organic solvent.

Worked example

The partition coefficient for the distribution of cyclohexanone between water and octanol is 24.



Calculate the mass of cyclohexanone that would be extracted if 20 cm³ of octanol was shaken with 100 cm³ of an aqueous solution containing 2.5 g of cyclohexanone.

Answer

Let [X] be the concentration of cyclohexanone expressed in g cm⁻³; let the mass of cyclohexanone extracted be x g; the mass remaining in the aqueous layer will therefore be $(2.5 - x)$ g

$$K = \frac{[X(\text{octanol})]}{[X(\text{aq})]}$$

$$[X(\text{octanol})] = [X(\text{aq})] \times K$$

$$\frac{x}{20} = \left(\frac{2.5 - x}{100} \right) \times 24$$

$$5x = (2.5 - x) \times 24$$

$$5x = 60 - 24x$$

$$x = 2.07 \text{ g}$$

This process has extracted about 83% of the 2.5 g of cyclohexanone that was in the water.

If we wanted to extract more cyclohexanone, we could repeat the process. But this would require another 20 cm³ of octanol. However, if we were to split the original 20 cm³ of octanol into two 10 cm³ portions, and use these for successive extractions, our yield of extracted material would increase. The following calculations will make this clear.

- 1 Let the mass of cyclohexanone extracted by the first 10 cm³ portion of octanol be y g. The mass remaining in the water will therefore be $(2.5 - y)$ g

$$\frac{y}{10} = \left(\frac{2.5 - y}{100} \right) \times 24$$

$$10y = (2.5 - y) \times 24$$

$$10y = 60 - 24y$$

$$y = 1.765 \text{ g}$$

This first extraction results in $2.5 - 1.765 = 0.735$ g of cyclohexanone remaining in the aqueous layer.

- 2 We can now calculate how much of this remaining cyclohexanone can be extracted by using the second 10 cm³ portion of octanol.

Let the mass of cyclohexanone extracted by the second 10 cm³ portion of octanol be z g. The mass remaining in the water will be $(0.735 - z)$ g.

$$\frac{z}{10} = \left(\frac{0.735 - z}{100} \right) \times 24$$

$$10z = 17.64 - 24z$$

$$z = 0.519 \text{ g}$$

The total mass of cyclohexanone extracted is $y + z = 1.765 + 0.519 = 2.28 \text{ g}$

The use of two successive extractions has now raised the percentage extracted from

$$83\% \text{ to } 100 \times \left(\frac{2.28}{2.5} \right) = 91\%$$

If a higher degree of extraction is required (when dealing with expensive perfumery components, for example), the process can be automated into a continuous extraction apparatus.

Now try this

When 100 cm³ of an aqueous solution containing 4.0 g of ketone **Y** was shaken with 25 cm³ of hexane, 3.0 g of **Y** was extracted into the hexane.

- Calculate the partition coefficient of **Y** between hexane and water.
- What volume of hexane would be needed to extract 90% of **Y** from the 100 cm³ of its aqueous solution, using only one extraction?

Summary

- In dilute aqueous solution, [H₂O] is a constant, 55.5 mol dm⁻³.
- For a weak acid, HA, its degree of ionisation may be calculated using the formula:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

- In aqueous solution, the product [H⁺][OH⁻] is a constant, the **ionic product of water**, K_w , whose value is $1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at room temperature.
- $\text{pH} = -\log_{10} [\text{H}^+]$
- For a strong acid or base, [H⁺] or [OH⁻] = c , where c is the concentration of the acid or base.
- For a weak acid, $[\text{H}^+] \approx \sqrt{K_a \times c}$
- A **buffer solution** is one that resists changes in pH on the addition of small quantities of acids or bases.
- A buffer solution is usually a mixture of a weak acid and the salt of that weak acid. The pH of the buffer solution can be found using the formula:

$$[\text{H}^+] = \frac{K_a [\text{acid}]_{\text{initial}}}{[\text{salt}]_{\text{initial}}}$$

- When an acid is titrated with base, there is a rapid change in pH at the equivalence point. An appropriate **indicator** can be used to find this equivalence point.
- When a solid salt M⁺X⁻ is in equilibrium with its saturated solution, the product [M⁺][X⁻] is a constant, the **solubility product**, K_{sp} .
- When an acid is titrated with base, there is a rapid change in pH at the equivalence point. An appropriate **indicator** can be used to find this equivalence point.
- If either excess M⁺ ions or X⁻ ions are added, the solubility of the salt decreases; this is called the **common ion effect**.
- When a substance X dissolves in two immiscible liquids A and B, the ratio:

$$\frac{\text{solubility of X in solvent A}}{\text{solubility of X in solvent B}}$$

is a constant; this constant is called the **partition coefficient**.

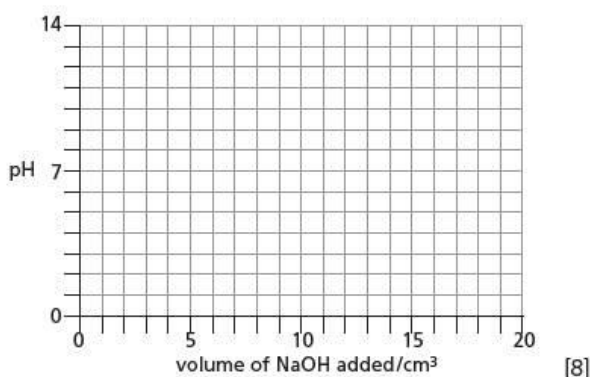
Examination practice questions

Please see the data section of the CD for any A_r values you may need.

1 a The K_a values for some organic acids are listed below.

Add	$K_a/\text{mol dm}^{-3}$
$\text{CH}_3\text{CO}_2\text{H}$	1.7×10^{-5}
$\text{ClCH}_2\text{CO}_2\text{H}$	1.3×10^{-3}
$\text{Cl}_2\text{CHCO}_2\text{H}$	5.0×10^{-2}

- Explain the trend in K_a values in terms of the structures of these acids.
- Calculate the pH of a 0.10 mol dm^{-3} solution of $\text{ClCH}_2\text{CO}_2\text{H}$.
- Use a copy of the following axes to sketch the titration curve you would obtain when 20 cm^3 of 0.10 mol dm^{-3} NaOH is added gradually to 10 cm^3 of 0.10 mol dm^{-3} $\text{ClCH}_2\text{CO}_2\text{H}$.



- Write suitable equations to show how a mixture of ethanoic acid, $\text{CH}_3\text{CO}_2\text{H}$, and sodium ethanoate acts as a buffer solution to control the pH when either an acid or an alkali is added.
 - Calculate the pH of a buffer solution containing 0.10 mol dm^{-3} ethanoic acid and 0.20 mol dm^{-3} sodium ethanoate. [4]

[Cambridge International AS & A Level Chemistry 9701, Paper 4 Q1 b & c June 2009]

- With the aid of a fully-labelled diagram, describe the standard hydrogen electrode.
 - Use the *Data Booklet* on the CD to calculate the standard cell potential for the reaction between Cr^{2+} ions and $\text{Cr}_2\text{O}_7^{2-}$ ions in acid solution, and construct a balanced equation for the reaction.
 - Describe what you would see if a blue solution of Cr^{2+} ions was added to an acidified solution of $\text{Cr}_2\text{O}_7^{2-}$ ions until reaction was complete.

- A buffer solution is to be made using 1.00 mol dm^{-3} ethanoic acid, $\text{CH}_3\text{CO}_2\text{H}$, and 1.00 mol dm^{-3} sodium ethanoate, $\text{CH}_3\text{CO}_2\text{Na}$.

Calculate to the nearest 1 cm^3 the volumes of each solution that would be required to make 100 cm^3 of a buffer solution with pH 5.50. Clearly show all steps in your working.

$$K_a(\text{CH}_3\text{CO}_2\text{H}) = 1.79 \times 10^{-5} \text{ mol dm}^{-3} \quad [4]$$

- Write an equation to show the reaction of this buffer solution with each of the following.
 - added HCl
 - added NaOH
 - Choose **one** reaction in organic chemistry that is catalysed by an acid, and write the structural formulae of the reactants and products. [3]

[Cambridge International AS & A Level Chemistry 9701, Paper 42 Q2 June 2013]