# Theories of acids and bases and salt hydrolysis

## THE IONIC THEORY

An acid was originally distinguished by its sour taste. Later it was said to be the oxide of a non-metal combined with water although hydrochloric acid does not fit into this definition. The ionic theory which is still commonly used today states that an acid is a substance which produces hydrogen ions, $H^+(aq)$, in aqueous solution, e.g.

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

In aqueous solution hydrogen ions are hydrated to form hydroxonium ions, $H_3O^+(aq)$. In the International Baccalaureate it is correct to write either $H^+(aq)$ or $H_3O^+(aq)$ to represent the hydrogen ions in an aqueous solution. Strictly speaking an acid gives a hydrogen ion concentration in aqueous solution greater than $1.0 \times 10^{-7}$ mol dm$^{-3}$. A base is a substance that can neutralize an acid. An alkali is a base that is soluble in water.

## BRØNSTED–LOWRY ACIDS AND BASES

A Brønsted–Lowry acid is a substance that can *donate* a proton. A Brønsted–Lowry base is a substance that can *accept* a proton.

Consider the reaction between hydrogen chloride gas and water.

$$\underset{\text{acid}}{HCl(g)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{acid}}{H_3O^+(aq)} + \underset{\text{base}}{Cl^-(aq)}$$

Under this definition both HCl and $H_3O^+$ are acids as both can donate a proton. Similarly both $H_2O$ and $Cl^-$ are bases as both can accept a proton. $Cl^-$ is said to be the **conjugate base** of HCl and $H_2O$ is the conjugate base of $H_3O^+$. The conjugate base of an acid is the species remaining after the acid has lost a proton. Every base also has a conjugate acid, which is the species formed after the base has accepted a proton. In the reaction with hydrogen chloride water is behaving as a base. Water can also behave as an acid.

$$\underset{\text{base}}{NH_3(g)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{acid}}{NH_4^+(aq)} + \underset{\text{base}}{OH^-(aq)}$$

Substances such as water, which can act both as an acid and as a base, are described as **amphiprotic**.

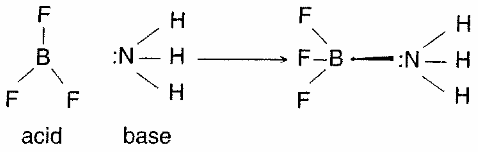
Strong acids (see next page) have weak conjugate bases, whereas weak acids have strong conjugate bases.

| acid strength ↑ | Acid | Equilibrium constant | Conjugate base | base strength ↓ |
|---|---|---|---|---|
| | ethanoic acid, $CH_3COOH$ | $1.8 \times 10^{-5}$ | ethanoate ion, $CH_3COO^-$ | |
| | phenol, $C_6H_5OH$ | $1.0 \times 10^{-10}$ | phenoxide ion, $C_6H_5O^-$ | |
| | water, $H_2O$ | $1.0 \times 10^{-14}$ | hydroxide ion, $OH^-$ | |
| | ethanol, $C_2H_5OH$ | approx. $1 \times 10^{-16}$ | ethoxide ion, $C_2H_5O^-$ | |

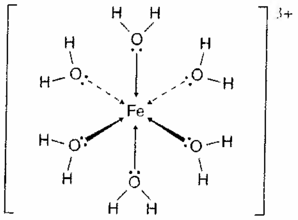
## LEWIS ACIDS AND BASES

Brønsted–Lowry bases must contain a non-bonding pair of electrons to accept the proton. The Lewis definition takes this further and describes bases as substances which can *donate* a pair of electrons, and acids as substances which can *accept* a pair of electrons. In the process a co-ordinate (both electrons provided by one species) covalent bond is formed between the base and the acid.

The Lewis theory is all-embracing, so the term Lewis acid is usually reserved for substances which are not also Brønsted–Lowry acids. Many Lewis acids do not even contain hydrogen.



$BF_3$ is a good Lewis acid as there are only six electrons around the central boron atom which leaves room for two more. Other common Lewis acids are aluminium chloride, $AlCl_3$, and also transition metal ions in aqueous solution which can accept a pair of electrons from each of six surrounding water molecules, e.g. $[Fe(H_2O)_6]^{3+}$.



# Properties of acids and bases

## TYPICAL PROPERTIES OF ACIDS AND BASES

A simple definition of an acid is that it is a substance that produces $H^+$ ions in aqueous solution. A base is a substance that can neutralize an acid. An alkali is a base that is soluble in water.

The typical reactions of acids are:

1. With indicators.

   Acid–base indicators can be used to determine whether or not a solution is acidic. Common indicators include:

| Indicator | Colour in acidic solution | Colour in alkaline solution |
|---|---|---|
| litmus | red | blue |
| phenolphthalein | colourless | pink |
| methyl orange | red | yellow |

2. Neutralization reactions with bases.

   **(a)** With hydroxides to form a salt and water,

   e.g. $CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$

   **(b)** With metal oxides to form a salt and water,

   e.g. $H_2SO_4(aq) + CuO(s) \rightarrow CuSO_4(aq) + H_2O(l)$

   **(c)** With ammonia to form a salt.

   e.g. $HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$

3. With reactive metals (those above copper in the reactivity series) to form a salt and hydrogen, e.g.

   $2HCl(aq) + Mg(s) \rightarrow$
   $MgCl_2(aq) + H_2(g)$

4. With carbonates (soluble or insoluble) to form a salt, carbon dioxide, and water, e.g.

   $2HNO_3(aq) + Na_2CO_3(aq) \rightarrow$
   $2NaNO_3(aq) + CO_2(g) + H_2O(l)$

   $2HCl(aq) + CaCO_3(s) \rightarrow$
   $CaCl_2(aq) + CO_2(g) + H_2O(l)$

5. With hydrogencarbonates to form a salt, carbon dioxide, and water, e.g.

   $HCl(aq) + NaHCO_3(aq) \rightarrow$
   $NaCl(aq) + CO_2(g) + H_2O(aq)$

## STRONG AND WEAK ACIDS AND BASES

A strong acid is completely dissociated (ionized) into its ions in aqueous solution. Similarly a strong base is completely dissociated into its ions in aqueous solution. Examples of strong acids and bases include:

| Strong acids | Strong bases |
|---|---|
| hydrochloric acid, $HCl$ | sodium hydroxide, $NaOH$ |
| nitric acid, $HNO_3$ | potassium hydroxide, $KOH$ |
| sulfuric acid, $H_2SO_4$ | barium hydroxide, $Ba(OH)_2$ |

Note: because one mole of HCl produces one mole of hydrogen ions it is known as a **monoprotic** acid. Sulfuric acid is known as a **diprotic** acid as one mole of sulfuric acid produces two moles of hydrogen ions.

Weak acids and bases are only slightly dissociated (ionized) into their ions in aqueous solution.

| Weak acids | Weak bases |
|---|---|
| ethanoic acid, $CH_3COOH$ | ammonia, $NH_3$ |
| 'carbonic acid' ($CO_2$ in water), $H_2CO_3$ | aminoethane, $C_2H_5NH_2$ |

The difference can be seen in their reactions with water:

Strong acid: $HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$
reaction goes to completion

Weak acid: $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$
equilibrium lies on the left

i.e. a solution of hydrochloric acid consists only of hydrogen ions and chloride ions in water, whereas a solution of ethanoic acid contains mainly undissociated ethanoic acid with only very few hydrogen and ethanoate ions.

Strong base: $KOH(s) \xrightarrow{H_2O(l)} K^+(aq) + OH^-(aq)$

Weak base: $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
equilibrium lies on the left

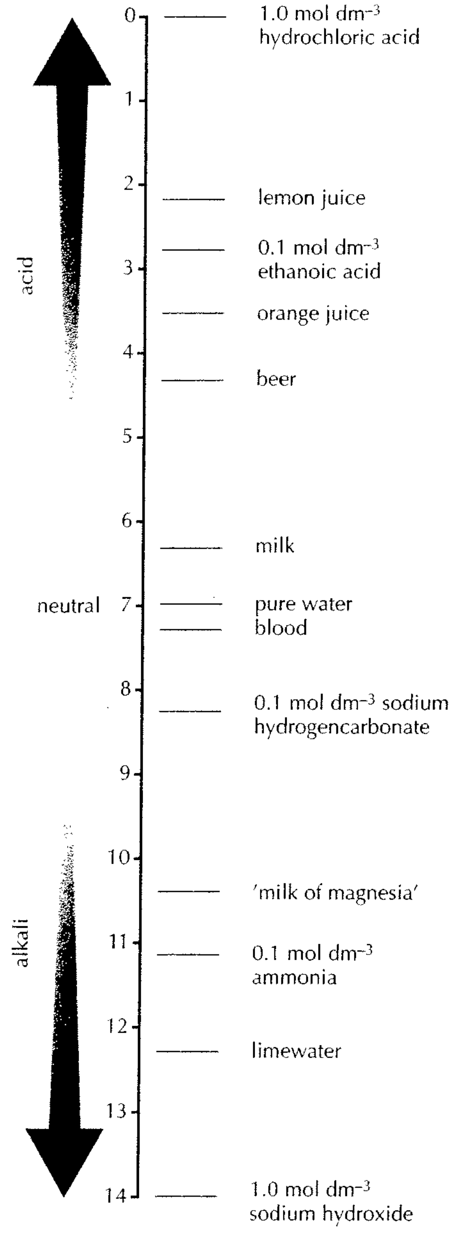
## EXPERIMENTS TO DISTINGUISH BETWEEN STRONG AND WEAK ACIDS AND BASES

1. pH measurement
   Because a strong acid produces a higher concentration of hydrogen ions in solution than a weak acid, with the same concentration, the pH of a strong acid will be lower than a weak acid. Similarly a strong base will have a higher pH in solution than a weak base, with the same concentration. The most accurate way to determine the pH of a solution is to use a pH meter.

   $0.10\ mol\ dm^{-3}\ HCl(aq)$ pH = 1.0
   $0.10\ mol\ dm^{-3}\ CH_3COOH$ pH = 2.9

2. Conductivity measurement
   Strong acids and strong bases in solution will give much higher readings on a conductivity meter than **equimolar** (equal concentration) solutions of weak acids or bases, because they contain more ions in solution.

# The pH scale



## THE pH SCALE

Pure water is very slightly dissociated:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

At 25 °C the equilibrium constant for this reaction is $1 \times 10^{-14}$ mol$^2$ dm$^{-6}$. The concentration of the hydrogen ions (which is the same as the concentration of the hydroxide ions) equals $1 \times 10^{-7}$ mol dm$^{-3}$.

pH (which stands for **p**ower of **H**ydrogen) is defined as being equal to minus the logarithm to the base ten of the hydrogen ion concentration. In practice this means that it is equal to the power of ten of the hydrogen ion concentration with the sign reversed. The pH of pure water is thus 7.

Pure water is neutral, so the pH of any neutral solution is 7. If the solution is acidic the hydrogen ion concentration will be greater than $10^{-7}$ mol dm$^{-3}$ and the pH will decrease. Similarly alkaline solutions will have a pH greater than 7.

The pH scale runs from 0 to 14. Because it depends on the power of ten a change in one unit in the pH corresponds to a tenfold change in the hydrogen ion concentration. A 0.1 mol dm$^{-3}$ solution of a strong monoprotic acid will have a pH of 1, a 0.001 mol dm$^{-3}$ solution of the same acid will have a pH of 3.

## THE LOG$_{10}$ SCALE AND p-SCALE

Normal scale – the distance between each number is equal

–5 –4 –3 –2 –1 0 1 2 3 4 5

Log$_{10}$ scale – the distances between powers of ten are equal

0.000 01 0.0001 0.001 0.01 0.1 1 10 100 1000 10 000 100 000

which can be written

$10^{-5}$ $10^{-4}$ $10^{-3}$ $10^{-2}$ $10^{-1}$ $10^{0}$ $10^{1}$ $10^{2}$ $10^{3}$ $10^{4}$ $10^{5}$

p-scale – sometimes used by chemists to express equilibrium constants and concentration. It is equal to minus the power of ten in the logarithmic scale so the scale becomes:

5 4 3 2 1 0 –1 –2 –3 –4 –5

## DETERMINATION OF pH

The pH of a solution can be determined by using a pH meter or by using 'universal' indicator, which contains a mixture of indicators which give a range of colours at different pH values.

| pH | [H$^+$]/ mol dm$^{-3}$ | [OH$^-$]/ mol dm$^{-3}$ | Description | Colour of universal indicator |
|---|---|---|---|---|
| 0 | 1 | $1 \times 10^{-14}$ | very acidic | red |
| 4 | $1 \times 10^{-4}$ | $1 \times 10^{-10}$ | acidic | orange |
| 7 | $1 \times 10^{-7}$ | $1 \times 10^{-7}$ | neutral | green |
| 10 | $1 \times 10^{-10}$ | $1 \times 10^{-4}$ | basic | blue |
| 14 | $1 \times 10^{-14}$ | 1 | very basic | purple |

## STRONG, CONCENTRATED, AND CORROSIVE

In English the words strong and concentrated are often used interchangeably. In chemistry they have very precise meanings:

- **strong**: completely dissociated into ions
- **concentrated**: a high number of moles of solute per litre (dm$^3$) of solution
- **corrosive**: chemically reactive.

Similarly weak and dilute also have very different chemical meanings:

- **weak**: only slightly dissociated into ions
- **dilute**: a low number of moles of solute per litre of solution.

# Calculations involving pH and pOH

## *THE IONIC PRODUCT OF WATER*

Pure water is very slightly ionized:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad \Delta H^\ominus = +57.3 \text{ kJ mol}^{-1}$$

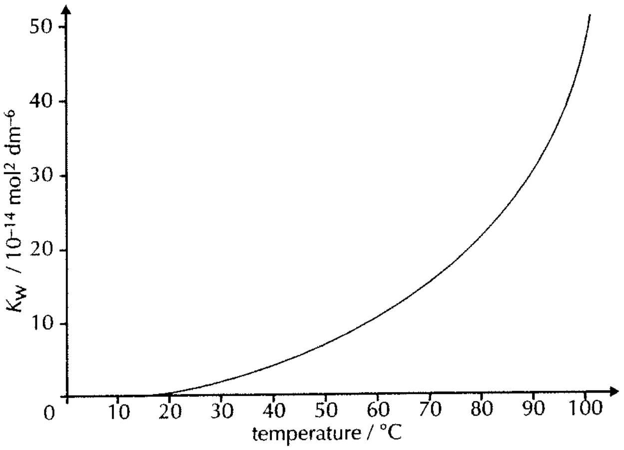
$$K_c = \frac{[H^+(aq)] \times [OH^-(aq)]}{[H_2O(l)]}$$

Since the equilibrium lies far to the left the concentration of water can be regarded as constant so

$K_w = [H^+(aq)] \times [OH^-(aq)] = 1.00 \times 10^{-14}$ mol$^2$ dm$^{-6}$ at 298 K, where $K_w$ is known as the ionic product of water.

The dissociation of water into its ions is an endothermic process, so the value of $K_w$ will increase as the temperature is increased.

**Variation of $K_w$ with temperature**



For pure water $[H^+(aq)] = [OH^-(aq)]$
$= 1.00 \times 10^{-7}$ mol dm$^{-3}$ at 298 K

From the graph the value for $K_w = 1.00 \times 10^{-13}$ at 334 K (61 °C)

At this temperature $[H^+(aq)] = \sqrt{1.00 \times 10^{-13}}$
$= 3.16 \times 10^{-7}$ mol dm$^{-3}$

## *pH, pOH, AND p$K_w$*

The pH of a solution depends only on the hydrogen ion concentration and is independent of the volume of solution.

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

**Strong acids**

For strong monoprotic acids $[H^+]$ will be equal to the concentration of the acid,

e.g. for 0.100 mol dm$^{-3}$ HCl

$[H^+] = 0.100$ mol dm$^{-3}$
$pH = -\log_{10} 0.100 = 1.0$

For a strong diprotic acid the hydrogen ion concentration will be equal to twice the acid concentration,

e.g. for 0.025 mol dm$^{-3}$ $H_2SO_4$

$[H^+] = 2 \times 0.025 = 0.050$ mol dm$^{-3}$
$pH = 1.3$

Note: it has been assumed that sulfuric acid is a strong acid. In reality the $HSO_4^-$ ion is only partially dissociated in aqueous solution.

**pOH for strong bases**

For a strong base the hydrogen ion concentration can be calculated using the ionic product of water,

e.g. for $1.00 \times 10^{-3}$ mol dm$^{-3}$ NaOH

$[OH^-] = 1.00 \times 10^{-3}$ mol dm$^{-3}$
$[H^+] \times [OH^-] = 1.00 \times 10^{-14}$

$$\Rightarrow [H^+] = \frac{1.00 \times 10^{-14}}{1.00 \times 10^{-3}} = 1.00 \times 10^{-11} \text{ mol dm}^{-3}$$

$pH = -\log_{10} 1.00 \times 10^{-11} = 11.0$

The pH of alkaline solutions can also be calculated by using pOH and the relationship between pOH, pH, and p$K_w$.

$$[H^+] \times [OH^-] = K_w \quad pOH = -\log_{10} [OH^-] \quad pK_w = -\log_{10} K_w = 14$$

$$pH + pOH = 14$$

e.g for $4.00 \times 10^{-2}$ mol dm$^{-3}$ $Ba(OH)_2$

$[OH^-] = 2 \times (4.00 \times 10^{-2}) = 8.00 \times 10^{-2}$ mol dm$^{-3}$

$pOH = 1.10$

$\Rightarrow pH = 14 - 1.10 = 12.9$

# Calculations with weak acids and bases

## WEAK ACIDS

The dissociation of a weak acid HA in water can be written:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

The equilibrium expression for this reaction is:

$$K_a = \frac{[H^+] \times [A^-]}{[HA]}$$ where $K_a$ is known as the acid dissociation constant

For example, to calculate the pH of 0.10 mol dm$^{-3}$ $CH_3COOH$ given that $K_a = 1.8 \times 10^{-5}$ mol dm$^{-3}$ at 298 K:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

Initial concentration / mol dm$^{-3}$

0.10 – –

Equilibrium concentration / mol dm$^{-3}$

$(0.10 - x)$ $x$ $x$

$$K_a = \frac{[CH_3COO^-] \times [H^+]}{[CH_3COOH]} = \frac{x^2}{(0.10 - x)}$$

$= 1.8 \times 10^{-5}$ mol dm$^{-3}$

$\Rightarrow x^2 + (1.8 \times 10^{-5}x) - 1.8 \times 10^{-6} = 0$

by solving the quadratic equation

$x = 1.33 \times 10^{-3}$ mol dm$^{-3}$

$pH = -\log_{10} 1.33 \times 10^{-3} = 2.88$

If the acids are quite weak the equilibrium concentration of the acid can be assumed to be the same as its initial concentration. Provided the assumption is stated it is usual to simplify the expression in calculations to avoid a quadratic equation. In the above example:

$$K_a = \frac{[CH_3COO^-] \times [H^+]}{[CH_3COOH]} \approx \frac{[H^+]^2}{0.10}$$

$= 1.8 \times 10^{-5}$ mol dm$^{-3}$

$\Rightarrow [H^+] = \sqrt{1.8 \times 10^{-6}} = 1.34 \times 10^{-3}$ mol dm$^{-3}$

pH = 2.87

**Examples of other weak acid calculations**

1. The pH of a 0.020 mol dm$^{-3}$ solution of a weak acid is 3.9. Find the $K_a$ of the acid.

$$K_a = \frac{[H^+]^2}{(0.020 - [H^+])} \approx \frac{10^{-3.9} \times 10^{-3.9}}{0.020}$$

$= 7.92 \times 10^{-7}$ mol dm$^{-3}$

2. An acid whose $K_a$ is $4.1 \times 10^{-6}$ mol dm$^{-3}$ has a pH of 4.5. Find the concentration of the acid.

$$[HA] = \frac{[H^+]^2}{K_a} = \frac{10^{-4.5} \times 10^{-4.5}}{4.1 \times 10^{-6}}$$

$= 2.44 \times 10^{-4}$ mol dm$^{-3}$

## WEAK BASES

The reaction of a weak base can be written:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

Since the concentration of water is constant:

$$K_b = \frac{[BH^+] \times [OH^-]}{[B]}$$

where $K_b$ is the base dissociation constant

If one considers the reverse reaction of $BH^+$ acting as an acid to give B and $H^+$ then:

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

then $$K_a \times K_b = \frac{[B] \times [H^+]}{[BH^+]} \times \frac{[BH^+] \times [OH^-]}{[B]}$$

$$= [H^+] \times [OH^-] = K_w$$

since $pK_a = -\log_{10} K_a$; $pK_b = -\log_{10} K_b$ and $pK_w = -\log_{10} K_w = 14$ this can also be expressed as:

$pK_a + pK_b = 14$

**Examples of calculations**

1. The $K_b$ value for ammonia is $1.8 \times 10^{-5}$ mol dm$^{-3}$. Find the pH of a $1.00 \times 10^{-2}$ mol dm$^{-3}$ solution.

Since $[NH_4^+] = [OH^-]$ then

$$K_b = \frac{[OH^-]^2}{[NH_3]} \approx \frac{[OH^-]^2}{1.00 \times 10^{-2}} = 1.8 \times 10^{-5}$$

$[OH^-] = \sqrt{1.8 \times 10^{-7}} = 4.24 \times 10^{-4}$ mol dm$^{-3}$

$\Rightarrow pOH = -\log_{10} 4.24 \times 10^{-4} = 3.37$

$\Rightarrow pH = 14 - 3.37 = 10.6$

2. The pH of a $3.00 \times 10^{-2}$ mol dm$^{-3}$ solution of weak base is 10.0. Calculate the $pK_b$ value of the base.

pH = 10.0 so pOH = 4.0

$$K_b = \frac{10^{-4} \times 10^{-4}}{3.00 \times 10^{-2}} = 3.33 \times 10^{-7} \text{ mol dm}^{-3}$$

$\Rightarrow pK_b = 6.48$

3. The IB data booklet value for the $pK_a$ of methylamine (aminomethane) is 10.64. Calculate the concentration of a solution of methylamine with a pH of 10.8.

$pK_b = 14 - 10.64 = 3.36$; pOH = 3.2

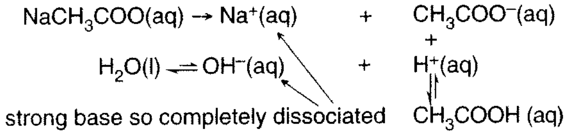
$$[CH_3NH_2] = \frac{[OH^-]^2}{K_b} = \frac{10^{-3.2} \times 10^{-3.2}}{10^{-3.36}}$$

$= 9.13 \times 10^{-4}$ mol dm$^{-3}$

# Salt hydrolysis and buffer solutions

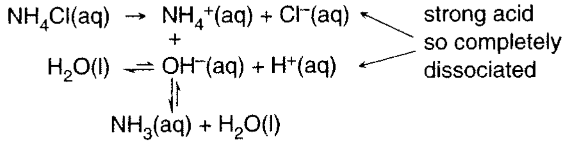
## SALT HYDROLYSIS

Sodium chloride is neutral in aqueous solution. It is the salt of a strong acid and a strong base. Salts made from a weak acid and a strong base, such as sodium ethanoate, are alkaline in solution. This is because the ethanoate ions will combine with hydrogen ions from water to form mainly undissociated ethanoic acid, leaving excess hydroxide ions in solution.



$$\begin{array}{lcl} NaCH_3COO(aq) \rightarrow Na^+(aq) & + & CH_3COO^-(aq) \\ & & + \\ H_2O(l) \rightleftharpoons OH^-(aq) & + & H^+(aq) \\ & & \updownarrow \\ \text{strong base so completely dissociated} & & CH_3COOH(aq) \end{array}$$

Similarly salts derived from a strong acid and a weak base will be acidic in solution.

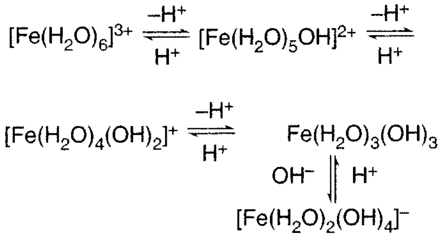


$$\begin{array}{ll} NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq) & \\ \qquad\qquad\quad + & \text{strong acid so completely dissociated} \\ H_2O(l) \rightleftharpoons OH^-(aq) + H^+(aq) & \\ \qquad\qquad\quad \updownarrow & \\ \qquad NH_3(aq) + H_2O(l) & \end{array}$$

The acidity of salts also depends on the size and charge of the cation. Aluminium chloride reacts vigorously with water to give an acidic solution.

$$AlCl_3(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3HCl(aq)$$

The +3 charge is spread over a very small ion, which gives the $Al^{3+}$ ion a very high charge density. The lone pair of one of the six water molecules surrounding the ion will be strongly attracted to the ion and the water molecule will lose a hydrogen ion in the process. This process will continue until aluminium hydroxide is formed. The equilibrium can be moved further to the right by adding $OH^-(aq)$ ions or back to the left by adding $H^+(aq)$ ions, which exemplifies the amphoteric nature of aluminium hydroxide. Similar examples of hydrolysis in aqueous solution occur with other small highly charged ions such as $Fe^{3+}$.



$$[Fe(H_2O)_6]^{3+} \underset{H^+}{\overset{-H^+}{\rightleftharpoons}} [Fe(H_2O)_5OH]^{2+} \underset{H^+}{\overset{-H^+}{\rightleftharpoons}}$$

$$\begin{array}{lc} [Fe(H_2O)_4(OH)_2]^+ \underset{H^+}{\overset{-H^+}{\rightleftharpoons}} & Fe(H_2O)_3(OH)_3 \\ & OH^- \updownarrow H^+ \\ & [Fe(H_2O)_2(OH)_4]^- \end{array}$$

Even $MgCl_2$ is slightly acidic in aqueous solution for the same reason.

| | Charge | Ionic radius / nm | Aqueous solution |
|---|---|---|---|
| $Na^+$ | +1 | 0.098 | neutral |
| $Mg^{2+}$ | +2 | 0.065 | acidic |
| $Al^{3+}$ | +3 | 0.045 | acidic |

## BUFFER SOLUTIONS

A buffer solution resists changes in pH when small amounts of acid or alkali are added to it.

An acidic buffer solution can be made by mixing a weak acid together with the salt of that acid and a strong base. An example is a solution of ethanoic acid and sodium ethanoate. The weak acid is only slightly dissociated in solution, but the salt is fully dissociated into its ions, so the concentration of ethanoate ions is high.

$$NaCH_3COO(aq) \rightarrow Na^+(aq) + CH_3COO^-(aq)$$
$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

If an acid is added the extra $H^+$ ions coming from the acid are removed as they combine with ethanoate ions to form undissociated ethanoic acid, so the concentration of $H^+$ ions remains unaltered.

$$CH_3COO^-(aq) + H^+(aq) \rightleftharpoons CH_3COOH(aq)$$

If an alkali is added the hydroxide ions from the alkali are removed by their reaction with the undissociated acid to form water, so again the $H^+$ ion concentration stays constant.

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

In practice acidic buffers are often made by taking a solution of a strong base and adding excess weak acid to it, so that the solution contains the salt and the unreacted weak acid.

$$\underset{\text{limiting reagent}}{NaOH(aq)} + CH_3COOH(aq) \rightarrow \underbrace{\underset{\text{salt}}{NaCH_3COO(aq)} + H_2O(l) + \underset{\text{excess weak acid}}{CH_3COOH(aq)}}_{\text{buffer solution}}$$

An alkali buffer with a fixed pH greater than 7 can be made from a weak base together with the salt of that base with a strong acid. An example is ammonia with ammonium chloride.

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$
$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

If $H^+$ ions are added they will combine with $OH^-$ ions to form water and more of the ammonia will dissociate to replace them. If more $OH^-$ ions are added they will combine with ammonium ions to form undissociated ammonia. In both cases the hydroxide ion concentration and the hydrogen ion concentration remain constant.

# Buffer calculations

## BUFFER CALCULATIONS

The equilibrium expression for weak acids also applies to acidic buffer solutions.

In the buffer made from an aqueous solution of sodium ethanoate and ethanoic acid the salt is completely dissociated but the acid is only slightly dissociated.

$$NaCH_3COO(aq) \rightarrow Na^+(aq) + CH_3COO^-(aq)$$

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

$$K_a = \frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]}$$

The essential difference is that now the concentrations of the two ions from the acid will not be equal. Since the sodium ethanoate is completely dissociated the concentration of the ethanoate ions in solution will be almost the same as the concentration of the sodium ethanoate as very little will come from the acid.

If logarithms to the base ten are taken then:

$$\log_{10}K_a = \log_{10}[H^+] + \log_{10}\frac{[CH_3COO^-]}{[CH_3COOH]}$$

or:

$$-\log_{10}[H^+] = -\log_{10}K_a + \log_{10}\frac{[CH_3COO^-]}{[CH_3COOH]}$$

Which gives:

$$pH = pK_a + \log_{10}\frac{[CH_3COO^-]}{[CH_3COOH]}$$

Two facts can be deduced from this expression. Firstly the pH of the buffer does not change on dilution as the concentration of the ethanoate ions and the acid will be affected equally. Secondly the buffer will be most efficient when $[CH_3COO^-] = [CH_3COOH]$. At this point, which equates to the half equivalence point when ethanoic acid is titrated with sodium hydroxide, the pH of the solution will equal the $pK_a$ value of the acid.

## WORKED EXAMPLES

(a) Calculate the pH of a buffer solution containing 0.2 mol of sodium ethanoate in 500 cm$^3$ of 0.10 mol dm$^{-3}$ ethanoic acid (given that $K_a$ for ethanoic acid = 1.8 x 10-5 mol dm$^{-3}$).

**Step 1.** Find the concentration of the ethanoate ion and the ethanoic acid.

$[CH_3COO^-] = 0.4$ mol dm$^{-3}$;
$[CH_3COOH] = 0.1$ mol dm$^{-3}$

**Step 2.** Make the assumptions that the equilibrium concentration of the acid is the same as the undissociated acid and that all the ethanoate ions come from the salt.

**Step 3.** Substitute the values into the expression for the acid dissociation constant.

$$K_a = \frac{[H^+] \times 0.4}{[CH_3COOH]}$$

$= 1.8 \times 10^{-5}$ mol dm$^{-3}$

**Step 4.** Calculate the value for $[H^+]$ and hence the pH

$[H^+] = 4.5 \times 10^{-6}$ mol dm$^{-3}$

$pH = -\log_{10}(4.5 \times 10^{-6}) = 5.4$

(b) Calculate what mass of sodium propanoate must be dissolved in 1.0 dm$^3$ of 1.0 mol dm$^3$ propanoic acid ($pK_a$ = 4.87) to give a buffer solution with a pH of 4.5.

**Step 1.** Determine the hydrogen ion concentration from the pH

$[H^+] = 10^{-4.5} = 3.16 \times 10^{-5}$ mol dm$^{-3}$ (although this can be kept as $10^{-4.5}$)

**Step 2.** Assume the acid concentration in the buffer is the same as the undissociated acid.

**Step 3.** Use the expression for $K_a$ to find the propanoate ion concentration.

$$[C_2H_5COO\text{-}] = \frac{K_a \times [C_2H_5COOH]}{[H^+]}$$

$$= \frac{10^{-4.87} \times 1.0}{10^{-4.5}} = 0.427 \text{ mol dm}^{-3}$$

**Step 4.** Calculate the $M_r$ for the salt and assume that all the propanoate ions come from the salt to determine the mass of salt required.

$M_r\ (NaC_2H_5COO) = [23 + (3 \times 12.01) + (5 \times 1.01) + (2 \times 16.00) = 96.08$

Mass of $NaC_2H_5COO$ required = 0.427 x 96.08 = 41.0g

(c) Calculate the pH of the buffer formed when 18.0 cm$^3$ of 0.100 mol dm$^{-3}$ hydrochloric acid is added to 32.0 cm$^3$ of 0.100 mol dm$^{-3}$ ammonia solution. ($pK_b$ for $NH_3$ = 4.75).

**Step 1.** Calculate the amount of the excess ammonia and the amount of salt formed.

$$HCl(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

Initial amount of

$$HCl = \frac{18.0}{1000} \times 0.100 = 1.80 \times 10^{-3} \text{ mol}$$

Initial amount of

$$NH_3 = \frac{32}{1000} \times 0.100 = 3.20 \times 10^{-3} \text{ mol}$$

Amount of ammonium salt = $1.80 \times 10^{-3}$ mol

Amount of excess ammonia
$= 3.20 \times 10^{-3} - 1.80 \times 10^{-3} = 1.6 \times 10^{-3}$ mol

**Step 2.** Calculate the equilibrium concentrations making the usual assumptions.

Since the combined volume = 50.0 cm$^3$

$[NH_4^+] = 3.6 \times 10^{-2}$ mol dm$^{-3}$ and $[NH_3]$
$= 3.2 \times 10^{-2}$ mol dm$^{-3}$

**Step 3.** Substitute into the expression for $K_b$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$= \frac{3.6 \times 10^{-2}}{3.2 \times 10^{-2}} \times [OH^-] = 10^{-4.75}$$

**Step 4.** Calculate $[OH^-]$ then pOH then pH

$[OH^-] = 0.889 \times 10^{-4.75} = 1.58 \times 10^{-5}$ mol dm$^{-3}$

$pOH = -\log_{10} 1.58 \times 10^{-5} = 4.80$

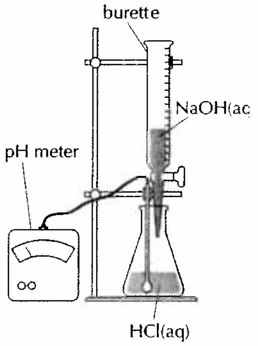
$pH = 14 - pOH = 9.2$

# HL Titration curves and indicators

## STRONG ACID – STRONG BASE TITRATION

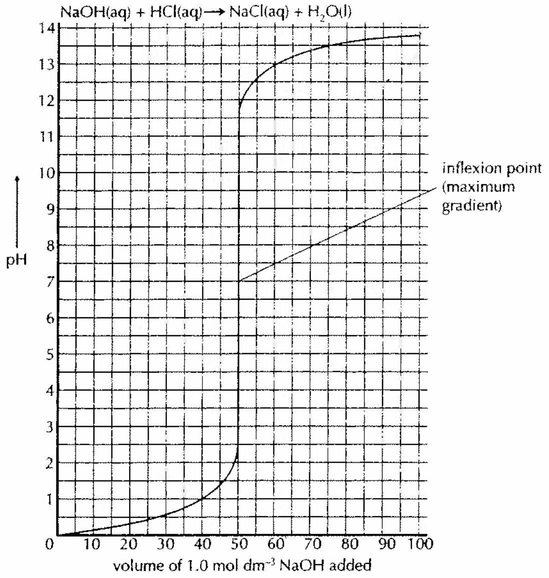
The change in pH during an acid–base titration can be followed using a pH meter. Consider starting with 50 cm$^3$ of 1.0 mol dm$^{-3}$ hydrochloric acid. Since $[H^+(aq)] = 1.0$ mol dm$^{-3}$ the initial pH will be 0. After 49 cm$^3$ of 1.0 mol dm$^{-3}$ NaOH have been added there will be 1.0 cm$^3$ of the original 1.0 mol dm$^{-3}$ hydrochloric acid left in 99 cm$^3$ of solution. At this point $[H^+(aq)] \approx 1.0 \times 10^{-2}$ mol dm$^{-3}$ so the pH = 2.

When 50 cm$^3$ of the NaOH solution has been added the solution will be neutral and the pH will be 7. This is indicated by the point of inflexion, which is known as the equivalence point. It can be seen that there is a very large change in pH around the equivalence point. Almost all of the common acid–base indicators change colour (reach their end point) within this pH region. This means that it does not matter which indicator is used.



This curve shows what happens when 1.0 mol dm$^{-3}$ sodium hydroxide is added to 50 cm$^3$ of 1.0 mol dm$^{-3}$ hydrochloric acid

$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$



## WEAK ACID – STRONG BASE TITRATION

Consider titrating 50.0 cm$^3$ of 1.0 mol dm$^{-3}$ $CH_3COOH$ with 1.0 mol dm$^{-3}$ NaOH.

$K_a = 1.8 \times 10^{-5}$. Making the usual assumptions the initial $[H^+] = \sqrt{K_a \times [CH_3COOH]}$ and pH = 2.37.

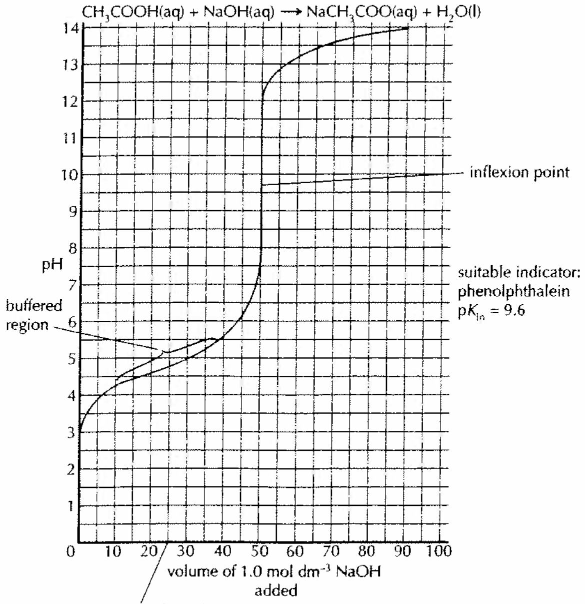
When 49.0 cm$^3$ of the 1.0 mol dm$^{-3}$ NaOH has been added $[CH_3COO^-] \approx 0.05$ mol dm$^{-3}$ and $[CH_3COOH] \approx 1.0 \times 10^{-2}$ mol dm$^{-3}$.

$$[H^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} \approx \frac{1.8 \times 10^{-5} \times 1 \times 10^{-3}}{0.05}$$

$$= 3.6 \times 10^{-7} \text{ mol dm}^{-3} \text{ and pH} = 6.44$$

After the equivalence point the graph will follow the same pattern as the strong acid – strong base curve as more sodium hydroxide is simply being added to the solution.

$CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$



When 25 cm$^3$ of alkali have been added, half the acid has been turned into its salt, so $pK_a$ = pH.

## INDICATORS

An indicator is a weak acid (or base) in which the dissociated form is a different colour to the undissociated form.

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

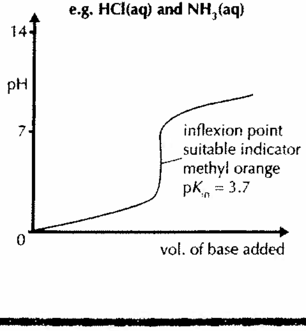
| | |
|---|---|
| colour A | colour B |
| (colour in acid solution) | (colour in alkali solution) |

$K_{in} = [H^+] \times \frac{[In^-]}{[HIn]}$ Assuming the colour changes when $[In^-] \approx [H_{in}]$ then the end point of the indicator will be when $[H^+] \approx K_{in}$, i.e. when pH $\approx pK_{in}$. Different indicators have different $K_{in}$ values and so change colour within different pH ranges.

| **Indicator** | **$pK_{in}$** | **pH range** | **Use** |
|---|---|---|---|
| methyl orange | 3.7 | 3.1–4.4 | titrations with strong acids |
| phenolphthalein | 9.6 | 8.3–10.0 | titrations with strong bases |

Similar arguments can be used to explain the shapes of pH curves for strong acid – weak base, and weak acid – weak base titrations. Since there is no sharp inflexion point titrations involving weak acids with weak bases should not be used in analytical chemistry.

**Strong acid – weak base**
**e.g. HCl(aq) and $NH_3$(aq)**



**Weak acid – weak base**
**e.g. $CH_3COOH$(aq) and $NH_3$(aq)**