Acid Base Equilibria

Introduction

Acids occur in natural systems. Citric acid is produced by a number of plants in their fruit. Early investigations of acids found them to have a sour taste. In the nineteenth century a Swedish chemistry by the name of Arrhenius suggested that acid were substances that dissolved in water forming hydrogen ions, H^+. For example in hydrochloric acid, the dissolved hydrogen chloride undergoes the following reaction:

$$HCl \rightarrow H^+ + Cl^-$$

Arrhenius also proposed that strong acid were fully dissociated into ions, but that weak acids were only partially dissociated.

As knowledge of atomic structure grew, it was understood that a hydrogen ions was simply a proton, and that it was unlikely that protons would exist independently in solution. Consequently it was proposed that the hydrogen ions join with water molecules in solution to form the hydroxonium ion, H_3O^+. So the reaction taking place when hydrogen chloride dissolves should be written:

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

This idea was taken further in the Bronstead Lowry theory of acids.

The Bronstead-Lowry Theory

When hydrogen bromide is dissolved in water, it forms an acid as the following reaction takes place:

$$HBr + H_2O \rightleftharpoons H_3O^+ + Br^-$$

In this reaction the hydrogen bromide transfers a proton to a water molecule. The Bronstead-Lowry theory uses this idea to form a more general theory of acids.
According to Bronstead-Lowry;

An acid is a proton donor
and **A base is a proton acceptor.**

So in the reaction between hydrogen bromide and water the HBr donates a proton to the water, so the HBr is the acid and the water is acting as a base.

Examples;

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$$

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$$

$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$

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

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

These reactions can be regarded as equilibrium. In the reverse reaction the proton moves back in the other direction, so the right hand side of the equation also has a proton donor and a proton acceptor (or acid and base).
The proton donor and proton acceptor on the right hand side of the equation are called the **conjugate acid** and **conjugate base**.

So

$$\underset{\text{ACID}}{HBr} + \underset{\text{BASE}}{H_2O} \rightleftharpoons \underset{\text{CONJ ACID}}{H_3O^+} + \underset{\text{CONJ BASE}}{Br^-}$$

Examples	ACID		BASE		Conjugate ACID		Conjugate BASE
	CH_3CO_2H	+	H_2O	$\rightleftharpoons$	H_3O^+	+	$CH_3CO_2^-$
	H_2O	+	NH_3	$\rightleftharpoons$	NH_4^+	+	OH^-
	H_2O	+	CO_3^{2-}	$\rightleftharpoons$	HCO_3^-	+	OH^-

The pH concept

Since it is the hydroxonium ion, H_3O^+, that causes a material to be acidic, the higher the concentration of this ion, the greater the acidity.
The concentration of this ion is measured on the pH scale.
This is a log scale defined as follows;

$$\mathbf{pH = -log[H^+]}$$

For a strong acid, it is assumed that all the molecules form H^+ ions.

Find the pH of

(a)	0.1 mol dm^{-3} HCl	*-log 0.1 = 1*
(b)	0.01 mol dm^{-3} HNO_3	*-log 0.01 = 2*
(c)	0.2 mol dm^{-3} HCl	*-log 0.2 = 0.7*
(d)	0.001 mol dm^{-3} HI	*-log 0.001 = 3*

Note – For strong acids a 10 fold ditultion (0.1 mol dm^{-3} to 0.01 mol dm^{-3}) results in a pH change of 1 unit.

Some acids, such as sulphuric are **dibasic**; this means they can release two hydrogen ions from each molecule. So a 1 mol dm^{-3} solution of $\mathbf{H_2}SO_4$ actually has a hydrogen ion concentration of 2 mol dm^{-3}.

Find the pH of

(e)	0.1 mol dm^{-3} H_2SO_4	*$[H^+]$ = 0.2 mol dm^{-3}*	*pH = -log 0.2 = 0.7*
(f)	0.01 mol dm^{-3} H_2SO_4	*$[H^+]$ = 0.02 mol dm^{-3}*	*pH = -log 0.02 = 1.7*

Note – Once again a 10 fold ditultion (0.2 mol dm^{-3} to 0.02 mol dm^{-3}) results in a pH change of 1 unit. Sulphuric acid is therefore a strong acid)

As a log scale the pH changes by one unit each time the concentration changes by 10 times.

Concentration of H_3O^+ in $moldm^-$	**pH**

3	
1	*0*
$1x10^{-1}$	*1*
$1x10^{-2}$	*2*
$1x10^{-3}$	*3*
$1x10^{-4}$	*4*
$1x10^{-5}$	*5*
$1x10^{-6}$	*6*
$1x10^{-7}$	*7*
$1x10^{-8}$	*8*
$1x10^{-9}$	*9*
$1x10^{-10}$	*10*
$1x10^{-11}$	*11*
$1x10^{-12}$	*12*
$1x10^{-13}$	*13*
$1x10^{-14}$	*14*

The dissociation constant (ionic product) K_w, for water.

Water molecules dissociate $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$
and the concentration of H_3O^+ ions at 25^oC is 1×10^{-7} mol dm^{-3}, that is pH 7, and this is taken as neutral.
This equilibrium exists in any solution in water.
If the material is an acid and increases the H_3O^+ concentration, the concentration of OH^- decreases correspondingly, so that when the H_3O^+ concentration is multiplied by the OH^- concentration the same value is always obtained.

In water the concentration of H_3O^+ and OH^- are both 1×10^{-7} mol dm^{-3}.

So when the two are multiplied $1 \times 10^{-7} \times 1 \times 10^{-7} = 1 \times 10^{-14}$ $mol^2\,dm^{-6}$

This value is always the same for any solution in water.
It is called the **water dissociation constant, K_w.**

K_w allows us to find the concentration of H_3O^+ in alkalis and consequently to calculate their pH.

$$\mathbf{K_w = [H_3O^+] \times [OH^-] = 1 \times 10^{-14}\ mol^2\,dm^{-6}}$$

$$\text{And}\quad [H_3O^+] = \frac{K_w}{[OH^-]}$$

So for sodium hydroxide solution of concentration $0.01 moldm^{-3}$

$$[H_3O^+] = \frac{1 \times 10^{-14}}{0.01} = 1 \times 10^{-12}$$

$$pH = -\log(1 \times 10^{-12}) = 12$$

Examples

1. For potassium hydroxide solution of concentration 0.2 mol dm^{-3}.

$$[H_3O^+] = \frac{1 \times 10^{-14}}{0.2} = 5 \times 10^{-14}$$

$pH = -\log 5 \times 10^{-14} = 13.3$

2. For sodium hydroxide solution of concentration 0.05 mol dm^{-3}.

$$[H_3O^+] = \frac{1 \times 10^{-14}}{0.05} = 2 \times 10^{-13}$$

$pH = -\log 2 \times 10^{-13} = 12.7$

Strong and weak acids and bases

The acidity of a solution is measured using the pH scale.
If the same concentration of hydrochloric acid and ethanoic acid were taken, they would **not** have the same pH value. This is because the hydrochloric acid **dissociates** (splits up) **completely** into H_3O^+ and Cl^- ions, whereas only a small fraction of ethanoic acid molecules dissociate.

When an acid is fully or near fully dissociated, it is said to be a strong acid, but one which is only slightly dissociated is said to be a weak acid. This should not be confused with concentration of the acid.
The same idea applies to bases. A strong base is one in which the particles **dissociate completely** to form hydroxide ions.

Solution	**Concentration of solution / moldm^{-3}**	**Concentration of H_3O^+ / moldm^{-3}**	**pH**
Hydrochloric acid	0.1	0.1	1
Ethanoic acid	0.1	0.0013	2.9
Hydrofluoric acid	0.1	0.024	1.6
Hydrocyanic acid	0.1	0.00002	4.7

Enthalpy of Neutralisation

When an acid is added to an alkali, there is a temperature change. This is due to the energy produced from the reaction; $H^+ + OH^- \rightarrow H_2O$ the enthalpy for this reaction is -57.3kJ mol^{-1}.

So whenever a strong acid and a strong base are added together this is the enthalpy change for the reaction. With a weak acid or base the enthalpy change for the reaction is less exothermic than this, as some energy is used in dissociating the acid.

Standard Molar Enthalpy of Neutralisation (ΔH_n) is the enthalpy change per mole of water formed in the neutralisation of an acid by an alkali, (298K and 1 atm).

Examples

Reaction	Enthalpy change /kJmol^{-1}	
Nitric acid + sodium hydroxide	-57.3	
Hydrochloric acid + ammonia	-52.2	Energy used to dissociate NH_3
Ethanoic acid + sodium hydroxide	-55.2	Energy used to dissociate CH_3CO_2H
Hydrocyanic acid + ammonia	-5.4	Energy used to dissociate HCN and NH_3

Acid dissociation constant K_a

We have seen that a strong acid, such as hydrochloric, is one which is fully dissociated.

The greater the dissociation, the stronger the acid. The amount of dissociation, and therefore an indication of the strength of an acid, is measured using the dissociation constant.
The dissociation of an acid is an equilibrium process, and the dissociation constant is derived from the equilibrium constant.

The equilibrium expression for the dissociation of acid, HA, is:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

The equilibrium constant is

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

In a dilute solution the concentration of the water is not going to change significantly during the dissociation process, and so for these reactions it can be taken as constant.
So;

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

This new constant is the acid dissociation constant, K_a

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

The lower of the acid dissociation constant, K_a, the weaker the acid.

This equation can then be used to find the pH of a weak acid.

Calculating the pH of a weak acid

The acid dissociation expression can be rearranged:

$$K_a[HA] = [H_3O^+][A^-]$$

Since every molecule of HA gives one A^- ion and one H_3O^+ ion, there must be equal numbers of the two ions in any solution, and so $[H_3O^+]$ is equal to $[A^-]$.

Since $[H_3O^+] = [A^-]$, then

$$K_a[HA] = [H_3O^+]^2$$

So $$[H_3O^+] = \sqrt{Ka[HA]}$$

From the $[H_3O^+]$ the pH can be found;

$$pH = -\log[H_3O^+] = -\log\sqrt{Ka[HA]}$$

All these calculations assume that;

i) because it is a weak acid and only partially dissociated, that the [HA] does not change significantly on dissociation.
ii) There are no extra H_3O^+ ions produced from the water in the acid.

Examples
Find the pH of the following solutions of ethanoic acid.
Ethanoic acid has a K_a value of 1.75×10^{-5} *mol dm*$^{-3}$

(a) 1 mol dm^{-3}

$$[H_3O^+] = \sqrt{1 \text{ x } 1.75 \text{ x } 10^{-5}} = 4.18 \text{ x } 10^{-3} \text{ moldm}^{-3}$$

$$pH = -\log 4.18 \text{ x } 10^{-3} = 2.38$$

(b) 2 mol dm^{-3}

$$[H_3O^+] = \sqrt{2 \text{ x } 1.75 \text{ x } 10^{-5}} = 5.92 \text{ x } 10^{-3} \text{ moldm}^{-3}$$

$$pH = -\log 5.92 \text{ x } 10^{-3} = 2.23$$

(c) 0.1 mol dm^{-3}

$$[H_3O^+] = \sqrt{0.1 \text{ x } 1.75 \text{ x } 10^{-5}} = 1.32 \text{ x } 10^{-3} \text{ moldm}^{-3}$$

$$pH = -\log 1.32\text{x } 10^{-3} = 2.88$$

(d) 0.2 mol dm^{-3}

$$[H_3O^+] = \sqrt{0.2 \text{ x } 1.75 \text{ x } 10^{-5}} = 1.87\text{x } 10^{-3} \text{ moldm}^{-3}$$

$$pH = -\log 1.87 \text{ x } 10^{-3} = 2.73$$

It is possible to find the K_a value of an acid by finding the pH of a solution of known concentration.

Example

(a) Nitrous acid of concentration 0.1 mol dm^{-3} has a pH of 2.17.
Calculate its K_a value.

$$[H_3O^+] = 10^{-2.17} = 6.76 \text{ x}10^{-3} \text{ moldm}^{-3}$$

$$K_a = \frac{[H_3O^+]^2}{[HA]} \qquad \frac{(6.76 \text{ x}10^{-3})^2}{0.1} \qquad = 4.57 \text{ x } 10^{-4} \text{ moldm}^{-3}$$

(b) Bromic(I) acid of concentration 1.0 moldm^{-3} has a pH of 4.35.
Calculate its K_a value.

$$[H_3O^+] = 10^{-4.35} = 4.47 \text{ x}10^{-5} \text{ moldm}^{-3}$$

$$K_a = \frac{[H_3O^+]^2}{[HA]} \qquad \frac{(4.47 \text{ x}10^{-5})^2}{1.0} \qquad = 2.00 \text{ x } 10^{-9} \text{ moldm}^{-3}$$

(c) Hydrofluoric acid of concentration 0.2 moldm^{-3} has a pH of 1.97.
Calculate its K_a value.

$$[H_3O^+] = 10^{-1.97} = 0.0107 \text{ moldm}^{-3}$$

$$K_a = \frac{[H_3O^+]^2}{[HA]} \qquad \frac{(0.0107)^2}{0.1} \qquad = 5.74 \text{ x } 10^{-4} \text{ moldm}^{-3}$$

Dilution of Strong and Weak Acids

Since strong acid are fully dissociated, as they are diluted, the hydrogen ions concentration falls in line with the dilution factor. **For each dilution of 10x, the pH increases by 1 unit.**

Weak acids are in equilibrium however, and so as they are diluted, some of the undissociated acid molecules split up, so the pH does not increase as fast as it does with the strong acid.
For each dilution of 10x, the pH increases by 0.5 unit, and for each dilution of 100x, the pH increases by 1 unit.

The table below shows how pH changes as an acid is diluted.

Dilution factor	Concentration of acid /moldm^{-3}	pH of strong acid (monobasic)	pH of weak acid (monobasic)
0	0.1	1	2.88
10x	0.01	2	3.38
100x	0.001	3	3.88
1000x	0.0001	4	4.38

pKa and pKw values

K_a and K_w quantities are normally very small inconvenient numbers.
e.g. K_a for ethanoic acid is about 10^{-5} mol dm^{-3} and K_w is about 10^{-14} mol^{2}dm^{-6}.

pK_a and pK_w give more convenient numbers in the same way that pH values are easier than hydrogen ion concentrations.

$$\mathbf{pKa = -logK_a}$$

$$\mathbf{pKw = -logK_w}$$

Examples - Find pK_a values for;

(a) Ethanoic acid $pK_a = -\log 1.75 \times 10^{-5} = 4.76$

(b) Nitrous acid $pK_a = -\log 4.57 \times 10^{-4} = 3.34$

(c) Bromic(I) acid $pK_a = -\log 2.00 \times 10^{-9} = 8.70$

The value of pK_w at room temperature is 14.

Notice that the <u>smaller</u> the pKa value, the <u>larger</u> the Ka value and the <u>stronger</u> the acid

Acid-base titrations

An acid/base titration is a procedure used in quantitative chemical analysis, in order to determine the concentration of either an acid or a base.

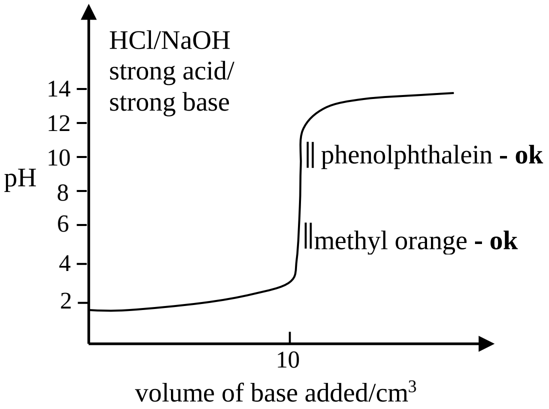
Generally, an alkaline solution of unknown concentration, and of known volume, is added to a conical flask, by means of a 25.0 cm^3 pipette. An acid of known concentration is then added to the conical flask using a burette, until the equivalence point is reached, i.e. when the stoichiometric amount of acid has been added to the base, this is when all the alkali has been neutralised and there is no excess acid or alkali present in the solution, this is called the **equivalence point**.

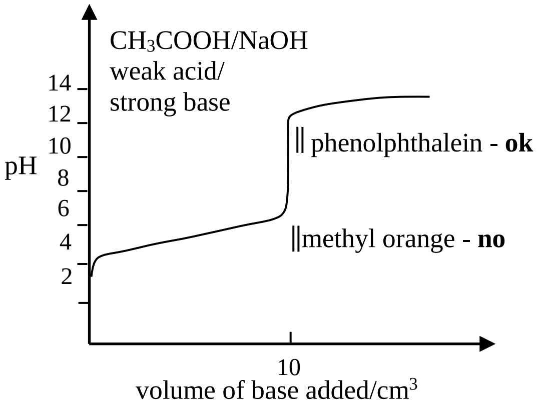
Normally, a visual indicator is used in order to help determine the equivalence point by noticing the exact point at which the colour of the solution changes. The point when the colour changes is the **end point** of the titration.
If the indicator is chosen correctly the end point and the equivalence point are the same.

A pH meter, or conductimetric method, can also be used to determine the equivalence point in an acid/base titration.

pH curves for titrations

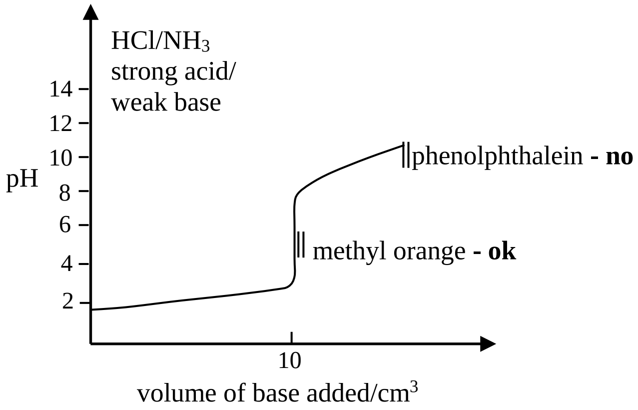
The characteristic shapes of these curves for the various strong/weak acid/base combinations are shown below, for 10 cm^3 of 0.10 mol dm^{-3} acid against 0.10 mol dm^{-3} base.

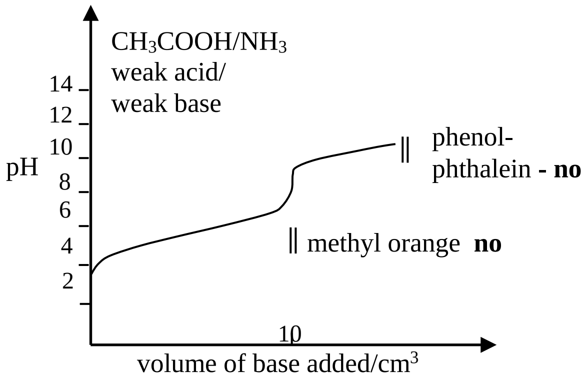




- On the left, for HCl/NaOH, the pH starts at 1, and the curve is almost horizontal up to the endpoint.
- Then it rises sharply (end-point = middle of vertical section = about 7) and quickly flattens out again, heading towards pH=13.
- Of the two most common indicators, **methyl orange** changes colour from about 3.5-5.0 (vertical line to left) and **phenolphthalein** from about 8.5-10: either is suitable as it changes completely over the vertical section around 10 cm^3.

- On the right, for CH$_3$COOH/NaOH, the curve starts higher at 2.9 since the acid is weak, then over the ***buffer region*** it rises slowly.
- The end-point is around pH=8.5,then the latter part of the curve is similar to the first one.
- Only **phenolphthalein** is suitable to detect the endpoint: methyl orange would change very slowly over the buffer region.





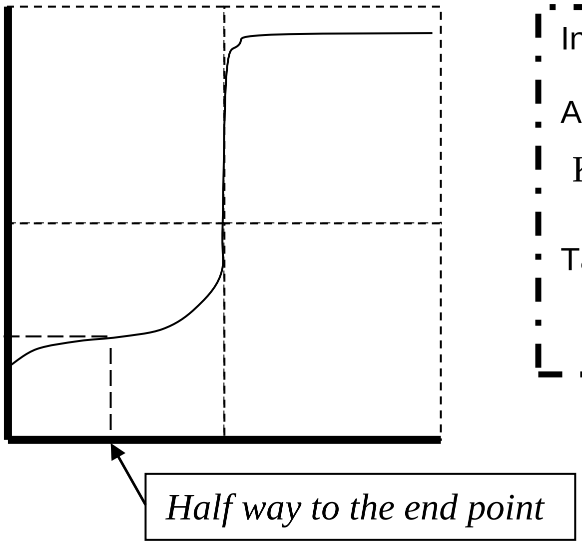
- On the left, strong acid against weak base can be titrated using **methyl orange**.
- While, on the right the weak acid and base give no sharp endpoint and there is no suitable indicator.

Summary:

- using a weak base, like ammonia, phenolphthalein is unsuitable because it doesn't start to change until after the endpoint.
- using a weak acid, like ethanoic acid, methyl orange is unsuitable because it changes steadily, and change is complete before the endpoint.

Determining pKa and Ka from titration curves

When a weak acid is titrated with a strong base, the following curve is obtained.



In the reaction:

$$HA + OH^- \rightarrow A^- + H_2O$$

At half way to the end point, [HA] = [A$^-$]

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]} = \frac{[H_3O^+]\,[1]}{[1]} = [H_3O^+]$$

Taking logs $-\log K_a = -\log [H_3O^+]$

So pKa = pH (@ half neutralization)

- pKa = pH at half neutralization
- Ka = antilog - pKa

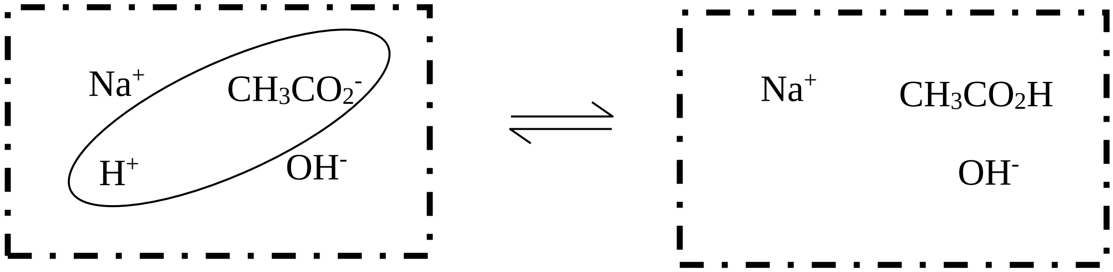
e.g. For ethanoic acid pH at half neutralization is 4.8.

Ka = antilog -pH = antilog -4.8 = **1.58 x 10^{-5} mol dm^{-3}**

Choice of indicator from pK_{In} values

Sodium ethanoate is the salt formed from ethanoic acid – a weak acid, and sodium hydroxide – a strong base. When it is placed in water it splits up completely into ions. Some water molecules also are dissociated, so the solution contains Na^+, $CH_3CO_2^-$, H^+ and OH^-.

Ethanoate ions and hydrogen ions tend to join to form undissociated ethanoic acid, leaving an excess of hydroxide ions.



This means that a solution of sodium ethanoate isin fact alkaline.
This is the case for any salt made from a weak acid and a strong base.
In the same way a salt made from a strong acid and a weak base is acidic in solution.
This means that at the point of neutralisation the pH is not 7.

When carrying out titrations using weak acid and strong base an appropriate indicator must be selected.

Titration	**Indicator**
Strong acid + strong alkali	Bromothymol blue
Weak acid + strong alkali	Phenolphthalein
Strong acid + weak alkali	Methyl orange

In a titration, when the moles of acid and moles of alkali are exactly the same, it is said to be at the **equivalence point.** The point at which the indicator changes colour is the **end point**.
It is clearly important that for a particular titration the end point should be the same as the equivalence point.

An indicator is in fact a weak acid, HIn. Like other weak acids, it dissociates, so it forms H^+ and In^- ions. The HIn will be one colour and the In^- will be a different colour.

$$\underset{\text{Colour 1}}{HIn} \rightleftharpoons \underset{\text{Colour 2}}{H^+ + In^-}$$

In an acid solution, the high concentration of H^+ will cause the equilibrium to move to the left, and so it will be colour 1.
When in alkali solution, the H^+ will be removed and the equilibrium will shift to the right and become colour 2.

When the amount of Hin and are exactly balanced the colour will be in between the two colours. One drop of acid or alkali, and the equivalence point should be able to change the colour of the indicator.

The end point for a particular indicator can be found.
As a weak acid, the K_a, or K_{In} expression can be written

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

At the end point, $[In^-] = [HIn]$, so $[In^-] / [HIn] = 1$

And $[H^+] = K_{In}$

$-\log [H^+] = -\log K_{In}$

$pH = pK_{In}$

So the end point for any indicator takes place at a pH equal to its Pk_{In} value.

To choose an indicator the pK_{In} value must be in the right pH range for the titration being done.

e.g. methyl orange pK_{In} = 5.1 for pH range 4.2 - 6.3 (pK_{In} + or - one pH unit)

- Strong acid and strong base - any indicator.
- Strong acid and weak base - low pH range 3.1- 4.4 e.g. methyl orange.
- Weak acid and strong base - high pH range 8.3 - 10.0 e.g. phenolphthalein.
- Weak acid and weak base - narrow pH range, very hard choice.

In each case pK_{In} must be matched to pH at equivalence point of titration.

End point = mid way between 2 colours of indicator (a property of the indicator).

Equivalence point = when the stoichiometric amounts of acid and alkali have been added.

End point and equivalence point must coincide for an effective titration.

Colours:

- **Phenolphthalein**: colourless from 1 to 8.5, turns pink from 8.5 to 10, remains pink above 10.
- **Methyl orange:** red from 1 to 3.5, then changes from red through orange to yellow between 3.5 and 5.0; yellow from 5.0 to 14.

Buffer Solutions

A buffer solution contains a weak acid or weak base and one of its salts.
It resists dramatic changes in pH if small quantities of acid or alkali is added to it.

Examples;

(i) a weak acid with its sodium salt (or similar) e.g. ethanoic acid and sodium ethanoate, giving high concentrations of CH_3COOH molecules and CH_3COO^- ions.

(ii) a weak base with one of its salts e.g. ammonia and ammonium chloride, giving high concentrations of NH_3 molecules and NH_4^+ ions.

Considering the dissociation of ethanoic acid, in the buffer we have deliberately made the concentrations of CH_3COOH molecules and CH_3COO^- ions large, and this determines the concentration of H^+ ions, and so the pH.

$$\mathbf{CH_3COOH \rightleftharpoons H^+ + CH_3COO^-}$$

- When a little additional strong acid is added, most of the H^+ ions react with some of the ethanoate to form ethanoic acid:

$$\mathbf{H^+ + CH_3COO^- \rightarrow CH_3COOH}$$

- Therefore the concentration of H^+ in the solution only rises slightly, and there is a very small drop in pH. Although the [$\mathbf{CH_3COO^-}$] decreases, it only does so by a small amount compared to the size of the reservoir of $\mathbf{CH_3COO^-}$ in the buffer, so the pH remains relatively constant.

- Conversely, if some alkali is added, most of the OH^- ions react with CH_3COOH molecules:

$$\mathbf{OH^- + CH_3COOH \rightarrow H_2O + CH_3COO^-}$$

- This time the H^+ doesn't fall by nearly as much as expected, and the pH remains relatively constant. Although the [$\mathbf{CH_3COO^-}$] increases, it only does so by a small amount compared to the size of the reservoir of $\mathbf{CH_3COO^-}$ in the buffer.

In the NH_3/NH_4Cl buffer, the NH_3 reacts with H^+, and the ammonium ions react with OH^-:

$$\mathbf{H^+ + NH_3 \rightarrow NH_4^+}$$

$$\mathbf{OH^- + NH_4^+ \rightarrow H_2O + NH_3}$$

Buffered solutions do change in pH upon addition of H^+ or OH^- ions.
However, the change is much less than that would occur if no buffer were present.

Calculating the pH of a buffer solution

(i) What is the pH of a buffer solution containing 0.500 mol dm^{-3} *sodium ethanoate and 0.800 mol dm*$^{-3}$ *ethanoic acid (*$K_a = 1.74 \times 10^{-5}$ *mol dm*$^{-3}$*)?*

In a buffer made up from a mixture of HA and NaA, it is a very good approximation that all of the acid HA will be undissociated, and all the A^- will come from the salt:

[HA] = conc. of acid; $[A^-]$ = conc. of salt

Then: $K_a = \frac{[H^+]\times[A^-]}{[HA]} = \frac{[H^+]\times 0.500}{0.800} = 1.74 \times 10^{-5}$ mol dm^{-3}

from which $[H^+] = 2.78 \times 10^{-5}$ mol dm^{-3}, and pH = **4.56**

In the alternative method, the **Henderson-Hasselbach** equation is derived as follows from the dissociation constant expression for the weak acid used in the buffer (representing the acid as HA):

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

Taking logs gives $\log K_a = \log[H^+] + \log \frac{[A^-]}{[HA]}$

and so $-\log K_a = -\log[H^+] - \log \frac{[A^-]}{[HA]}$

or $pK_a = pH - \log \frac{[A^-]}{[HA]}$

from which $pH = pK_a + \log \frac{[A^-]}{[HA]}$

Since the acid is weak it is present almost entirely in the form of molecules, and virtually all the A^- comes from the salt present; so, to a good approximation, $[A^-]$ is the same as the concentration of the salt and [HA] is the same as the concentration of the acid, giving

$$\mathbf{pH = pK_a + \log} \frac{[\text{concentration of salt}]}{[\text{concentration of acid}]}$$

from which it is clear that if the concentration of salt is equal to the concentration of acid, the pH of the buffer is equal to pK_a for the acid.

Examples using pK_a:

(ii) What is the pH of the solution obtained when 41g of sodium ethanoate is dissolved in 1dm^3 of 0.800 mol dm^{-3} ethanoic acid (pK_a = 4.76)?

Molar mass of CH_3COONa = 82 g mol^{-1}

Amount of CH_3COONa in 41g = $\frac{41\,\text{g}}{82\,\text{g mol}^{-1}}$ = 0.500 mol; conc. = 0.500 mol dm^{-3}

$$\text{pH} = \text{p}K_a + \log\frac{[\text{A}^-]}{[\text{HA}]}$$

$$= 4.76 + \log\frac{0.500}{0.800} = \mathbf{4.56}$$

(ii) What is the pH of the buffer solution obtained when 100 cm^3 of 0.100 mol dm^{-3} ethanoic acid is mixed with 20cm^3 of 0.300 mol dm^3 sodium ethanoate solution?

Amount of ethanoic acid = $\frac{100}{1000} \times 0.100$ = 0.0100 mol

Amount of sodium ethanoate = $\frac{20}{1000} \times 0.300$ = 0.0060 mol

$$\text{pH} = \text{p}K_a + \log\frac{[\text{A}^-]}{[\text{HA}]} = 4.76 + \log\frac{0.0060}{0.0100} = \mathbf{4.54}$$

Buffering Biological Systems

In order to work effectively blood needs to be at a pH of 7.4. This pH is maintained by a number of buffering systems including plasma, proteins, haemoglobin and carbonate/hydrogencarbonate conjugate acid-base pairs.
The proteins are able to act as buffers because of the amine and carboxylic acid side chains of the amino acids composing them.

The carbonate/hydrogencarbonate conjugate acid-base pairs buffer the blood by the equilibrium:

$$H_2CO_{3(aq)} \rightleftharpoons HCO_3{}^-{}_{(aq)} + H^+{}_{(aq)}$$

If the pH of the blood drops, as H^+ increases, this equilibrium shifts to the left reducing the H^+ again and consequently raising the blood pH. On its own this equilibrium would be of limited value as the increasing level of H_2CO_3 would mean that the movement to the left would stop, but there is a second equilibrium involving the H_2CO_3:

$$H_2CO_{3(aq)} \rightleftharpoons CO_{2(aq)} + H_2O_{(l)}$$

At the level of H_2CO_3 increases it produces carbon dioxide which is then removed by gas exchange in the lungs.

If the pH of the blood increases, as H^+ decreases, the $H_2CO_{3(aq)}/HCO_3{}^-{}_{(aq)}$ equilibrium shifts to the right increasing the H^+ again and consequently lowering the blood pH.