

## Equilibrium

### Introduction

Many chemical reactions go to completion. This means that the reactants ultimately form 100% products.

Many reactions, however, never go to completion but are in a state of equilibrium, with reactants and products always present.

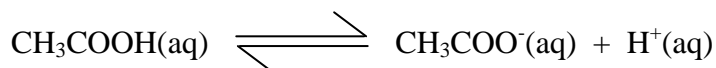
A chemical reaction is said to be in equilibrium when the composition of the reactants and products remains constant over time. i.e. at equilibrium the **concentration** of the reactants and products remains constant.

For an equilibrium to be established the reaction must take place in a **closed system**.

A closed system is one that allows energy to be transferred to or from the surroundings but not the reactants or products. Reactants and products are trapped in the reaction vessel and reactant molecules form the products and product molecules react to reform the starting materials.

The concept of a closed system can be illustrated using the following examples:

- 1) Ethanoic acid in solution. Ethanoic acid is a weak acid and shows little tendency to dissociate

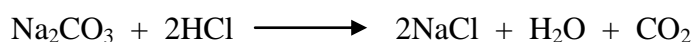


None of the three species in the equation leave the container. This system is closed.

Eventually, a point will be reached where the forward and reverse reaction rates are equal.

At this point, the concentration of all three species are constant.

- 2) Sodium carbonate reacting with dilute acid



The carbon dioxide gas formed leaves the system. The system is not closed. The constant removal of a product means that equilibrium can never be reached and the reaction goes to completion.

When a system is in equilibrium and the concentration of reactants and products is constant, the forward reaction (reactants to products) and the reverse reaction (products to reactants) do not stop. At equilibrium the rate of the forward reaction is equal to the rate of the reverse reaction. This means that there is no overall change in the composition of the reaction mixture when equilibrium has been established.

### Introducing another chemical expression

The study of equilibrium and chemical kinetics later on involves a lot of equations involving concentration. The way that chemists express this is to put the name, or more likely the formula, of the substance inside **square brackets**. e.g. 1 mol l<sup>-1</sup> hydrochloric acid would be written as

$$[\text{HCl}] = 1 \text{ mol l}^{-1}$$

a 0.05 mol l<sup>-1</sup> solution of iron (II) ions would be written as

$$[\text{Fe}^{2+}] = 0.05 \text{ mol l}^{-1}$$

### The equilibrium constant

In Higher Grade, you learned that if a change is imposed on a system at equilibrium, the system would adjust itself in order to oppose the change.

If the concentration of a reactant were increased, more product would be formed (to remove the extra reactant added).

In Advanced Higher, we now introduce the theory that when a system is at equilibrium, the concentrations of all species involved in the equilibrium will, when put into an equation, will produce a constant value. This value is called the **equilibrium constant** and has the symbol **K**.

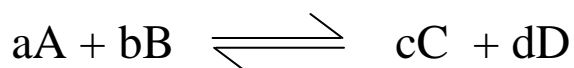
It also means that,

when a system is at equilibrium and the concentration of a reactant or product is changed, **the system will adjust itself not to oppose the change, but to re-establish the value of K.**

The equation

For the reaction of a molecules of A reacting reversibly with b molecules of B to produce c molecules of C and d molecules of D

i.e.



the equilibrium constant is calculated by

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

i.e. the number of molecules of each becomes a power. [ ] of each species is given in mol l<sup>-1</sup>.

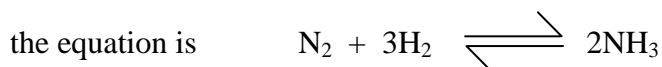
In any equilibrium constant equation, the products are always on the top and divided by the reactants.

Worked example.

The Haber produces ammonia from nitrogen and hydrogen. The reaction is reversible.

A 1 litre sample removed from the catalyst chamber was found to contain 0.8 mol hydrogen, 0.2 mol nitrogen and 0.03 mol ammonia.

Calculate K



the equation for calculation the equilibrium constant therefore becomes

$$K = \frac{[NH_3]^2}{[N_2]^1 [H_2]^3} = \frac{[0.03]^2}{[0.2]^1 [0.8]^3} = \frac{9 \times 10^{-4}}{0.2 \times 0.512} = 8.789 \times 10^{-3}$$

The effect of temperature on K

Again from Higher Grade, if a system at equilibrium is heated, the reaction will move in the endothermic direction to absorb the heat added.

The Advanced Higher explanation is that temperature has an effect on K.

Changing the temperature alters the value of K and the concentrations of reactants and products adjust themselves to produce this new value when put into the equation.

**For an endothermic reaction, increasing temperature causes an increase in product formed, therefore K will increase (larger number on the top line, smaller number on the bottom line).**

**And applying the same mathematical principle will produce the fact that for an exothermic reaction, an increase in temperature lowers the value of K.**

The effect of a catalyst on K

As you already know from Higher Grade, a catalyst has no effect on the position of equilibrium, therefore it has no effect on the value of K

Calculation of K from gas pressures

In a gas mixture at a given pressure, the total pressure is made up of the pressure produced by each gas i.e. each gas has a *partial pressure*. The easiest way to handle partial pressures is simply to say that partial pressure is directly related to concentration, and put these values into the equation.

*You have to be aware of this, but you will not be asked to calculate K from partial pressures, although you are likely to come across it at University. Partial pressures play an important part in systems involving gas mixtures. In medicine, arterial blood gases are measured by their partial pressure. PaO<sub>2</sub> and PaCO<sub>2</sub> are important measurements as they give an indication of how well the lungs get oxygen into the blood and how well they remove carbon dioxide.*

K and the position of equilibrium

Whether K is calculated from concentrations or partial pressures its value gives an indication of how far the equilibrium lies to one side of a reaction or the other.

It is important to note that the value of K gives no indication about the rate at which the state of dynamic equilibrium is established.

The following table gives an illustration of K and equilibrium position

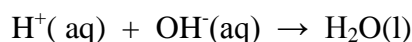
System	Value of K	Position of equilibrium
$\text{Ag}^+(\text{aq}) + 2\text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+(\text{aq})$	$1.7 \times 10^7$ at 25°C	Because $K \gg 1$ , equilibrium lies to the right
$\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$	$1.8 \times 10^{-5}$ at 25°C	Because $K \ll 1$ , equilibrium lies to the left
$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$	0.87 at 55°C	Because $K \approx 1$ , equilibrium lies close to the middle

The words strong and weak have a quite different meaning from concentrated and dilute.

## Equilibria involving ions

### Acid/base equilibria

Historically acids were defined as producing hydrogen ions in solution and bases as producing hydroxide ions in solution. These two ions combine in the neutralisation equation:



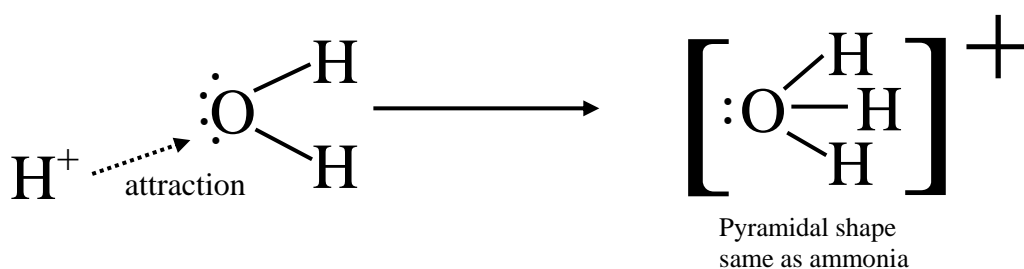
As research continued throughout the nineteenth and early twentieth centuries, the definitions had to be refined.

For example, pure hydrogen chloride is a gas that contains no  $\text{H}^+$  ions and ammonia has no  $\text{OH}^-$  ions but can neutralise an acid.

It was also discovered that the  $\text{H}^+$  ion could not exist in aqueous solution.

*The  $\text{H}^+$  ion is nothing more than a proton. It is therefore much smaller than any other positive ion. This very small size makes it more strongly attracted to anything negative (the 1+ charge is more "concentrated" in a smaller space) than any other positive ion (cation – cathode seeking ion).*

It is very strongly attracted to the lone pairs of electrons on water molecules. Water forms a dative bond with one of its lone pairs of electrons to form  $\text{H}_3\text{O}^+$ , which is called the hydronium ion (or the oxonium ion or the hydroxonium ion):



The shorthand  $\text{H}^+(\text{aq})$  is always used in stoichiometric and equilibrium equations, although this is not strictly accurate.

In 1925 the new discoveries led two chemists, Brønsted and Lowry, to define acids and bases in a different way:

**An acid is any substance capable of donating a proton.**

**A base is any substance capable of accepting a proton.**

When an acid donates a proton the species left (the negative ion) is itself capable of accepting a proton back (given the right conditions) and is called the **conjugate base** of that acid.

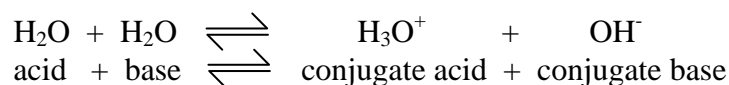
When a base accepts a proton the species formed is capable of donating a proton back (given the right conditions) and is called the **conjugate acid** of that base. This is shown in the table.

acid	+	base	$\rightleftharpoons$	conjugate base	+	conjugate acid
HCl	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{Cl}^-$	+	$\text{H}_3\text{O}^+$
$\text{CH}_3\text{COOH}$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{CH}_3\text{COO}^-$	+	$\text{H}_3\text{O}^+$
$\text{H}_2\text{O}$	+	$\text{NH}_3$	$\rightleftharpoons$	$\text{OH}^-$	+	$\text{NH}_4^+$
$\text{H}_2\text{O}$	+	$\text{CH}_3\text{COO}^-$	$\rightleftharpoons$	$\text{OH}^-$	+	$\text{CH}_3\text{COOH}$

The table also illustrates the **amphoteric** nature of water since it can act both as a proton acceptor and a proton donor (specific learning outcome – water is amphoteric).

### The dissociation of water

In Brønsted-Lowry terms the ionisation of water is represented by:



The equilibrium constant is therefore expressed as

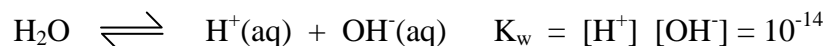
$$K = \frac{[\text{H}_3\text{O}^+] [\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

Since water is a liquid, and by definition liquids and insoluble solids always have [ ] = 1, the equation becomes:

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

This particular equilibrium is known as the **ionic product of water** and has the symbol **K<sub>w</sub>**. It has the value of **1.0 X 10<sup>-14</sup>** at 25°C

The water equilibrium is usually written as



In pure water, since one of each ion must be formed when it ionises, the [ ] of each ion must be the same.

### The mathematics

In pure water,  $[\text{H}^+] [\text{OH}^-] = 10^{-14}$

since both concentrations are equal, the equation can become  $[\text{H}^+]^2 = 10^{-14}$

taking square roots,  $[\text{H}^+] = 10^{-7}$

and  $[\text{OH}^-] = 10^{-7}$

What is important to understand is that in any solution (whether acidic, alkaline or neutral)  $[\text{H}^+] [\text{OH}^-]$  always =  $10^{-14}$  at 25°C, although this value varies with temperature as shown:

Temperature (°C)	K <sub>w</sub> (X 10 <sup>-14</sup> )
18	0.6
25	1.0
40	2.9
75	16.9

The dissociation of water is an endothermic process. Increasing temperature causes a move in the endothermic direction, and therefore the value of K increases.

It also means that true neutrality (pH 7) only occurs in pure water at 25°C.

## The pH scale

You learned in Higher Grade that pH is a measure of  $[H^+]$  in an aqueous solution, and that a change of 1 pH unit = a change in  $[H^+]$  by a factor of 10, a change of 2 units = a change by a factor of 100 and so on.

pH change was mathematically related to  $[H^+]$  by a “power”.

It was explained this way because your mathematical knowledge at that time may not have extended to an important mathematical function – logarithms (or logs to the base of 10), which you should now know.

To refresh your knowledge of this, the actual definition is:

*the log of a number is the power that 10 must be raised to get that number*  
to get 100, 10 must be raised to the power of 2, so the log of 100 is 2

In water,  $[H^+] = 10^{-7} \text{ mol l}^{-1}$

The log of  $10^{-7} = -7$

The negative of this is 7

Giving the definition of pH as

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

(or  $-\log_{10}[H_3O^+]$  to be absolutely accurate)

### Examples

1.0 mol l <sup>-1</sup> HCl	$[H^+] = 1.0 \text{ mol l}^{-1}$	$\log_{10} 1.0 = 0$	pH = 0
0.2 mol l <sup>-1</sup> HCl	$[H^+] = 0.2 \text{ mol l}^{-1}$	$\log_{10} 0.2 = -0.7$	pH = 0.7
0.01 mol l <sup>-1</sup> NaOH from $K_w$ ,	$[OH^-] = 0.01 \text{ mol l}^{-1} = 10^{-2} \text{ mol l}^{-1}$ $[H^+] = 10^{-12} \text{ mol l}^{-1}$	$\log_{10} 10^{-12} = -12$	pH = 12
0.5 mol l <sup>-1</sup> NaOH from $K_w$ ,	$[OH^-] = 0.5 \text{ mol l}^{-1}$ $[H^+] = 2 \times 10^{-14} \text{ mol l}^{-1}$	$\log_{10} (2 \times 10^{-14}) = -13.7$	pH = 13.7

For calculations involving strong acids and alkalis it can be assumed that they are 100% dissociated and that the small number of hydrogen ions supplied by the water are so insignificant that they can be ignored.

### Practice questions

Calculate the pH of the following solutions:

- 1) 0.35 mol l<sup>-1</sup> nitric acid
- 2) 0.14 mol l<sup>-1</sup> sulphuric acid
- 3) 0.78 mol l<sup>-1</sup> potassium hydroxide

## Strong and weak acids

A strong acid can be either concentrated or dilute depending on the number of moles of acid per litre of solution. The same applies to a weak acid.

**A strong acid is one in which almost all the molecules are dissociated (ionised) when dissolved in water.**

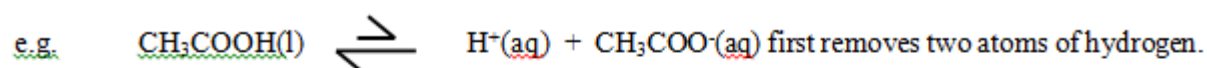


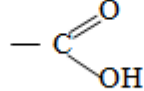
Almost all the HCl molecules break up into ions when dissolved in water.

*This happens because the polar water molecules are attracted strongly to the polar HCl molecules. The attraction is so strong that the HCl molecules are pulled apart and form ions.*

A solution of hydrogen chloride gas will exist almost entirely as hydrogen and chloride ions. There will be almost no hydrogen chloride molecules present. Other strong acids include sulphuric and nitric acids.

**A weak acid is one in which only some of the molecules are dissociated (ionised) when dissolved in water.**



The carboxyl group has the structure  and this is much more difficult for water molecules to break into ions

In practice, if ethanoic acid is added to water to make a concentration of  $1 \text{ mol l}^{-1}$ , less than 1% of the molecules are dissociated. The equilibrium lies very much to the left.

The mixture contains mostly undissociated molecules and very few ions.

As a rule, almost all organic acids are weak (citric, tartaric, malic, lactic etc.)

Carbonic acid ( $\text{CO}_2$  dissolved in water) and sulphurous acid ( $\text{SO}_2$  dissolved in water) are also weak.

*Natural rainwater is and always has been slightly acidic due to raindrops absorbing  $\text{CO}_2$  from the atmosphere as they fell, but the burning of fossil fuels also puts  $\text{SO}_2$ , nitrogen oxides and more  $\text{CO}_2$  into the air, so the acidity of rainwater has increased to the point where it is damaging to the environment in the form of acid rain. Steps are now being taken to reduce these emissions; catalytic converters in car exhausts, extra refining to remove the sulphur from petrol and diesel before it leaves the refinery, and FGD (flue gas desulphurisation) plant installed in coal-fired power stations to remove the  $\text{SO}_2$  from flue gases before discharge into the atmosphere.*

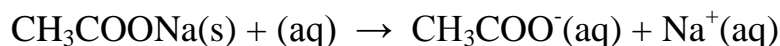




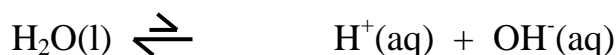
## Acidic, Basic and Neutral Salts

Salts derived from weak acids and strong bases produce **alkaline** solutions.

Consider sodium ethanoate. When it dissolves in water, it dissociates completely into **ethanoate ions** ( $\text{CH}_3\text{COO}^-$ ) and **sodium ions**.

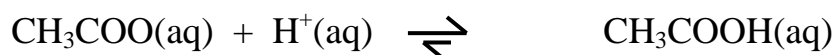


The aqueous solution will also contain a few **hydrogen** and **hydroxide** ions due to the slight **ionisation** of water molecules.



Ethanoate ions and hydrogen ions are found in **ethanoic acid** which is a weak acid and therefore exists mainly as **molecules** in aqueous solution.

The **ethanoate** ions therefore react with the hydrogen ions to establish the equilibrium:

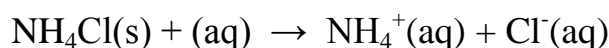


As the concentration of hydrogen ions in the water equilibrium decreases, due to the ethanoic acid equilibrium, the water equilibrium shifts to the **right**

As more hydroxide ions are produced, the pH **increases**.

Salts derived from strong acids and weak bases produce **acidic** solutions.

Consider ammonium chloride. When it dissolves in water, it dissociates completely into **ammonium ions** ( $\text{NH}_4^+$ ) and **chloride ions**.

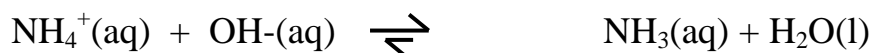


There is an **equilibrium** between hydrogen ions, hydroxide ions and **water** molecules.



**ammonium ions** and **hydroxide ions** are found in ammonia solution which is a **weak base** and therefore exists mainly as molecules in aqueous solution.

The ammonium ions therefore react with the **hydroxide** ions to establish the equilibrium:



As the concentration of hydroxide ions in the water equilibrium decreases due to the ammonia equilibrium, the water equilibrium shifts to the **right**.

As more hydrogen ions are produced, the pH **decreases**.

### Dealing with weak acids

A weak acid (such as ethanoic or most organic acids) is one in which only about 1 or 2% of the molecules are dissociated.

It is also convenient to represent an acid with the general formula **HA**

The equilibrium constant for a weak acid therefore becomes

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

For any acid, this value is called the **dissociation constant** and has the symbol **K<sub>a</sub>**

In the case of ethanoic acid, K<sub>a</sub> has the value 1.8 X 10<sup>-5</sup>.

There is a list of K<sub>a</sub> values in the Data Book

The lower the value of K<sub>a</sub>, the weaker the acid.

Calculating [H<sup>+</sup>] and pH of a weak acid

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

If the acid is weak and only slightly dissociated, we can safely assume that the change in [HA] is negligible and can be safely ignored. For a 1 mol l<sup>-1</sup> solution after dissociation, [HA] is still 1 mol l<sup>-1</sup>

since [H<sup>+</sup>] = [A<sup>-</sup>], the equation now becomes

$$K_a = \frac{[\text{H}^+]^2}{[\text{HA}]}$$
 if we now let [HA] = c and rearrange

$$[\text{H}^+]^2 = K_a c$$

taking the square root, the equation now becomes

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

the pH would then be the negative log of this value

This important equation allows the calculation of [H<sup>+</sup>] in a weak acid of **any** concentration provided K<sub>a</sub> is known. K<sub>a</sub> values are widely available from any data source.

*Note that this equation is only valid for **monobasic** acids – ones which donate one proton. Knowledge of di or tri-basic acids is not required for Advanced Higher.*

Since pH is a logarithmic scale, it makes sense to calculate directly in logs, and there is another value associated with dissociation constant - the negative log. This value is called the **pK<sub>a</sub>** and is also listed in the Data Book or in any data source.

To calculate correctly, you should already know that multiplying with logs involves addition, dividing involves subtraction, and the square root of a number involves dividing the log by 2 (remember that the square root is the number to the power 1/2)

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

$$-\log_{10} [\text{H}^+] = \frac{1}{2} (-\log_{10} K_a) + \frac{1}{2} (-\log_{10} c)$$

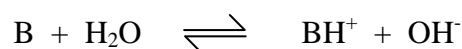
$$\text{pH} = \frac{1}{2} \text{pK}_a - \frac{1}{2} \log_{10} c$$

so the pH of **any** weak acid of **any** concentration can be calculated directly from its pK<sub>a</sub> value.

## Weak bases

Weak bases such as ammonia also have an equilibrium constant.

If the base is represented by the letter B, the equation becomes:



The ion  $BH^+$  is the conjugate acid, and can react with water



and this also has a  $K_a$  value

$$K_a = \frac{[B][H_3O^+]}{[BH^+]}$$

In the Data Booklet, the  $K_a$  and  $pK_a$  values of three weak bases are shown at the bottom.

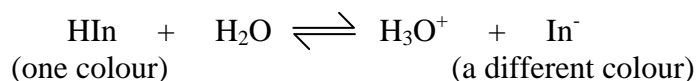
*You will not usually be expected to calculate pH values of weak bases.*

## Indicators

Indicators are used to determine the end-point in an acid-alkali titration.

A suitable indicator must be chosen for any given reaction.

Indicators are dyes whose colours are sensitive to pH. An indicator is usually a weak acid represented by the general formula **HIn** that dissociates as shown:



The dissociation constant has the symbol  $K_{in}$ , and the negative log of this is  $pK_{in}$ .

$$K_{in} = \frac{[H_3O^+][In^-]}{[HIn]}$$

If  $[H_3O^+]$  changes (as it would in a neutralisation titration),  $[HIn]$  and  $[In^-]$  will also change to maintain the value of  $K_{in}$ .

If a point is reached where  $[HIn]$  and  $[In^-]$  are equal, then  $[In^-]$  divided by  $[HIn]$  becomes 1. and  $K_{in} = [H_3O^+]$ .

Therefore  $pK_{in} = pH$ .

At this point, the colour seen will be a mixture of the two colours and is *not* usually a good indication of the end-point of a titration.

Colour change is able to be positively seen when the concentrations of the two different coloured species differ by a factor of 10. This happens one pH unit either side of  $pK_{in}$ .

Therefore, the pH range over which any indicator will change colour is defined as  $pK_{in} \pm 1$ .

This does not seem like a very accurate way of determining the end-point of a neutralisation, but when an acid is neutralised with an alkali or vice versa, the pH change at the end-point is very rapid. One drop of titrant from the burette can cause the pH to change by several units, so if an indicator changes colour over 2 pH units, the end-point is easily determined.

## Titration curves

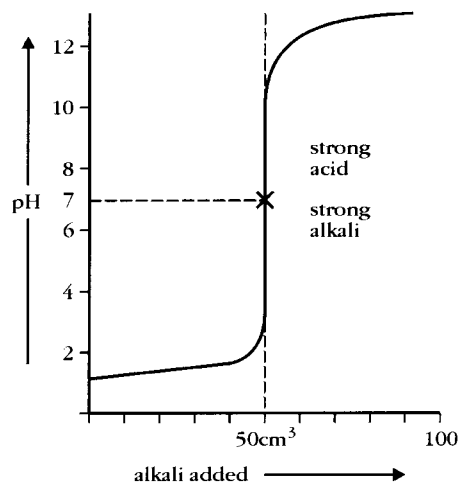
1) strong acid titrated with strong base (e.g. 50 ml 1.0 mol<sup>-1</sup>HCl titrated with 1.0 mol<sup>-1</sup> NaOH)

Initially, there is only a small change in pH

As the end-point approaches, the pH changes rapidly

Halfway up this rapid change, the exact equivalence point occurs at pH 7

When excess base is added, the pH change returns to being small.



2) strong acid titrated with a weak base (e.g. HCl titrated with NH<sub>3</sub>)

Initially, there is only a small change in pH

As the end-point approaches, the pH changes rapidly, but not as rapidly as strong-strong

Halfway up this rapid change, the exact equivalence point occurs at pH <7

When excess base is added, the pH change returns to being small.

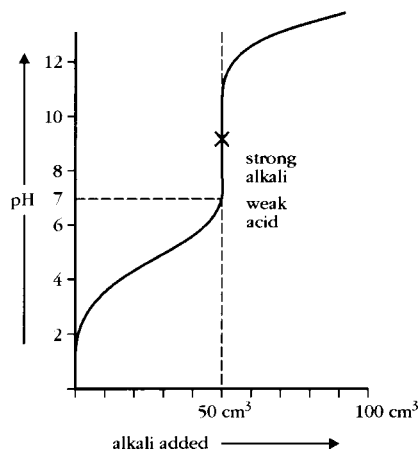
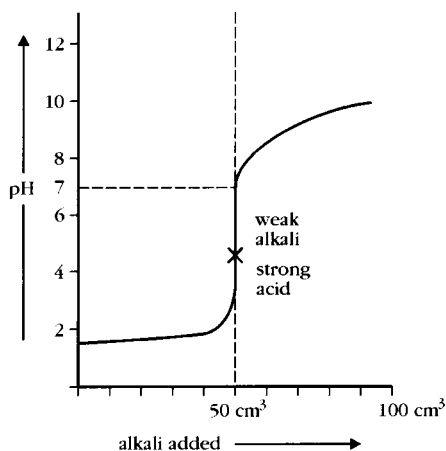
3) weak acid titrated with a strong base (e.g. CH<sub>3</sub>COOH titrated with NaOH)

Initially, there is only a small change in pH

As the end-point approaches, the pH changes rapidly, but not as rapidly as strong-strong

Halfway up this rapid change, the exact equivalence point occurs at pH >7

When excess base is added, the pH change returns to being small.

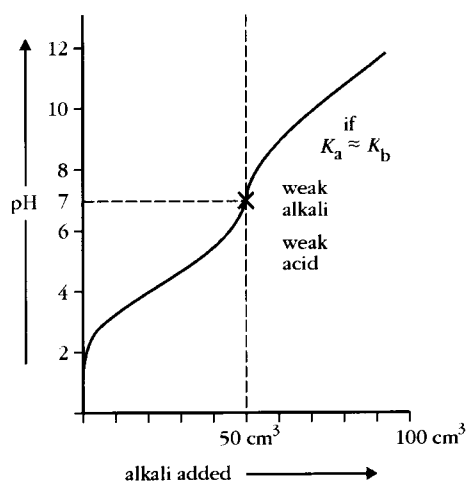


#### 4) weak acid titrated with weak base (e.g. $\text{CH}_3\text{COOH}$ titrated with $\text{NH}_3$ )

Throughout the titration, there is *no* point where the pH changes rapidly.

This means that it is not possible to determine the end-point accurately using an indicator.

It may take several drops of base to change the pH by 2 units near the end-point



#### Choice of indicator

Each titration curve shown has the equivalence point marked with an X.

A suitable indicator for each titration should have a  $\text{pK}_{\text{in}}$  the same as, or close to, the pH shown by X.

*You would not usually be expected to determine which indicator to use for a titration as there are many to choose from, but if you are given the conditions of a titration and the pH ranges of various indicators, you would be expected to choose the correct one.*

#### Buffer solutions

A buffer solution is one in which the pH of the solution remains approximately constant when small amounts of acid or base are added or the solution is diluted with water.

An acidic buffer consists of a solution of a weak acid and one of its salts with a strong alkali.

A basic buffer consists of a solution of a weak base and one of its salts with a strong acid.

Both types of buffer solution work in the same way.

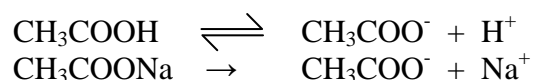
In an acid buffer solution, the weak acid supplies more hydrogen ions when the existing ones are removed by a base being added, while the salt of the weak acid provides the conjugate base to react with the hydrogen ions when small amounts of acid are added.

In a basic buffer solution, the weak base reacts with the hydrogen ions when acid is added and the salt provides the conjugate acid, which dissociates to replace the hydrogen ions when these are removed by addition of small amounts of base.

In consequence, the pH hardly changes in both cases.

This principle is illustrated by an acid buffer of weak acid ( $\text{CH}_3\text{COOH}$ ) and its sodium salt ( $\text{CH}_3\text{COONa}$ ).

In solution the following occurs:



Ethanoic acid is only slightly ionised, so there is a large number of  $\text{CH}_3\text{COOH}$  molecules  
Sodium ethanoate is an ionic compound, so ionises fully in solution

The solution therefore contains a large number of  $\text{CH}_3\text{COOH}$  molecules and  $\text{CH}_3\text{COO}^-$  ions  
According to Brønsted-Lowry theory, the solution contains a large quantity of acid *and* a large quantity of conjugate base.

The solution should therefore be able to donate protons *and* accept protons.

What happens in practice

If an acid is added to an ethanoic acid-sodium ethanoate buffer solution, the large number of  $\text{CH}_3\text{COO}^-$  ions (the conjugate base) “mop up” the hydrogen ions and become undissociated  $\text{CH}_3\text{COOH}$  molecules, so the pH is held constant (or almost constant).

If an alkali is added, the large number of ethanoic acid molecules will supply protons to react with the hydroxide ions and form water, so the pH is held almost constant.

Calculating the pH of a buffer solution.

Consider the weak acid HA and its sodium salt NaA. NaA provides almost all the A<sup>-</sup> ions

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

rearranging

$$\begin{aligned} [\text{H}^+] &= \frac{K_a [\text{HA}]}{[\text{NaA}]} \\ &= K_a \times \frac{[\text{acid}]}{[\text{salt}]} \end{aligned}$$

taking negative logs

$$\text{pH} = \text{p}K_a - \log \frac{[\text{acid}]}{[\text{salt}]}$$

This formula allows the calculation of the pH of any acid buffer solution. It also allows a buffer solution of a specific pH to be prepared.

The pH of a basic buffer solution can also be calculated, but this is not required for Advanced Higher.

## Applications of buffer solutions

### 1) in the blood

Blood must be buffered, otherwise a small quantity of acid or alkali (e.g. inhalation of HCl or ammonia) would cause the pH to change enough to stop enzymes from working, which could be fatal.

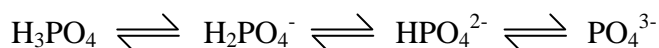
Blood is buffered with a mixture of carbon dioxide and hydrogencarbonate ions.

### 2) in the seas and oceans

Seawater also contains carbonate and hydrogencarbonate ions, which act as buffers and maintain the pH within the limits which allow marine life to exist.

*Studies have shown that increasing levels of carbon dioxide in the atmosphere are slowly turning the pH of the world's oceans more acidic. This could be disastrous for marine life, especially crustaceans and shellfish as these creatures require a delicate balance between these two ions to allow shell to form. Shell is almost pure calcium carbonate. Increasing carbon dioxide dissolving in seawater reduces the concentration of carbonate and increases the concentration of hydrogencarbonate, making it more difficult for the creature to form a shell.*

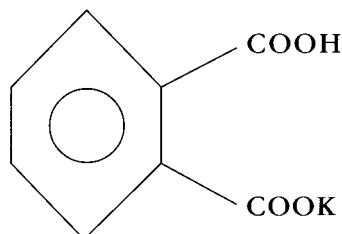
Phosphoric acid and its ions can also act as a buffer



In some organisms, buffering is carried out by a mixture of  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$

*Can you explain why this mixture will act as a buffer?*

In the laboratory, a buffer can be made with the potassium hydrogen salt of phthalic acid.



This particular buffer is useful as it is the weak acid and its potassium salt all in one.

### Practice questions

- 1 Calculate the pH of the buffer solution made from  $1.0 \text{ mol l}^{-1}$  methanoic acid and  $1.78 \text{ mol l}^{-1}$  sodium methanoate solution. The pKa of methanoic acid is 3.7.
- 2 Calculate the pH of the buffer solution made from  $0.1 \text{ mol l}^{-1}$  solution of ethanoic acid and  $0.5 \text{ mol l}^{-1}$  potassium ethanoate. The pKa of ethanoic acid is 4.8.
- 3 100 ml of a buffer solution is required. Its specifications are as follows:
  - Its pH is to be 3.5
  - It is to be made with chloroethanoic acid and its potassium salt
  - The acid concentration is to be  $0.1 \text{ mol l}^{-1}$Calculate the concentrations of the acid and salt required to make this buffer solution, and then calculate the masses of each required.  
Chloroethanoic acid has the formula  $\text{CH}_2\text{ClCOOH}$  and has a pKa of 2.87.  
Its potassium salt has the formula  $\text{CH}_2\text{ClCOOK}$