

Topic 4.3

ACIDS AND BASES

Bronsted-Lowry theory
Acids and bases in water
Calculating pH
Buffer solutions
Acid-alkali titrations
Indicators

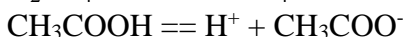
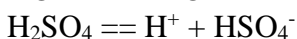
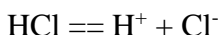
BRONSTED-LOWRY ACIDS AND BASES

1. The Bronsted-Lowry definition

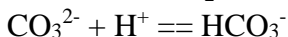
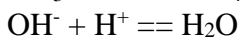
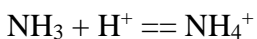
There are many definitions of acids and bases in existence, but the most useful one is the Bronsted-Lowry definition:

An acid is a substance which can behave as a proton donor. A proton can be represented as a hydrogen ion, H^+ .

Any substance which contains hydrogen bonded to a more electronegative element can thus behave as an acid:

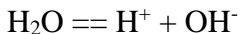
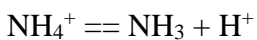
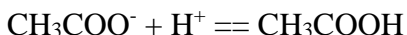
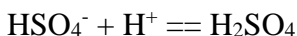
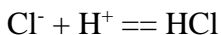


A base is a substance which can behave as a proton acceptor. Any species which has a lone pair of electrons can thus behave as a base:



2. Conjugate acid-base pairs

Since all the above reactions are reversible, the species formed when an acid gives up a proton can accept a proton and thus behave as a base. The species formed when a base accepts a proton can give up a proton and behave as an acid:



Acids and bases thus come in pairs; every acid can lose a proton to become a base and every base can accept a proton to become an acid. Species related in this way are known as **conjugate acid-base pairs**.

Eg Cl^- is the conjugate base of HCl ; HCl is the conjugate acid of Cl^-

Eg NH_3 is the conjugate base of NH_4^+ ; NH_4^+ is the conjugate acid of NH_3

Not all acids are equally good proton donors; in fact some give up their protons very reluctantly; conversely, some bases accept protons readily whereas others accept protons very reluctantly.

The better an acid is at losing protons, the worse its conjugate base will be at accepting them. The better a base is at accepting protons, the worse its conjugate acid will be at losing them. Thus a strong acid will have a weak conjugate base, and a weak acid will have a strong conjugate base.

Acids and bases can be ranked in order of decreasing strength; a list of common acids and their conjugate bases ranked in such a way is shown below:

ACID		BASE	
H_2NO_3^+ ($\text{NO}_2^+ + \text{H}_2\text{O}$)	==	HNO_3	+ H^+
H_2SO_4	==	HSO_4^-	+ H^+
HNO_3	==	NO_3^-	+ H^+
HCl	==	Cl^-	+ H^+
H_3O^+	==	H_2O	+ H^+
H_2SO_3 ($\text{SO}_2 + \text{H}_2\text{O}$)	==	HSO_3^-	+ H^+
HSO_4^-	==	SO_4^{2-}	+ H^+
H_3PO_4	==	H_2PO_4^-	+ H^+
HF	==	F^-	+ H^+
HNO_2	==	NO_2^-	+ H^+
CH_3COOH	==	CH_3COO^-	+ H^+
H_2PO_4^-	==	HPO_4^{2-}	+ H^+
H_2CO_3 ($\text{CO}_2 + \text{H}_2\text{O}$)	==	HCO_3^-	+ H^+
HSO_3^-	==	SO_3^{2-}	+ H^+
NH_4^+	==	NH_3	+ H^+
HCN	==	CN^-	+ H^+
HCO_3^-	==	CO_3^{2-}	+ H^+
HPO_4^{2-}	==	PO_4^{3-}	+ H^+
H_2O	==	OH^-	+ H^+
OH^-	==	O^{2-}	+ H^+

The strongest acids are at the top; these have the weakest conjugate bases.

The strongest bases are at the bottom; these have the weakest conjugate acids.

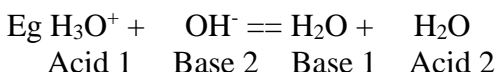
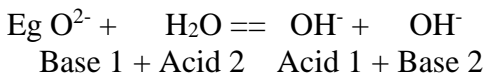
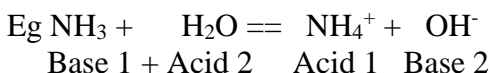
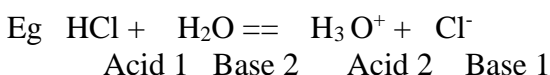
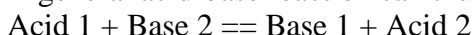
Note that some species (eg H_2O , HSO_3^- , HCO_3^- amongst others) appear in both columns. Such species can behave as either acids or bases and are said to be **amphoteric**.

3. Acid-base reactions

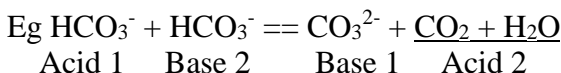
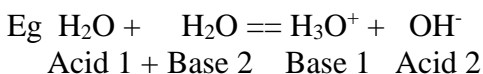
Protons are not given up by acids unless there is a base which can accept them; and bases can only accept protons if there is an acid present to provide them. Reactions between acids and bases thus involve proton transfer from acid to base.

In acid-base reactions, acids react with bases to give the conjugate base of the reactant acid and the conjugate acid of the reactant base. The reactant acid is given the label "acid 1" and its conjugate base is given the label "base 1". The reactant base is given the label "base 2" and its conjugate acid is given the label "acid 2".

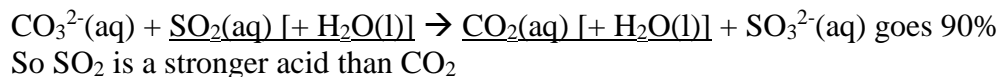
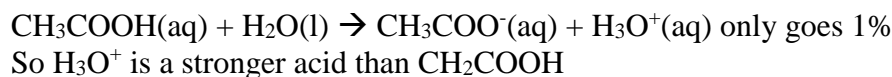
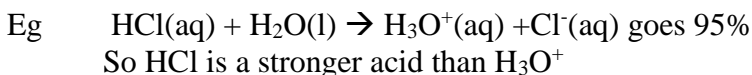
A general acid-base reaction can thus be represented as follows:



Amphoteric substances can undergo acid-base reactions with themselves:



Any acid-base reaction which takes place in aqueous solution will reveal which of two acids is the stronger:

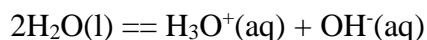


ACIDS AND BASES IN WATER

Most common acid-base reactions take place in aqueous solution, and thus acids and bases are generally defined by the way in which they react with water.

1. Auto-ionisation of water

Water can behave both as an acid and a base: in aqueous solution a small fraction of the water molecules undergo acid-base reactions with each other to produce the equilibrium:



This is known as the **auto-ionisation of water**. The equilibrium expression for this reaction can be written:

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

The concentration of water under these conditions is not changed significantly, since the proportion of water which dissociates into its ions is small. The water concentration can thus be assumed to be constant and it can be incorporated into K_c :

$$K_c[\text{H}_2\text{O}] = \mathbf{K_w = [H_3O^+][OH^-]}$$

$\mathbf{K_w = [H_3O^+][OH^-]}$

The expression $[\text{H}_3\text{O}^+][\text{OH}^-]$ is known as the **ionic product of water** and has a value of $1.0 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$ at 25°C . This value is a constant at a given temperature. The ionic product of water is slightly higher at higher temperatures, suggesting that the dissociation is endothermic.

In pure water, the $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ concentrations are equal.

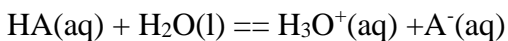
It follows that $[\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}_3\text{O}^+]^2 = K_w$.

So $[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{K_w} = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$.

Any solution in which the concentrations of H_3O^+ and OH^- are equal is said to be **neutral**.

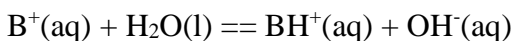
2. Acidic and alkaline solutions

An acid can be regarded as a substance which reacts with water by forcing it to accept a proton and behave as a base:



The resulting solution contains an excess of H_3O^+ ions. Any solution which contains more H_3O^+ ions than OH^- ions is said to be **acidic**. The measure of the acidity of the solution is the H_3O^+ concentration. The greater the H_3O^+ concentration, the more acidic the solution.

A base can be regarded as a substance which reacts with water by accepting a proton from water, forcing it to behave as an acid:



The resulting solution contains an excess of OH^- ions. Any solution which contains more OH^- ions than H_3O^+ ions is said to be **alkaline**. The measure of the alkalinity of the solution is the OH^- concentration. The greater the OH^- concentration, the more alkaline the solution.

The concentration of OH^- ions can be deduced from the concentration of H_3O^+ ions and vice versa. The following table shows some examples:

$[\text{H}_3\text{O}^+]$	$[\text{OH}^-]$	Type of solution
0.1	1×10^{-13}	Acidic
1×10^{-3}	1×10^{-11}	Acidic
1×10^{-5}	1×10^{-9}	Acidic
1×10^{-7}	1×10^{-7}	Neutral
1×10^{-9}	1×10^{-5}	Alkaline
1×10^{-11}	1×10^{-3}	Alkaline
1×10^{-13}	0.1	Alkaline

3. The pH scale

The acidity and alkalinity of a solution is often measured by its pH.

The pH of a solution is the negative logarithm to the base ten of the H_3O^+ concentration.
 $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$.

If $[\text{H}_3\text{O}^+] = 1.0\text{M}$, the pH of the solution is 0.

If $[\text{H}_3\text{O}^+] = 0.1\text{M}$, the pH of the solution is 1.

If $[\text{H}_3\text{O}^+] = 0.01\text{M}$, the pH of the solution is 2.

$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$
--

In alkaline solutions, the OH^- concentration is known. The concentration of H_3O^+ can be deduced from the ionic product of water:

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}. [\text{H}_3\text{O}^+] = K_w/[\text{OH}^-].$$

If $[\text{OH}^-] = 1.0\text{M}$, $[\text{H}_3\text{O}^+] = 1 \times 10^{-14} \text{ M}$ and the pH of the solution is 14.

If $[\text{OH}^-] = 0.1\text{M}$, $[\text{H}_3\text{O}^+] = 1 \times 10^{-13} \text{ M}$ and the pH of the solution is 13.

If $[\text{OH}^-] = 0.01\text{M}$, $[\text{H}_3\text{O}^+] = 1 \times 10^{-12} \text{ M}$ and the pH of the solution is 12.

Note that an increase in pH of one unit is equivalent to a tenfold fall in the H_3O^+ concentration, and a decrease in pH of one unit is equivalent to a tenfold increase in the H_3O^+ concentration.

Calculating the pH of water:

In pure water, $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M}$ and the $\text{pH} = 7$.

It follows that the pH of acidic solutions is less than 7 and the pH of alkaline solutions is greater than 7.

At higher temperatures, the ionic product of water is greater and $[\text{H}_3\text{O}^+]$ is greater than $1 \times 10^{-7} \text{ M}$. The pH of pure water is thus slightly less than 7 at higher temperatures. The solution is still neutral, since the concentrations of H_3O^+ and OH^- are still the same. The pH of a neutral solution is just lower at higher temperatures.

STRONG AND WEAK ACIDS

Acids can be classified as one of two types; strong acids and weak acids. Each must be considered separately:

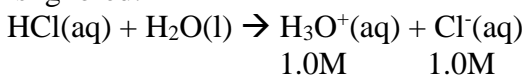
1. Strong acids

A strong acid is one which dissociates completely in water into H_3O^+ and A^- . A strong acid must therefore be a better proton donor than H_3O^+ . Examples of strong acids are HCl , HNO_3 and H_2SO_4 .

Calculating the pH of strong acids:

Since strong acids dissociate fully, the concentration of H_3O^+ will be the same as the concentration of the acid (ignoring the auto-ionisation of water).

A 1.0M solution of HCl will therefore be 1.0M with respect to both H_3O^+ and Cl^- ions if the H_3O^+ present due to the auto-ionisation of water (which will be small in comparison) is ignored:



The pH of 1.0M HCl is thus 0.

If $[\text{H}_3\text{O}^+] = 1.0\text{M}$, the pH of 1.0M HCl is thus 0.

The $[\text{H}_3\text{O}^+]$ in a 0.10M solution of HCl is 0.10M. The pH of 0.10M HCl is thus 1.

The $[\text{H}_3\text{O}^+]$ in a 0.05M solution of HCl is 0.05M. The pH of 0.05M HCl is thus 1.3.

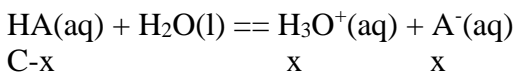
The $[\text{H}_3\text{O}^+]$ in a 2M solution of HCl is 2M. The pH of 2M HCl is thus -0.3.

In theory, there is no minimum pH as the molarity of the acid can increase indefinitely. In practice, the pH rarely falls below -0.5 as even strong acids do not dissociate fully at very high concentrations (there is not enough water). Strong acids can thus only be said to be fully dissociated if the solution is reasonably dilute (ie less than 0.1M).

Diluting the acid tenfold causes the pH to rise by one unit.

2. Weak acids

A weak acid is one which only dissociates partially in water. It reaches equilibrium as follows:



A weak acid is one which is a worse proton donor than H_3O^+ . Examples are CH_3COOH (ethanoic acid), NaHSO_4 (sodium hydrogensulphate) and CO_2 (carbon dioxide).

The equilibrium expression for the dissociation of a weak acid is as follows:

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

The water is in large excess, so its concentration is not significantly affected by this equilibrium and so can be assumed to remain constant. The equilibrium expression can thus be re-written:

$$K_c[\text{H}_2\text{O}] = K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

K_a is known as the **acid dissociation constant** for the acid and has units of mol dm^{-3} .

It is often quoted as $\text{p}K_a = -\log_{10} K_a$.

$$\text{p}K_a = -\log_{10} K_a$$

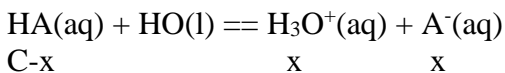
Some K_a and $\text{p}K_a$ values for different acids are shown below:

ACID	$K_a/\text{mol dm}^{-3}$	$\text{p}K_a$
HSO_4^-	1.0×10^{-2}	2.0
CH_3COOH	1.7×10^{-5}	4.8
$\text{CO}_2 + \text{H}_2\text{O}$	4.5×10^{-7}	6.3
NH_4^+	5.8×10^{-10}	9.2
HCO_3^-	4.8×10^{-11}	10.3

The larger the K_a , the greater the degree to which the acid dissociates into its ions and the stronger the acid.

Calculating the pH of weak acids

The H_3O^+ concentration can be calculated by the following method:



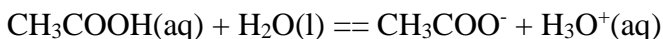
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

Ignoring the H_3O^+ present due to the auto-ionisation of water, the H_3O^+ and A^- concentrations can be assumed to be the same. Therefore $[\text{H}_3\text{O}^+][\text{A}^-] = [\text{H}_3\text{O}^+]^2$.

If the degree of dissociation of HA is assumed to be small, then the molarity of the HA can be assumed to be the same as that of the solution (assume C-x is approximately equal to C).

$$K_a = \frac{[\text{H}_3\text{O}^+]^2}{[\text{HA}]} \quad \text{so } [\text{H}_3\text{O}^+]^2 = K_a[\text{HA}] \quad \text{and } [\text{H}_3\text{O}^+] = \sqrt{K_a[\text{HA}]}$$

eg Calculate the pH of 0.1 mol dm^{-3} ethanoic acid, $K_a = 1.7 \times 10^{-5} \text{ mol dm}^{-3}$



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Ignoring auto-ionisation of water, $[\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-]$ so

$$[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-] = [\text{H}_3\text{O}^+]^2.$$

Assuming degree of dissociation of CH_3COOH is small, $[\text{CH}_3\text{COOH}] = 0.1 \text{ mol dm}^{-3}$.

$$[\text{H}_3\text{O}^+]^2 = K_a \times 0.1, \text{ so } [\text{H}_3\text{O}^+] = \sqrt{K_a \times 0.1} = 1.304 \times 10^{-3} \text{ mol dm}^{-3} \text{ and pH} = 2.9$$

By the same method, the pH of 0.01M CH₃COOH can be shown to be 3.4, and the pH of 0.001M CH₃COOH can be shown to be 3.9.

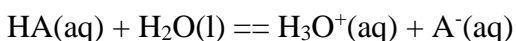
Note that when a weak acid is diluted tenfold, the pH does not increase by one unit as expected. In fact it increases only by 0.5 units. This suggests that the weak acid compensates for the dilution by dissociating to a greater extent:

In 0.1M ethanoic acid, approximately 1.3% of the molecules are dissociated into ions.

In 0.01M ethanoic acid, approximately 4.1% of the molecules are dissociated into ions.

In 0.001M ethanoic acid, approximately 13% of the molecules are dissociated into ions.

Thus the more dilute the solution, the greater the extent to which the acid dissociates into its ions. This is in accordance with Le Chatelier's principle:



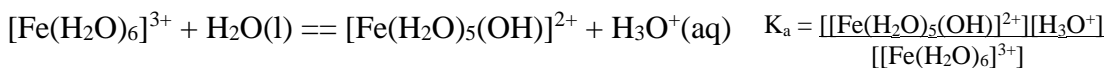
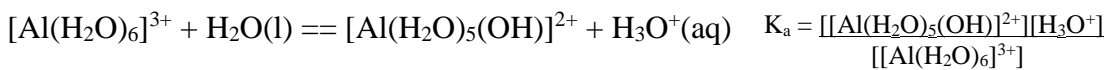
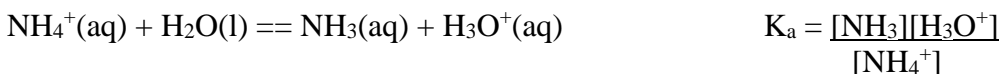
As the amount of water increases, the equilibrium is shifted to the right and the degree of dissociation is greater. This is not the case with strong acids, since they are fully dissociated even at relatively high concentrations and are thus unable to respond to dilution in the same way.

3. Acidic salts

Salts of weak bases can behave as acids.

Examples of acidic salts are: NH₄⁺(aq), Al³⁺(aq), Fe³⁺(aq)

Expressions for K_a are deduced in the normal way:



4. Dilute and concentrated solutions

A dilute solution of an acid is a solution with a low molarity (eg 0.001M HCl). A concentrated solution of an acid is a solution with a high molarity (eg 1M CH₃COOH).

It is important to realise that the concentration of the solution is not necessarily a good measure of the acidity of the solution, since concentrated solutions of weaker acids may be less acidic than more dilute solutions of stronger acids:

Eg the pH of 0.1 M CH₃COOH ($K_a = 1.7 \times 10^{-5}$ M) is 2.88, but the pH of 0.05 M HCOOH ($K_a = 1.6 \times 10^{-4}$ M) is 2.55.

Thus the solution of HCOOH is more acidic, even though it is more dilute. This is because it is a stronger acid (ie it has a larger K_a) and so dissociates to a greater extent.

It is not, however, always true that the stronger acid will give the more acidic solution. Often concentrated solutions of weaker acids are more acidic than more dilute solutions of stronger acids:

Eg the pH of 0.1M CH₃COOH ($K_a = 1.7 \times 10^{-5}$ M) is 2.88, but the pH of 0.001M HCl is 3.0. Thus the solution of CH₃COOH is more acidic, even though it is a weaker acid. This is because the molar concentration of the acid is higher.

The acidity of a solution (ie the concentration of H₃O⁺) therefore depends on both the concentration of the solution and the strength of the acid.

5. Very dilute solutions

In all the calculations considered so far, the H₃O⁺ present due to the auto-ionisation of water has been ignored. This is normally a reasonable assumption, since water only ionises very slightly ($[H_3O^+] = 1 \times 10^{-7}$ M in pure water).

In very dilute solutions, however, the H₃O⁺ present due to the auto-ionisation of water is significant and cannot be ignored. This is generally the case if the concentration of the solution is less than 1×10^{-6} M.

The pH of 1×10^{-6} M HCl = 6.00

The pH of 1×10^{-7} M HCl is not, however, equal to 7, since the solution is very slightly acidic, and the pH of 1×10^{-8} M HCl is certainly not 8.

At such low concentrations the H₃O⁺ present due to the auto-ionisation of water is significant and must be taken into consideration.

From a more thorough consideration of the equilibrium mixture, it can be shown that the pH of a 1×10^{-7} M solution of HCl is 6.79 and the pH of a 1×10^{-8} M solution of HCl is 6.98.

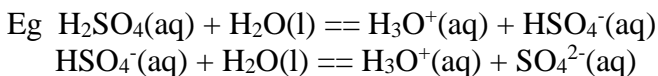
6. polybasic acids

Acids which are capable of losing more than one proton are said to be polybasic.

Examples of polybasic acids are H_2SO_4 , H_3PO_4 and $\text{CO}_2 + \text{H}_2\text{O}$.

Acids which can lose two protons in solution are said to be dibasic, and acids which can lose three protons in solution are said to be tribasic.

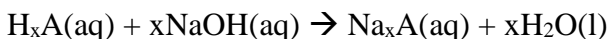
Polybasic acids dissociate more than once in aqueous solution:



Each H_2SO_4 therefore gives two moles of H_3O^+ ions

Polybasic acids such as H_2SO_4 thus form more than one salt; H_2SO_4 , a dibasic acid, forms two sodium salts, NaHSO_4 and Na_2SO_4 . H_3PO_4 , a tribasic acid, forms three sodium salts, NaH_2PO_4 , Na_2HPO_4 and Na_3PO_4 .

The number of protons which an acid loses can be determined from its reaction with alkali:



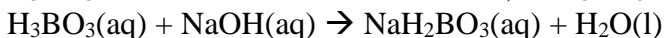
Monoprotic acids react with sodium hydroxide in a 1:1 ratio.

Diprotic acids react with sodium hydroxide in a 2:1 ratio.

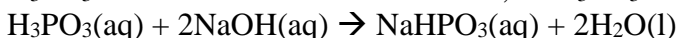
Triprotic acids react with sodium hydroxide in a 3:1 ratio, etc.

With many acids, not all of the available hydrogen is lost and thus the number of replaceable hydrogens must be determined experimentally:

H_3BO_3 reacts with NaOH in a 1:1 ratio, so H_3BO_3 is monobasic:



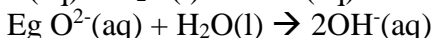
H_3PO_3 reacts with NaOH in a 1:2 ratio, so H_3PO_3 is dibasic:



BASES

1. Strong bases

A strong base is one which fully dissociates into its ions in water:



A strong base in water must therefore be a stronger base than OH^- .

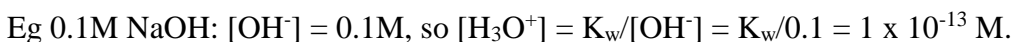
Strong bases in water are, in fact, quite rare as water is a very weak acid and will not readily give up protons to other species. The oxide ion is one of the only common examples of a strong base.

The hydroxide ion is, however quite stable and there are many examples of ionic substances containing OH^- ions. If these substances are soluble, they will completely dissociate in aqueous solution. Though they do not actually react with water, they are regarded as strong bases since they completely dissociate to give OH^- ions. Examples of these substances are NaOH, KOH and $Ba(OH)_2$.

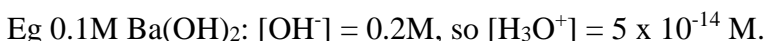
Substances which dissolve in water to produce an excess of OH^- ions are said to be **alkaline**.

Calculating the pH of strong bases:

The pH of strong bases can be calculated if the concentration of the solution is known:



Thus the pH of 0.1M NaOH is 13.0



Thus the pH of 0.1M $Ba(OH)_2$ = 13.3

Note that in these calculations the OH^- present due to the auto-ionisation of water has been ignored.

Since these compounds are ionic, they are fully dissociated at all concentrations. The alkalinity of the solution is thus limited only by the solubility of the hydroxide. The maximum possible pH at room temperature is 14.5, corresponding to a solution of approx 3M NaOH.

2. Weak bases

Weak bases do not dissociate fully in water. They behave in a similar way to weak acids but pH calculations involving weak bases are not required at A-level.

BUFFER SOLUTIONS

A buffer solution is a solution which can resist changes in pH on addition of small quantities of acid or alkali or on dilution.

1. How buffers work

A buffer solution is a mixture of an acid and an alkali. The acid neutralises the alkali added and the alkali neutralises the acid added.

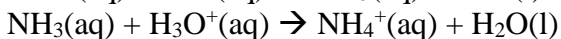
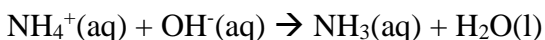
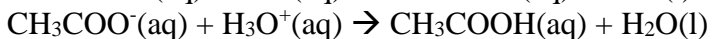
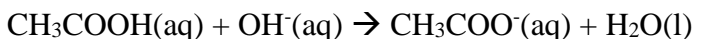
The mixture cannot be a mixture of a strong acid and a strong alkali, or the two will react with each other (eg a mixture of NaOH and HCl would react with each other and thus not behave as an effective buffer). If the acid and alkali in the buffer are too weak, however, they will not react effectively with the acid or alkali that are added.

A suitable mixture is one which contains a mixture of acid and alkali strong enough to react with H_3O^+ and OH^- , but weak enough not to react with each other.

An ideal mixture for this purpose is a mixture of a weak acid and its conjugate base. For example CH_3COOH and CH_3COONa , or NH_4Cl and NH_3 . The acids and bases in these mixtures will react with OH^- and H_3O^+ respectively but not with each other.

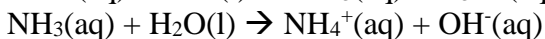
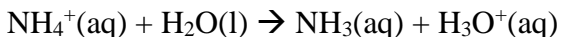
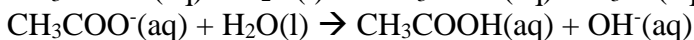
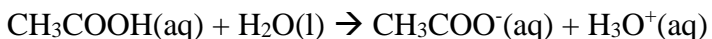
a) Resisting pH change on addition of acid and alkali

These mixtures will react with acid and alkali as follows:



b) Resisting pH change on dilution

On dilution, both the weak acid and the weak base can dissociate more to compensate for the dilution:

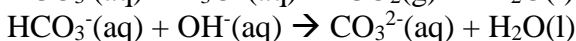
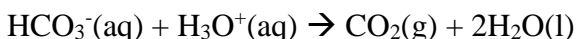


c) Other buffer solutions

A buffer does not have to be a mixture of a weak acid and its conjugate base; any mixture of a weak acid and a weak base will have the same effect.

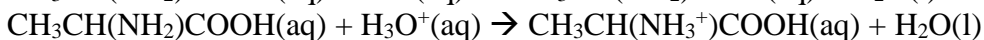
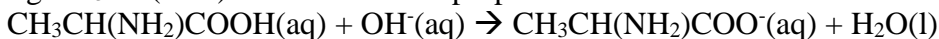
Substances which can behave as both weak acids and weak bases can also behave as buffers.

One important example is sodium hydrogencarbonate; the HCO_3^- ion can behave as either an acid or a base:



Amino acids can also behave as buffers:

Eg $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$ - 2-aminopropanoic acid



2. Calculating the pH of buffer solutions

If a mixture of a weak acid and its conjugate base is used as a buffer, the pH of the buffer can be calculated by the following method:

Consider the mixture $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$:

The K_a of the acid can be written: $K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$

$$\text{so } [\text{H}_3\text{O}^+] = \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

In general, $[\text{H}_3\text{O}^+]$ can be calculated from the formula:

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{acid}]}{[\text{base}]}$$

$[\text{H}_3\text{O}^+] = K_a \frac{[\text{acid}]}{[\text{base}]}$
--

For example, a mixture containing 0.2M CH_3COOH ($K_a = 1.7 \times 10^{-5}$ M) and 0.1M CH_3COONa has a $[\text{H}_3\text{O}^+]$ concentration of 1.7×10^{-5} ($0.2/0.1$) = 3.4×10^{-5} M.
Therefore the pH of the solution is 4.5.

For example, a mixture containing 0.1M NH_4Cl ($K_a = 5.6 \times 10^{-10}$ M) and 0.1M NH_3 has a $[\text{H}_3\text{O}^+]$ concentration of 5.6×10^{-10} ($0.1/0.1$) = 5.6×10^{-10} M.
Therefore the pH of the solution is 9.3.

To prepare a buffer solution of a given pH, it is necessary to have the acid and base concentrations in a suitable ratio.

Eg to prepare an $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer of $\text{pH} = 10$

$$\frac{[\text{H}_3\text{O}^+]}{K_a} = \frac{[\text{acid}]}{[\text{base}]} \quad \text{so} \quad \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = \frac{1 \times 10^{-10}}{5.6 \times 10^{-10}} = 1/5.6$$

So 5.6 moles of NH_3 are required for every 1 mole of NH_4Cl

Given equimolar solutions of both, 100 cm^3 of this buffer could be made by taking 10 cm^3 of NH_4Cl , adding 56 cm^3 of ammonia and the total volume made up to 100 cm^3 .

It is possible to express the pH directly in terms of the concentrations of the reactants:

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{acid}]}{[\text{base}]}$$

$$\text{so } \log_{10}[\text{H}_3\text{O}^+] = \log_{10}K_a + \log_{10}([\text{acid}]/[\text{base}])$$

$$\text{so } -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}K_a + \log_{10}([\text{base}]/[\text{acid}])$$

$$\text{so } \text{pH} = \text{p}K_a + \log_{10}([\text{base}]/[\text{acid}])$$

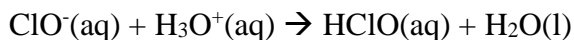
$$\text{pH} = \text{p}K_a + \log_{10}([\text{base}]/[\text{acid}])$$

3. Showing how buffer solutions limit changes in pH.

It is possible to show quantitatively the ability of buffer solutions to limit changes in pH:

Eg a mixture of 0.6M HClO ($K_a = 3.7 \times 10^{-8} \text{ M}$) and 0.2M NaClO has a pH of 7.0.

If 0.01 moles of HCl are added to 100 cm^3 of the buffer:



Initially: $0.02 \quad 0.01 \quad 0.06$

Finally: $0.01 \quad - \quad 0.07$

So the $[\text{base}]/[\text{acid}]$ ratio is $0.01/0.07$

$$\text{pH} = \text{p}K_a + \log_{10}([\text{base}]/[\text{acid}]) = 6.58 \text{ (a change of 0.4 units)}$$

If 0.01 moles of HCl were added to 100 cm^3 of pure water, the pH of the resulting solution would be 1.0 (a change of 6 units)

If 0.01 moles of NaOH are added to the buffer:

	$\text{HClO}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{ClO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$		
Initially:	0.06	0.01	0.02
Finally:	0.05	-	0.03

So the $[\text{base}]/[\text{acid}]$ ratio is 0.03/0.05

$$\text{pH} = \text{pK}_a + \log_{10}([\text{base}]/[\text{acid}]) = 7.21 \text{ (a change of 0.2 units)}$$

If 0.01 moles of NaOH were added to 100 cm³ of pure water, the pH of the resulting solution would be 13.0.

So buffer solutions do not change their pH much on adding small quantities of acid or alkali.

NB it is possible to exceed the buffering capacity of a buffer solution by adding too much acid or alkali; in such cases the buffer will be unable to maintain the pH and the pH will change dramatically. This would be the case of more than 0.02 moles of HCl or more than 0.06 moles of NaOH were added to the above mixture.

It can be shown that buffer solutions are most efficient at resisting changes in pH when the concentrations of acid and alkali are the same.

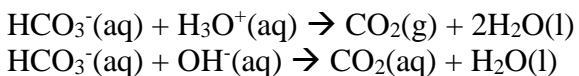
If there is much more acid than base in a buffer solution, then it is not very able to resist changes in pH on adding acid. Similarly if there is much more base than acid in a buffer solution it is not very able to resist changes in pH on adding alkali.

4. Natural buffers

There are many biological systems which rely on a fairly constant pH, and which rely on the use of buffer solutions to maintain this pH.

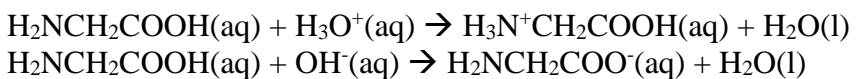
a) blood

The pH of blood must be maintained at around 7.4. Hydrogencarbonate ions are used for this purpose:



b) tears

The pH of tears must also be maintained at around 7.4, in this case by the use of amino acids:



ACID-ALKALI TITRATIONS

A reaction between an acid and an alkali is known as a **neutralisation**.

The concentration of an acid can be determined by titrating it against a standard alkali solution using a suitable indicator, and the concentration of an alkali can be determined by titrating against a standard acid solution.

If solution A is titrated against solution B, it means that solution A is in the conical flask and solution B is in the burette.

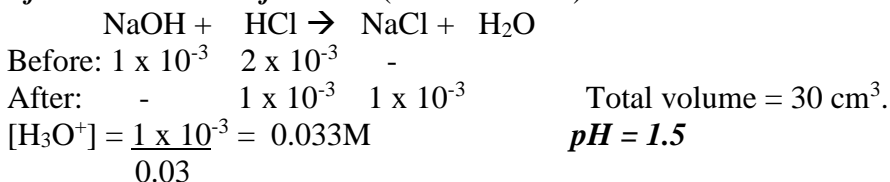
The behaviour of acid-alkali mixtures during titrations depends on whether the acids and bases are strong or weak.

1. pH changes during strong acid - strong alkali titrations

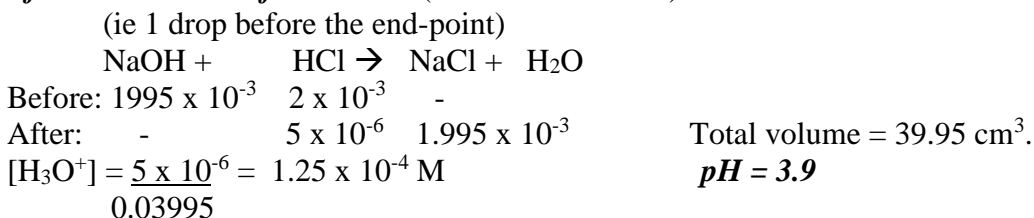
If 0.1M NaOH is added dropwise to 20 cm³ of 0.1M HCl (2 x 10⁻³ moles), the change in pH of the solution can be calculated by considering the reaction taking place.

Before the addition of NaOH, the pH of the solution is 1.0.

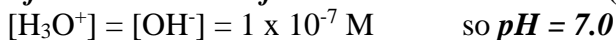
After the addition of 10 cm³ (1 x 10⁻³ moles) of 0.1M NaOH:



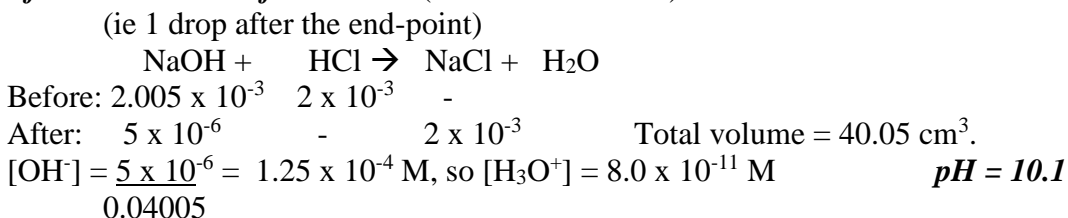
After the addition of 19.95 cm³ (1.995 x 10⁻³ moles) of 0.1M NaOH:



After the addition of 20.0 cm³ of 0.1M NaOH (ie at the end-point)

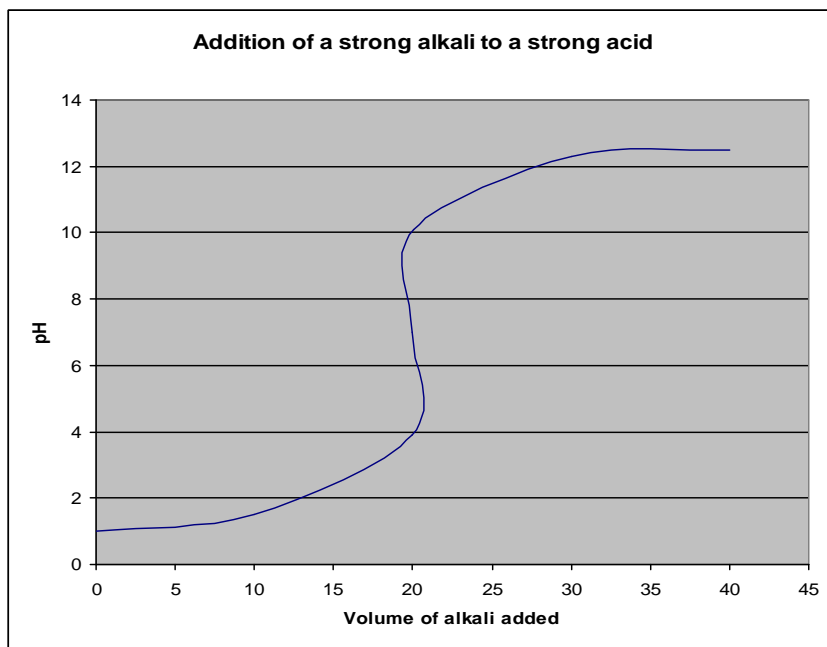


After the addition of 20.05 cm³ (2.005 x 10⁻³ moles) of 0.1M NaOH:



The pH of the solution during a strong acid - strong alkali titration therefore changes from around 4 to 10 over two drops at the end-point.

A titration curve for a strong acid - strong alkali titration can be sketched as follows:

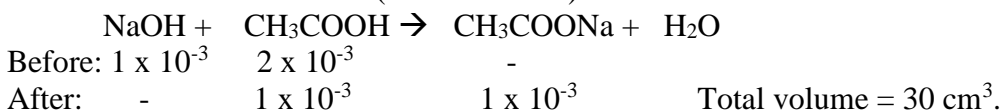


2. pH changes during weak acid - strong alkali titrations

If 0.1M NaOH is added dropwise to 20 cm³ of 0.1M CH₃COOH (2 x 10⁻³ moles), the change in pH of the solution can be calculated by considering the reaction taking place.

Before the addition of NaOH, the pH of the solution is 2.9.

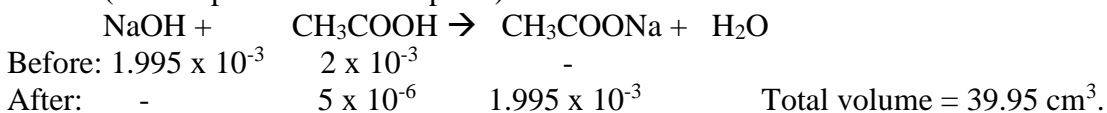
After the addition of 10 cm³ (1 x 10⁻³ moles) of 0.1M NaOH:



The solution now contains a mixture of a weak acid (CH₃COOH) and its conjugate base (CH₃COO⁻). It thus behaves as a **buffer solution**. The pH of the mixture can thus be calculated by considering the relative concentrations of the CH₃COOH and CH₃COO⁻.

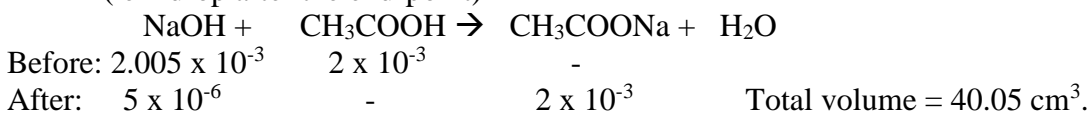
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \text{ so } [\text{H}_3\text{O}^+] = \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = 1.7 \times 10^{-5} \text{ M and pH} = 4.8$$

After the addition of 19.95 cm³ (1.995 x 10⁻³ moles) of 0.1M NaOH:
(ie 1 drop before the end-point)



$$[\text{H}_3\text{O}^+] = \frac{K_a \times (5 \times 10^{-6} / 0.3995)}{(1.995 \times 10^{-3} / 0.3995)} \quad \text{pH} = 7.4$$

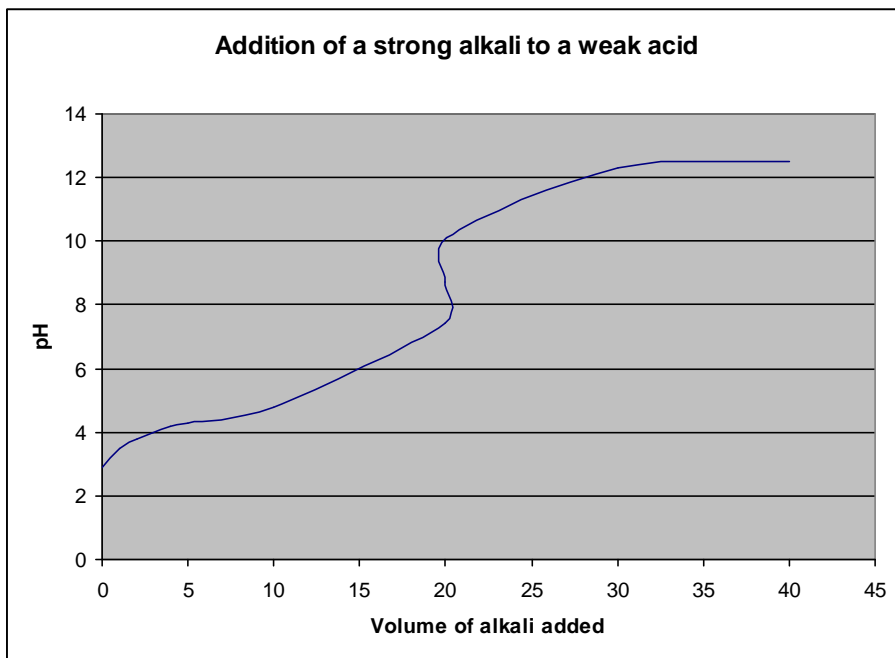
After the addition of 20.05 cm³ (2.005 x 10⁻³ moles) of 0.1M NaOH:
(ie 1 drop after the end-point)



$$[\text{OH}^-] = \frac{5 \times 10^{-6}}{0.04005} = 1.25 \times 10^{-4} \text{ M, so } [\text{H}_3\text{O}^+] = 8.0 \times 10^{-11} \text{ M} \quad \text{pH} = 10.1$$

The pH of the solution during a weak acid - strong alkali titration therefore changes from around 7 to 10 over two drops at the end-point.

A titration curve for a weak acid - strong alkali titration can be sketched as follows:



Note that the pH increases fairly fast at the beginning of the titration, until there is enough of the salt formed for an effective buffer solution.

The end-point of the titration is the mid-point of the vertical section of the graph.

Note that in this titration the pH of the solution at the end-point is not 7. The ethanoate ion is basic: $\text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOH}(\text{aq}) + \text{OH}^-(\text{aq})$
The pH of this solution at the end-point is between 8 and 9

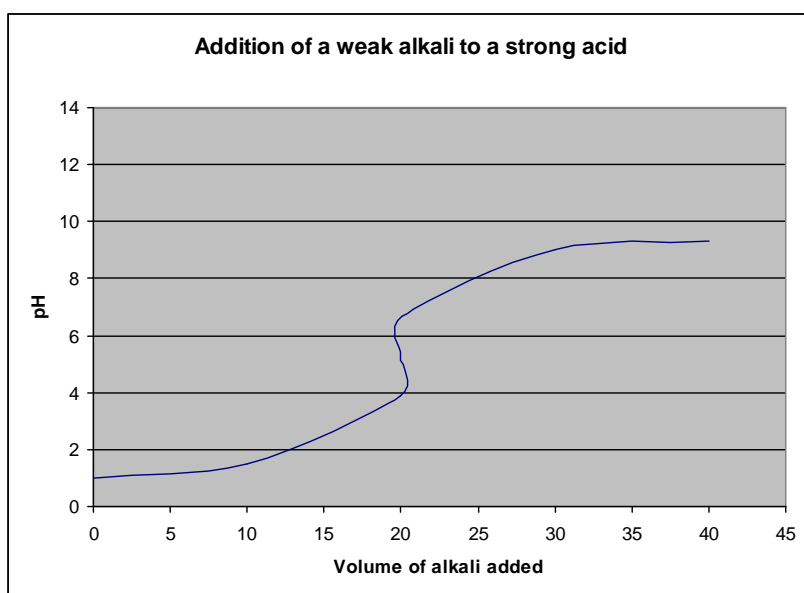
4. Strong acid - weak alkali titrations

If 0.1M NH_3 is added to 20 cm^3 0.1M HCl , the mixture behaves in a similar way to a strong acid - strong alkali titration until the end-point is reached.

After the end-point, the solution contains a mixture of NH_4^+ and NH_3 and thus behaves as a buffer solution.

The pH of the solution during a strong acid - weak alkali titration changes from around 4 to 7 at the end-point.

A titration curve for a strong acid - weak alkali titration can be sketched as follows:



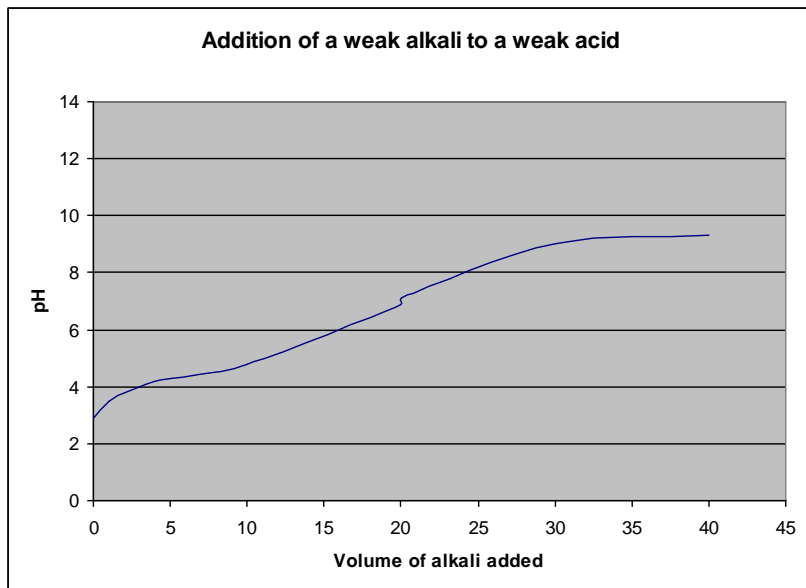
The solution at the end-point contains 0.05M NH_4Cl . It is not neutral, since the NH_4^+ ion is acidic: $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

The pH at the end-point is between 5 and 6.

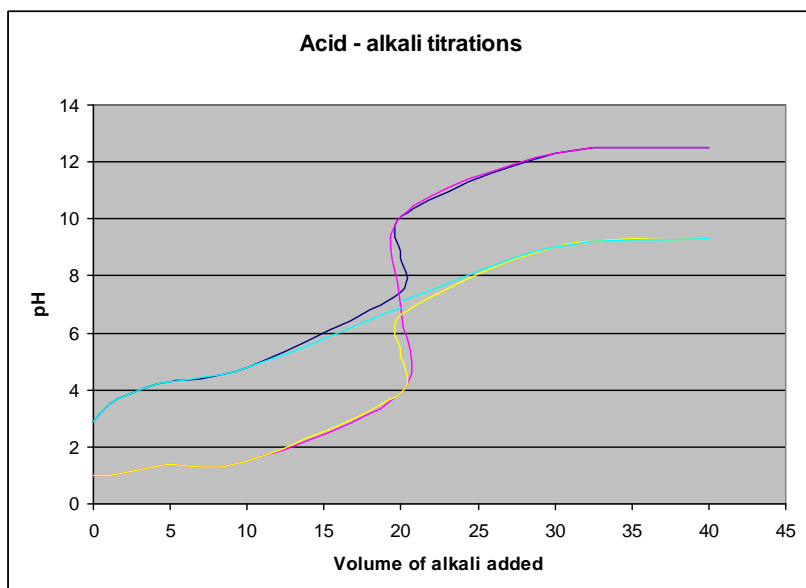
5. Weak acid - weak alkali titrations

Weak acid - weak alkali titrations behave as buffer solutions throughout the titration. Unlike titrations involving strong acids or strong alkalis, there is no dramatic pH change at the end-point. The pH of the end-point is usually around 7, but it depends on the relative strengths of the acid and the alkali.

A titration curve for a weak acid - weak alkali titration can be sketched as follows:

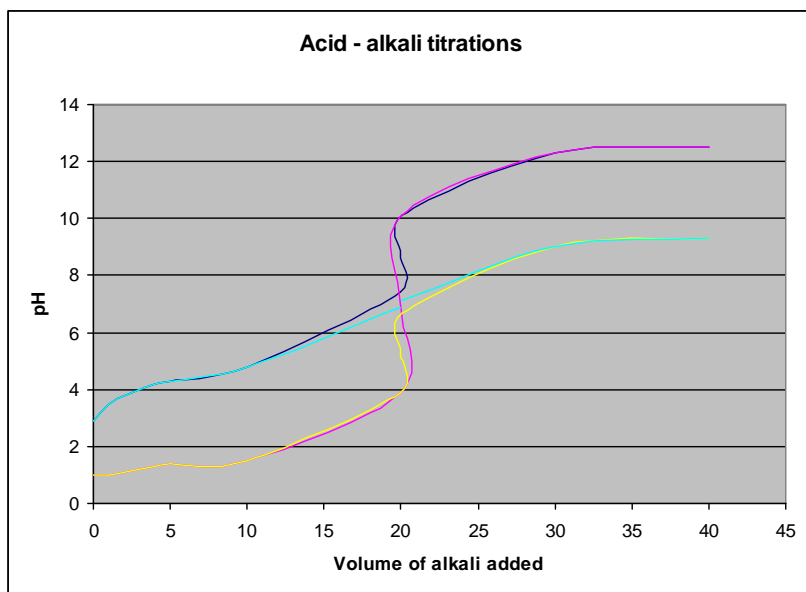


The titration curves for all the different possible titrations can be sketched on the same graph as follows:



SUMMARY OF ACID-ALKALI TITRATION CURVES

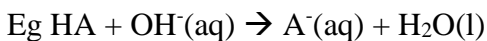
The titration curves for all the different possible titrations can be sketched on the same graph as follows:



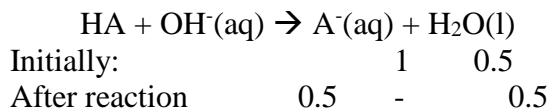
Type of titration	pH at end-point	pH change at end-point
Strong acid - strong alkali	7.0	4 to 10
Weak acid - strong alkali	Approx 8.5	7 to 10
Strong acid - weak alkali	Approx 5.5	4 to 7
Weak acid - weak alkali	Approx 7	No sudden change

6. Half -neutralisation

A weak acid is half-neutralised when exactly half the volume of alkali required for neutralisation has been added.



If 0.5 moles of OH^- ions is added to 1 mole of HA, half of the acid will be converted into its salt.



At half-neutralisation the number of moles, and hence concentration, of the salt and acid will be the same. $[\text{HA}] = [\text{A}^-]$

Given that $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$ $[\text{H}_3\text{O}^+] = \frac{K_a[\text{HA}]}{[\text{A}^-]}$

If $[\text{HA}] = [\text{A}^-]$ then $[\text{H}_3\text{O}^+] = K_a$ and therefore $\text{pH} = \text{p}K_a$.

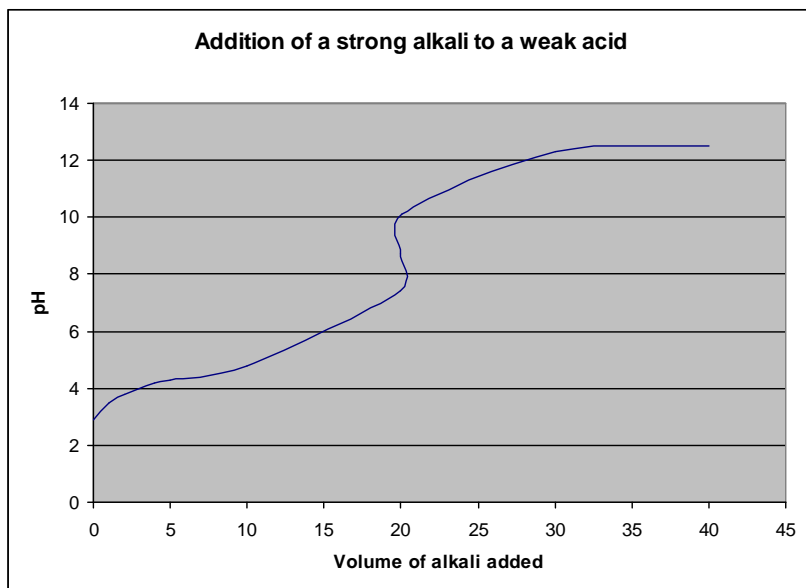
Therefore at half-neutralisation: $[\text{H}_3\text{O}^+] = K_a$ and $\text{pH} = \text{p}K_a$.

at half-neutralisation: $\text{pH} = \text{p}K_a$

The K_a of an acid can be deduced from a graph of pH against volume of alkali added.

The pH of the mixture after exactly half the required amount of alkali has been added corresponds to the $\text{p}K_a$ of the acid.

You calculate the K_a of the acid as follows:



The end-point of the titration is the centre of the steep vertical section of the curve.

This occurs at 20 cm³ in this case.

Therefore half-neutralisation occurs at 10 cm³ in this case.

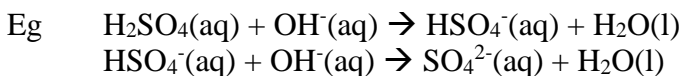
The pH at half-neutralisation is 4.7.

So the pK_a of the acid is 4.7

So the K_a of the acid = $10^{-4.7} = 1.7 \times 10^{-5} \text{ mol dm}^{-3}$.

7. Titrations with polybasic acids

When polybasic acids are titrated against strong alkalis, the reaction proceeds through more than one stage.

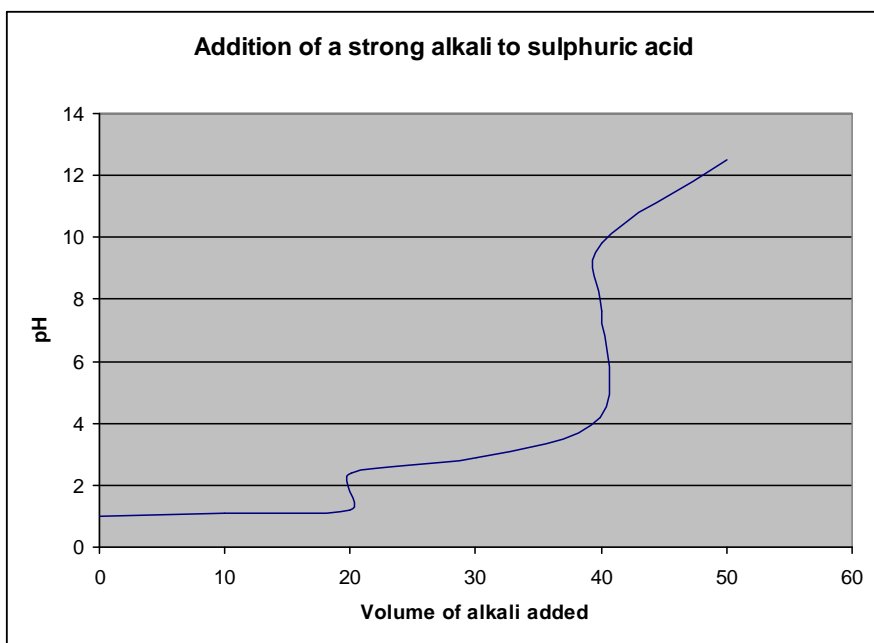


These reactions do not occur simultaneously – they take place one at a time.

Each of these stages has its own end-point, and thus the reaction will have two end-points.

Eg if 20 cm^3 0.1M H_2SO_4 is titrated against 0.1M NaOH , the first end-point will be reached after 20 cm^3 NaOH has been added and the second end-point will be reached after 40 cm^3 NaOH has been added.

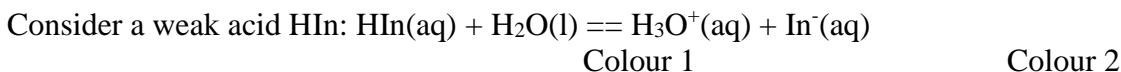
The titration curve for the above titration can be sketched as follows:



ACID-BASE INDICATORS

1. Theory of indicators

An acid-base indicator is a weak acid which dissociates to give an anion of a different colour.



HIn and its conjugate base In⁻ are different colours. The colour of the solution depends on the relative concentrations of the two species.

If the solution is strongly acidic, the above equilibrium will be shifted to the left and HIn will dominate. Colour 1 will thus dominate. If the solution is strongly alkaline, the above equilibrium will shift to the right and In⁻ will dominate. Colour 2 will thus dominate. The colour of the indicator thus depends on the pH of the solution.

The colour will not change suddenly at a certain pH, but will change gradually over a pH range. The colour of the indicator depends on the ratio of [HIn] to [In⁻].

In general, if [HIn]/[In⁻] > 10, then colour 1 will dominate. If [In⁻]/[HIn] > 10, then colour 2 will dominate. The pH at which these transitions will occur depends on the K_{In} of the indicator.

$$K_{\text{In}} = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} \text{ so } [\text{H}_3\text{O}^+] = \frac{K_{\text{In}}[\text{HIn}]}{[\text{In}^-]}$$

If [H₃O⁺] > 10 x K_{In}, then [HIn]/[In⁻] > 10 and colour 1 dominates.

If [H₃O⁺] < 0.1 x K_{In}, then [HIn]/[In⁻] < 0.1 and colour 2 dominates.

At intermediate H₃O⁺ concentrations, neither colour dominates.

K_{In} values are often expressed as pK_{In} values, where pK_{In} = -log₁₀K_{In}.

This equation can also be expressed in terms of pH:

$$\text{pH} = \text{pK}_{\text{In}} - \log_{10}[\text{HIn}]/[\text{In}^-]$$

$$\text{pH} = \text{pK}_{\text{In}} + \log_{10}[\text{In}^-]/[\text{HIn}]$$

For colour 1 to dominate, [In⁻]/[HIn] < 0.1 so pH must be less than pK - 1.

For colour 2 to dominate, [In⁻]/[HIn] > 10 so pH must be greater than pK + 1.

So the colour of the indicator changes over the pH range pK_{In} ± 1

Eg If the K_a of an indicator is $1.0 \times 10^{-5} \text{ mol dm}^{-3}$.

If $[\text{H}_3\text{O}^+] > 1 \times 10^{-4}$ ($\text{pH} < 4$), then $[\text{HIn}]/[\text{In}^-] > 10$ and colour 1 dominates.

If $[\text{H}_3\text{O}^+] < 1 \times 10^{-6}$ ($\text{pH} > 6$), then $[\text{HIn}]/[\text{In}^-] < 0.1$ and colour 2 dominates.

If the pH is between pH 4 and 6, then neither colour dominates.

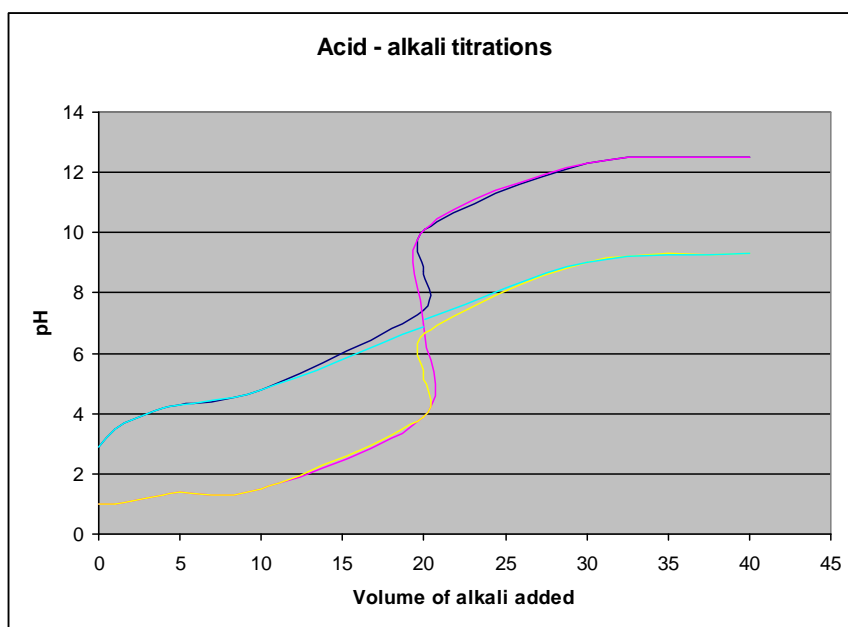
The pK_{In} values of some indicators is shown below:

Indicator	Colour in acid	Colour in alkali	pK_a	pH range of colour change
Thymol blue	Red	Yellow	1.7	1.2 - 2.8
Methyl orange	Red	Yellow	3.7	3.2 - 4.4
Methyl red	Red	Yellow	5.1	4.2 - 6.3
Litmus	Red	Blue	6.3	5.0 - 8.0
Phenolphthalein	Colourless	Pink	9.3	8.2 - 10.0

2. Use of indicators

Indicators are used in acid - alkali titrations in order to find the end-point of the titration. If they are to determine the end-point accurately, they must undergo a complete colour change at the end-point. This means that the pH range of the colour change must fall completely within the pH range of the end-point. Not all indicators can therefore be used for all titrations, and indicators must be chosen carefully so that the pH range of the colour change matches that of the pH range at the end-point.

The titration curves of various different types of titration are shown below:



- In strong acid - strong alkali titrations, the pH changes from 4 to 10 at the end-point so a suitable indicator must change colour within this range.

Methyl red, litmus and phenolphthalein are suitable indicators for these titrations. Methyl orange is not ideal but it shows a significant enough colour change at the end point to be widely used.

- In weak acid - strong alkali titrations, the pH changes from 7 to 10 at the end-point so a suitable indicator must change colour within this range.

Phenolphthalein is only suitable indicator for weak acid - strong alkali titrations that is widely available.

- In strong acid - weak alkali titrations, the pH changes from 4 to 7 at the end-point so a suitable indicator must change colour within this range.

Methyl red is the most suitable indicator for these titrations. However methyl orange is often used since it shows a significant enough colour change at the end-point and is more widely available than methyl red.

- In weak acid -weak alkali titrations, there is no sudden pH change at the end-point and thus there are no suitable indicators for these titrations. The end-points of these titrations cannot be easily determined.

When carrying out these titrations, only one or two drops of indicators should be used since they are themselves acidic and will themselves influence the end-point if too much is added.

An indicator is suitable for a titration if the most part of the pH range over which it changes colour falls within the pH change at the end-point of the titration.