Acids, Bases and Buffers

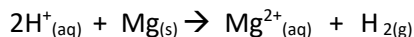## Bronsted – Lowry theory of acids and bases

An acid is a proton donor, e.g. $HCl \rightarrow H^+ + Cl^-$
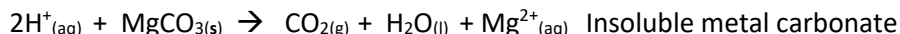A base is a proton acceptor, e.g. $NH_3 + H^+ \rightarrow NH_4^+$

Ionic equations can be used to show the role of H^+ in the reactions of acids with

1. **Metals**
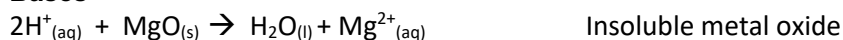
   $2H^+_{(aq)} + Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + H_{2(g)}$

2. **Carbonates**

   $2H^+_{(aq)} + MgCO_{3(s)} \rightarrow CO_{2(g)} + H_2O_{(l)} + Mg^{2+}_{(aq)}$ Insoluble metal carbonate

   $2H^+_{(aq)} + CO_3^{2-}_{(aq)} \rightarrow CO_{2(g)} + H_2O_{(l)}$ Soluble metal carbonate (eg Na_2CO_3)

3. **Bases**

   $2H^+_{(aq)} + MgO_{(s)} \rightarrow H_2O_{(l)} + Mg^{2+}_{(aq)}$ Insoluble metal oxide

   $2H^+_{(aq)} + O^{2-}_{(aq)} \rightarrow H_2O_{(l)}$ Soluble metal oxide (eg Na_2O)

4. **Alkalis**

   $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$ Soluble acid (eg HCl) and alkali (eg NaOH)

Conjugate acid base pairs are chemicals which have the same formula except that the acid has an extra H^+ in its formula

conjugate acid	conjugate base
HCl	Cl^-
H_2O	OH^-
HNO_2^{2+}	NO_2^+
H_3O^+	H_2O

Note that chemicals which are normally found as acids can behave as bases in some reactions e.g. HNO_3 has a conjugate acid $H_2NO_3^+$ as well as a conjugate base NO_3^-

Strong and weak acids

Strong acids are completely dissociated (broken down) into ions, e.g. hydrochloric and sulphuric acids

eg $HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$ $H_2SO_{4(aq)} \rightarrow 2H^+_{(aq)} + SO_4^{2-}_{(aq)}$

Weak acids are only partially dissociated into ions, e.g. ethanoic acid (vinegar).

eg $CH_3COOH \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$

There are many more H^+ ions in 1 dm^3 1M hydrochloric acid than there are in the same volume of 1M ethanoic acid.

K_a The acid dissociation constant is the equilibrium constant for the ionisation of a weak acid.

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

$$K_a = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]} \qquad \text{units= mol dm}^{-3}$$
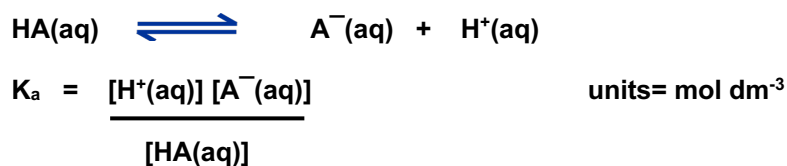
pK$_a$ pK$_a$ = -log$_{10}$ K$_a$

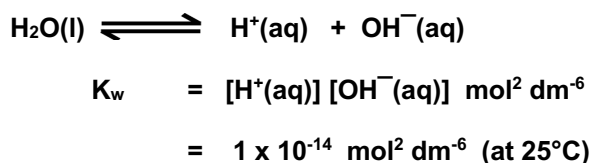*NB if an acid has pKa 4.00 that does not mean that its pH is 4.00*

pH and [H$^+$(aq)]

pH shows the hydrogen ion concentration of a solution in an easily written form

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

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

The use of logs for pH and pKa allows us to produce a manageable scale from very small numbers.

K$_w$ the ionic product of water   is the equilibrium constant for the ionisation of water.
At room temperature its value is 1.00×10^{-14} mol^2 dm^{-6}

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

$$K_w = [H^+(aq)][OH^-(aq)] \text{ mol}^2 \text{ dm}^{-6}$$

$$= 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ (at 25°C)}$$

Because the constant is based on an equilibrium, **K$_w$ VARIES WITH TEMPERATURE**

pOH can be a useful idea for working out the pH of alkalis.

$$pOH = -log_{10}[OH^-]$$
$$pH + pOH = 14.00$$

pH of strong monobasic acids assume that the concentration of hydrogen ions is the same as the acid

pH of strong monobasic bases assume that the concentration of hydroxide ions is the same as the alkali. Two methods

   a)   Work out pOH the subtract from 14.00 to get pH.

   b)   Using K$_w$ directly. Remember K$_w$ = [H$^+$(aq)][OH$^-$(aq)] so if you know [OH$^-$(aq)] then you can work out [H$^+$(aq)] by:

$$[H^+(aq)] = \frac{1 \times 10^{14}}{[OH^-(aq)]}$$

[In fact both a and b use the same equations. Mathematicians should be able to work this out.]

pH of weak monobasic acids   assume that [H$^+$] = [A$^-$] and   equilibrium acid concentration is equal to initial acid concentration so we can use

$$[H^+] = \sqrt{(Ka \times C)} \qquad \text{(C is the initial concentration of the acid)}$$

Buffers: action, uses and calculations

A **buffer solution** is a system that minimises pH changes on addition of small amounts of an acid or base.

A buffer solution can be made from a weak acid and a salt of the weak acid eg CH_3COOH/CH_3COONa.

CH_3COOH/CH_3COO^- from ethanoic acid and sodium ethanoate:

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$
$$CH_3COONa \rightarrow Na^+ + CH_3COO^-$$
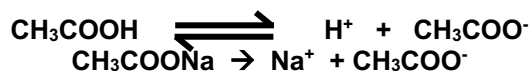
Adding Alkali (OH⁻)
The H^+ reacts with the **added alkali** to produce water. This therefore neutralises any added OH^-. Equilibrium moves to **right** to replace the H^+ used.

Adding Acid (H⁺)
The CH_3COO^- reacts with the **added acid** to produce CH_3COOH. This therefore neutralises any added H^+. The Equilibrium moves to **left.**

The pH of a buffer can be calculated using
$$pH = pK_a + \log_{10} [\text{conjugate base}]/[\text{conjugate acid}]$$

Blood pH is kept reasonably constant (between 7.35-7.45) using the carbonic acid-hydrogencarbonate buffer. The H_2CO_3/HCO_3^- conjugate pair is the most important of these.

Neutralisation

Titration curves show how pH changes during a titration. An indicator can give a sharp end-point if there is a sudden pH change covering the pH at which the indicator changes colour.

Strong acids give a sudden pH change between 3-7 (matches **methyl orange**)
Strong alkalis give a sudden change between 7-11 (matches **phenolphthalein**)

Weak acids or alkalis never give a sudden pH change. Titration Curves are shown on the following pages. You need to learn these.

It is essential that the correct indicators is chosen eg phenolphthalein can only be used in titrations with a strong alkali - the nature of the acid is immaterial.

The **standard enthalpy change of neutralisation** is the change in enthalpy that occurs when an acid and base undergo a neutralisation reaction to form one mole of water under standard conditions.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$
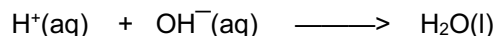
 A value of -57 kJ mol⁻¹ is obtained when strong acids react with strong alkalis.

Calculating standard enthalpy change of neutralisation from experimental results

Example:
25.0 cm³ of 2.00 mol dm⁻³ HCl was added to 25.0 cm³ of 2.00 mol dm⁻³ NaOH in an insulated beaker.

The initial temperature of both solutions was 20.0 °C.
The highest temperature reached by the solution was 33.0 °C.
The specific heat capacity (c) of water is 4.18 J K^{-1} g^{-1}

$$NaOH \quad + \quad HCl \quad \rightarrow \quad NaCl \quad + \quad H_2O$$
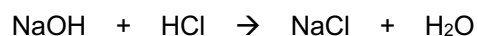
Temperature rise $\qquad = \quad 306K - 293K \qquad = \quad 13.0$ K

Volume of resulting solution $\quad = \quad 25.0 + 25.0 \ = 50.0$ cm^3

Equivalent mass of water $\qquad\qquad = \quad 50.0$ g
(density is 1g per cm^3)

Heat absorbed by the water $\quad = \quad m \times c \times \Delta T \ = \quad 50.0 \times 4.18 \times 13 = \ 2717$ J

Moles of HCl reacting $\qquad = \ 2 \ \times \ 25/1000 \qquad = \quad 0.05$ mol
Moles of NaOH reacting $\qquad = \ 2 \ \times \ 25/1000 \qquad = \quad 0.05$ mol

Enthalpy change per mol $(\Delta H) \ = \ $ heat energy / moles of water $\ = \ 2717 / \ 0.05 = 54\ 340$ J mol^{-1}
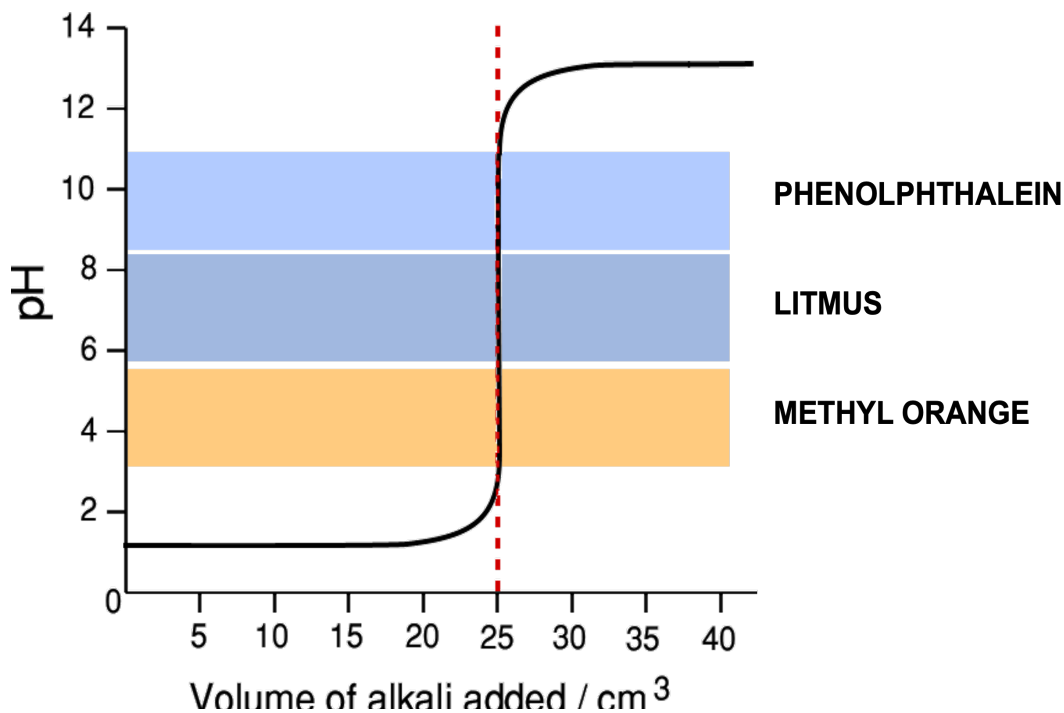$\qquad\qquad\qquad\qquad\qquad = \ $ **- 54.3 kJ mol^{-1}**

Titration Curves

These titration curves assume that the alkali (in burette) is being added to the acid (in conical flask).
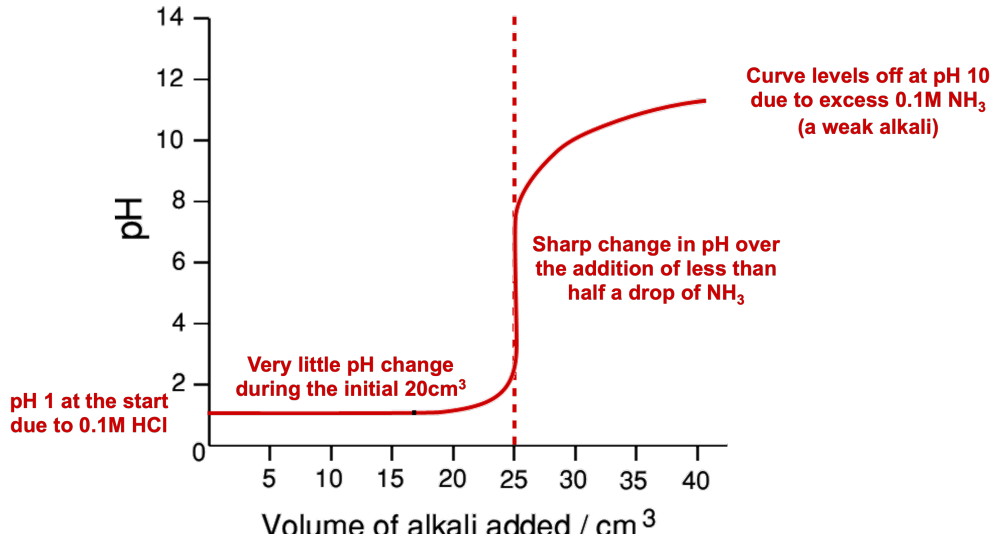You merely need to reverse them if the question specifies the acid is being added to alkali.

strong acid (HCl) v. strong base (NaOH)

Curve levels off at pH 13 due to excess 0.1M NaOH (a strong alkali)

Very sharp change in pH over the addition of less than half a drop of NaOH

Very little pH change during the initial 20cm^3

pH 1 at the start due to 0.1M HCl (strong monoprotic acid)

strong acid (HCl) v. strong base (NaOH)

PHENOLPHTHALEIN

LITMUS

METHYL ORANGE

strong acid (HCl) v. weak base (NH₃)

Curve levels off at pH 10
due to excess 0.1M NH₃
(a weak alkali)

Sharp change in pH over
the addition of less than
half a drop of NH₃

Very little pH change
during the initial 20cm³

pH 1 at the start
due to 0.1M HCl

strong acid (HCl) v. weak base (NH₃)

PHENOLPHTHALEIN

LITMUS

METHYL ORANGE

weak acid (CH₃COOH) v. strong base (NaOH)

Curve levels off at pH 13 due to excess 0.1M NaOH (a strong alkali)

Sharp change in pH over the addition of less than half a drop of NaOH

Steady pH change

weak acid (CH₃COOH) v. strong base (NaOH)

PHENOLPHTHALEIN

LITMUS

METHYL ORANGE

weak acid (CH$_3$COOH) v. weak base (NH$_3$)

pH 4 due to 0.1M CH$_3$COOH (weak monoprotic acid)

Steady pH change

NO SHARP CHANGE IN pH

Curve levels off at pH 10 due to excess 0.1M NH$_3$ (a weak alkali)

Volume of alkali added / cm^3

PHENOLPHTHALEIN

LITMUS

METHYL ORANGE

NOTHING SUITABLE

Volume of alkali added / cm^3