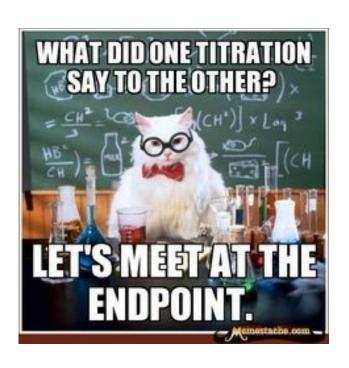
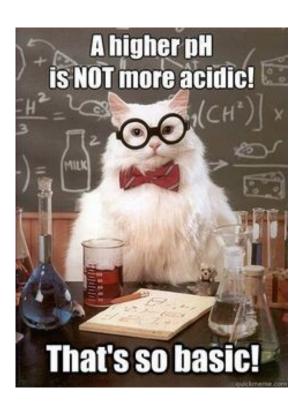


Acids and Bases (Teacher)





WEEK	TOPIC	UNIT CONTENT	ASSESSMENT
5 – 10	Acids and Bases	models and theories are contested and refined or replaced when new evidence challenges them, or when a new model or theory has greater explanatory scope.	
		Davy initially proposed that acids were substances that contained replaceable hydrogen (hydrogen that could be partly or totally replaced by metals) and bases were substances that reacted with acids to form salts and water.	
		Arrhenius model, which includes only soluble acids and bases, identified acids as substances which produce hydrogen ions in solution and bases as substances which produce hydroxide ions in solution	
		the Brønsted-Lowry model describes acid-base behaviour in terms of proton donors and proton acceptors. This approach includes a wider range of substances and can be more broadly applied.	
		acids are substances that can act as proton (hydrogen ion) donors and can be classified as monoprotic or polyprotic, depending on the number of protons available for donation	
		the relationship between acids and bases in equilibrium systems can be explained using the Brønsted-Lowry model and represented using chemical equations that illustrate the transfer of protons between conjugate acid- base pairs	
		• the strength of acids is explained by the degree of ionisation at equilibrium in aqueous solution which can be represented by chemical equations and acidity constants (Ka)	
		the hydrolysis of salts of weak acids and weak bases can be represented using equations; the Brønsted-Lowry model can be applied to explain the acidic, basic and neutral nature of salts derived from bases and monoprotic and	

polyprotic acids water is a weak electrolyte; the self-ionisation of water is represented by $K_w = [H^+][OH^-]$ where $K_w = 1.0 \times 10^{-14} \text{ at } 25 \text{ °C}$ K_w can be used to calculate the concentration of hydrogen ions or hydroxide ions in solutions of strong acids or bases the pH scale is a logarithmic scale and the pH of a solution can be calculated from the concentration of hydrogen ions using the Practical 2 relationship pH = $-\log_{10} [H^{+}]$ acid-base indicators are weak acids, or weak Test 2 bases, in which the acidic form is a different colour from the basic form buffer solutions are conjugate in nature and resist changes in pH when small amounts of strong acid or base are added to the solution;

buffering capacity can be explained

equivalence point by measuring the

observable end point

involved

qualitatively; Le Châtelier's Principle can be applied to predict how buffers respond to the addition of hydrogen ions and hydroxide ions

volumetric analysis methods involving acidbase reactions rely on the identification of an

associated change in pH, using appropriate acid-base indicators or pH meters, to reveal an

data obtained from acid-base titrations can be used to calculate the masses of substances and concentrations and volumes of solutions

Chemical and Physical Properties of Acids and Bases

Acidic solutions generally:

- conduct an electric current
- turn litmus red
- taste sour

Basic solutions generally:

- also conduct an electric current
- turn litmus blue
- taste bitter
- have a slippery feel

Fill in the chemical equation and the net ionic equation for the reactions below illustrating some of the **chemical properties** of acids and bases.

1. Acidic solutions dissolve most metals forming a salt and hydrogen gas. Au, Ag, Pt and Cu are unaffected by dilute acids.

ACID + METAL
$$\rightarrow$$
 SALT + H_{2(q)}

(Eg: Some hydrochloric acid solution is poured onto a strip of nickel metal)

(Eg: Calcium hydroxide solution is added to a solution of nitric acid)

$$2HNO_{3(aq)} + Ca(OH)_{2(aq)} \rightarrow Ca(NO_3)_{2(aq)} + 2H_2O_{(I)}$$

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(I)}$$

3. ACID + METAL OXIDE
$$\rightarrow$$
 SALT + H_2O

(Eg: Some solid copper (II) oxide is added to a solution of sulfuric acid)

$$H_2SO_{4(aq)} + CuO_{(s)} \rightarrow CuSO_{4(aq)} + H_2O_{(l)}$$

 $2H^+_{(aq)} + CuO_{(s)} \rightarrow Cu^{2+}_{(aq)} + H_2O_{(l)}$

4. ACID + CARBONATE
$$\rightarrow$$
 SALT + H₂O + CO_{2(g)}

(Eg: Hydrochloric acid solution is added to nickel carbonate solid)

$$2HCI_{(aq)} + NiCO_{3(s)} \rightarrow NiCI_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$$

 $2H^+_{(aq)} + NiCO_{3(s)} \rightarrow Ni^{2+}_{(aq)} + H_2O_{(l)} + CO_{2(q)}$

5. ACID + HYDROGENCARBONATE \rightarrow SALT + H₂O + CO_{2(g)} (Eg: Ethanoic acid solution is added to solid zinc hydrogencarbonate)

$$2CH_{3}COOH_{(aq)} + Zn(HCO_{3})_{2(s)} \rightarrow Zn^{2+}_{(aq)} + 2CH_{3}COO^{-}_{(aq)} + 2H_{2}O_{(l)} + 2CO_{2(g)}$$

6. ACID + METAL SULFITE \rightarrow SALT + H_2O + $SO_{2(g)}$ (Eg: Hydrochloric acid solution and sodium sulphite powder are mixed)

$$2HCI_{(aq)} + Na_2SO_{3(s)} \rightarrow 2NaCI_{(aq)} + H_2O_{(l)} + SO_{2(g)}$$

 $2H^+_{(aq)} + Na_2SO_{3(s)} \rightarrow 2Na^+_{(aq)} + H_2O_{(l)} + SO_{2(q)}$

7. BASE + AMMONIUM SALT \rightarrow SALT + H_2O + $NH_{3(g)}$ (Eg: A potassium hydroxide solution is mixed with an ammonium chloride solution)

$$KOH_{(aq)} + NH_4CI_{(aq)} \rightarrow KCI_{(aq)} + H_2O_{(l)} + NH_{3(g)}$$

 $NH_4^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} + NH_{3(q)}$

8. BASE + NON-METAL OXIDE → SALT + H₂O (Eg: Sulfur dioxide gas is bubbled through a potassium hydroxide solution)

$$SO_{2(g)}$$
 + $2KOH_{(aq)}$ \rightarrow $K_2SO_{3(aq)}$ + $H_2O_{(l)}$ $SO_{2(q)}$ + $2OH^{-}_{(aq)}$ \rightarrow $SO_3^{2-}_{(aq)}$ + $H_2O_{(l)}$

Theories of Acids and Bases

Davy Theory

<u>Acids</u>: Have replaceable H (hydrogen could be partly or totally replaced by metals).

eg hydrochloric acid:

$$2HCI_{(aq)} + \ Mg_{(s)} \ \rightarrow \ MgCI_{2(aq)} \ + \ H_{2(g)}$$

Bases: Reacted with acids to form salt and water.

eg sodium hydroxide:

$$NaOH_{(s)} + HNO_{3(aq)} \rightarrow NaNO_{3(aq)} + H_2O_{(l)}$$

Arrhenius Theory

Acids: Have H in their formula and produce hydrogen ions (H⁺) when dissolved in water.

eg hydrochloric acid: $HCI_{(g)} \rightarrow H^+_{(aq)} + C\Gamma_{(aq)}$

eg ethanoic acid: $CH_3COOH_{(s)} \rightarrow H^+_{(aq)} + CH_3COO^-_{(aq)}$

Bases: Have OH in their formula and produce hydroxide ions (OH⁻) when dissolved in water.

eg sodium hydroxide: $NaOH_{(s)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$

eg strontium hydroxide: $Sr(OH)_{2(s)} \rightarrow Sr^{2+}_{(aq)} + 2OH^{-}_{(aq)}$

<u>Neutralisation</u>: an acid plus a base produces a neutral solution (ie $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$)

Problems with the theory:

- Some bases produce OH⁻ ions in solution yet do not have OH in their formula (eg NH₃ and CO₃²-).
- Restricted to aqueous solutions.
- Not all salts are neutral.
- Does not allow for the existence of hydronium ions (H₃O⁺).

Brønsted-Lowry Theory

Acids are proton (H⁺) donors.

```
Strong acid: HCI_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + CI^-_{(aq)}
```

HCI is donating a proton and acting as an acid. The H_2O is accepting a proton and acting as a base.

```
Weak acid: CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}
```

 $CH_3COOH_{(aq)}$ is donating a proton and acting as an acid. The H_2O is accepting a proton and acting as a base.

Bases are proton (H⁺) acceptors.

```
eg ammonia: NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}
```

 $NH_{3(aq)}$ is accepting a proton and acting as a base. The H_2O is donating a proton and acting as an acid.

eg hydrogencarbonate ion: $HCO_3^-_{(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} + OH^-_{(aq)}$

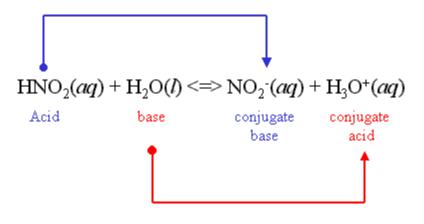
 $HCO_{3(aq)}$ is accepting a proton and acting as a base. The H_2O is donating a proton and acting as an acid.

<u>Neutralisation</u>: reaction between a proton donor and a proton acceptor. eg carbonate ion plus water: $CO_3^{2^-}(aq) + H_2O_{(l)} \rightleftharpoons HCO_3^{-}(aq) + OH^{-}(aq)$

Conjugate acid- base pairs

Brønsted-Lowry theory recognises the reversibility of proton transfer reactions.

- Once an acid has donated a proton it has the potential to act as a base. We say it has formed its conjugate base.
- Once a base has accepted a proton it has the potential to act as an acid. We say it has formed its conjugate acid.
- This means both the forward and the reverse reactions are acid-base reactions. eg $NH_{3(g)} + H_2O_{(l)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)} \qquad H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$
- The acid and the base it forms (or the base and the acid it forms) are called a conjugate acid-base pair.
- In any conjugate acid- base pair the formula of the acid is always greater by the equivalent of H⁺.
- The stronger the acid the weaker its conjugate base.



(Blaber, 2000)

Acidity constant (Ka) and acid strength

An acid- base transfer reaction is an example of an equilibrium process. The extent to which an acid ionises in aqueous solutions can be determined from the equilibrium constant K_a also known as the acidity constant. It is a measure to which the proton transfer goes to completion.

- The larger the K_a the greater the tendency of the acid to donate a proton to water ie the stronger the acid is the greater the degree of its ionisation. (Strong acids fully ionise in water.)
- Eg the proton transfer equation for ethanoic acid is:

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

$$\frac{\left[\text{CH}_{3}\text{COO}^{-}\right]\!\!\left[H_{3}O^{+}\right]}{\left[\text{CH}_{3}\text{COOH}\right]}$$
 its K_a expression is: K_a =

The K_a value at 25°C is 1.8 x 10⁻⁵. This indicates the reaction only proceeds to a very limited extent and only about 1% of ethanoic acid molecules are ionised.

- The larger the value of K_a the more the equilibrium position favours products, hence the greater the tendency of the acid to form hydrogen ions and so the stronger the acid is.
- The K_a value also indicates the strength of the acid's conjugate base to accept a proton back from water so, if K_a is large (strong acid) its conjugate base is weak. As K_a is progressively smaller, the acid is progressively weaker and the conjugate base becomes progressively stronger. (**The** stronger the acid is the weaker its conjugate-base.)
- Acid-base reactions tend to occur in the direction in which the stronger acid and stronger base react to form a weaker acid and weaker base.

Eg
$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$$
 Equilibrium lies to the left

$$HCN_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CN^-_{(aq)}$$
 Equilibrium lies to the left

Polyprotic Acids

Monoprotic acids can donate only one proton (hydrogen ion) per molecule. Eg HCl; CH₃COOH; HNO₃

While weak monoprotic acids produce fewer hydrogen ions in solution than strong acids, they react to the same extent with bases, providing that the concentration is the same.

$$HCI_{(aq)} + H_2O_{(I)} \rightarrow H_3O^+_{(aq)} + CI^-_{(aq)}$$

<u>Diprotic acids</u> contain two acidic protons per molecule. Eg H₂SO₄; H₂CO₃

Explain (using equations) why one mole of H₂SO₄ yields between one and two moles of H₃O⁺ ions in solution.

$$H_2SO_{4(aq)} + H_2O_{(l)} \rightarrow HSO_4^-_{(aq)} + H_3O^+_{(aq)}$$

 $HSO_4^-_{(aq)} + H_2O_{(l)} \rightleftharpoons SO_4^{2^-_{(aq)}} + H_3O^+_{(aq)}$

This process of becoming ions over multiple steps is called successive ionisation.

<u>Polyprotic acids</u> are acids which contain two or more acidic protons. Use equations to show the successive ionisation of phosphoric acid.

$$H_3PO_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_2PO_4^-_{(aq)} + H_3O^+_{(aq)}$$
 $H_2PO_4^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HPO_4^{2-}_{(aq)} + H_3O^+_{(aq)}$
 $HPO_4^{2-}_{(aq)} + H_2O_{(l)} \rightleftharpoons PO_4^{3-}_{(aq)} + H_3O^+_{(aq)}$

Acid-Base Properties of Salts

When an acid reacts with a base a salt and water are produced. Although this is called a neutralisation reaction, the salt formed in the reaction is not always neutral. The acid-base properties of the salt can be understood in terms of Bronsted-Lowry theory. If one of the ions present in the salt reacts with water (and the ion acts as a proton donor) then its solution will be acidic. If one of the ions present reacts with water (and its ion acts as a proton acceptor) then its solution is basic. The reaction of the ions with water is also known as hydrolysis.

Eg 1

An ammonium chloride solution (NH₄Cl_(aq)) is acidic. The ammonium ion (NH₄⁺) is a weak acid in water as acts as a proton donor and hydrolyses to produce hydronium ions (H₃O⁺). The chloride ion (Cl⁻) is neutral.

$$NH_4^+_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+_{(aq)}$$

Eg 2

A sodium ethanoate solution (NaCH₃COO_(aq)) is basic. The ethanoate ion (CH₃COO⁻) is a weak base in water as it acts as a proton acceptor and hydrolyses to produce hydroxide ions (OH⁻). The sodium ion (Na⁺) is neutral.

$$CH_3COO^{-}_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^{-}_{(aq)}$$

Summary

The table below classifies common ions according to whether they cause aqueous solutions to be acidic, basic or neutral.

Type of Ion	Acidic	Basic	Neutral
Anions	Anions produced in	Anions from	Anions from
	first stage of	weak acids:	strong acids:
	ionisation of polyprotic	F ⁻ , CO ₃ ²⁻ , HS ⁻ , S ²⁻ ,	Cl ⁻ , Br ⁻ , l ⁻ , NO ₃ ⁻
	acids: HSO ₄ -, H ₂ PO ₄ -	HPO ₄ ²⁻ , PO ₄ ³⁻ , HCO ₃ ⁻ ,	
		CH₃COO⁻ , SO₄²⁻	
Cations	NH ₄ +, Fe ³⁺ , Al ³⁺ , Cr ³⁺	Not common	Li ⁺ , Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ , Ba ²⁺
	Sn ⁴⁺		Ca ²⁺ , Ba ²⁺

Predict whether aqueous solutions of the following salts will be acidic, basic or neutral and justify your choice by writing suitable chemical equations.

- a) Ammonium nitrate
- b) Calcium hydrogencarbonate
- c) Potassium ethanoate
- d) Magnesium bromide
- e) Calcium hydrogensulfate
- a) Acidic

NO₃ ions are neutral

$$NH_4^+_{(aq)} + H_2O_{(l)} = NH_{3(aq)} + H_3O^+_{(aq)}$$

b) Basic

Ca²⁺ ions are neutral

$$HCO_3^-(aq) + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} + OH^-(aq)$$

c) Basic

K⁺ ions are neutral

$$CH_3COO^{-}_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^{-}_{(aq)}$$

d) Neutral

Mg²⁺ and Br ions are both neutral

e) Acidic

Ca2+ ions are neutral

$$HSO_{4(aq)}^{-} + H_2O_{(l)} \rightleftharpoons SO_{4(aq)}^{-2} + H_3O_{(aq)}^{+}$$

Complete Essential Chemistry Set 4

Self- Ionisation of Water, Kw and pH

Water is an extremely weak electrolyte. The ionisation of water molecules into hydronium and hydroxide ions is very small. This is known as self-ionisation. It is given by:

$$2H_2O_{(I)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

At hh, the equilibrium constant for the ionisation of water (K_w) equals 1.00 ×10⁻¹⁴. It is given by: $K_w = [H_3O^+][OH^-]$

In water or any solution where H_3O^+ and OH^- have the same concentration, the solution is said to be neutral. $[H_3O^+] = [OH^-] = 1.00 \times 10^{-7} \text{ mol L}^{-1}$ at 25 °C.

From this, an acidic solution must have $[H_3O^+] > [OH^-]$ and a basic solution must have $[H_3O^+] < [OH^-]$. Also, since $[H_3O^+] \times [OH^-] = 1.00 \times 10^{-14}$ for all solutions at 25 °C, the concentration of one of these ions can be calculated given the concentration of the other.

Eg. Calculate the concentration of hydrogen ions in a 0.001 mol L⁻¹ NaOH solution.

```
[OH^{-}] = [NaOH] = 1 \times 10^{-3} \text{ mol L}^{-1}

[H_3O^{+}] \times [OH^{-}] = 1.00 \times 10^{-14} \text{ mol L}^{-1}

[H_3O^{+}] = 1.00 \times 10^{-14} / 1 \times 10^{-3}

= 1.00 \times 10^{-11} \text{ mol L}^{-1}
```

Eg. Calculate the concentration of hydroxide and hydrogen ions in a solution made by dissolving 2.34 g of Ba(OH)₂ solid in 543 mL of water.

```
\begin{split} n_{\text{Ba(OH)2}} &= 2.34/171.316 = 0.01366 \text{ mol} \\ n_{\text{(OH-)}} &= 2 \times n_{\text{Ba(OH)2}} \\ &= 2 \times 0.01366 \text{ mol} = 0.02732 \text{ mol} \\ [\text{OH-]} &= \text{n/v} = 0.02732/\ 0.543 = \textbf{5.03} \times \textbf{10}^{-2} \text{ mol } \text{L}^{-1} \\ [\text{H+]} &\times [\text{OH-]} = 1.00 \times 10^{-14} \text{mol } \text{L}^{-1} \\ [\text{H+]} &= 1.00 \times 10^{-14} / [\text{OH-]} \\ &= \textbf{1.99} \times \textbf{10}^{-13} \text{ mol } \text{L}^{-1} \\ [\text{OH-]} &= \textbf{5.03} \times \textbf{10}^{-2} \\ [\text{H+]} &= \textbf{1.99} \times \textbf{10}^{-13} \end{split}
```

pН

pH is a number indicating how acidic or basic a solution is. It was developed by Søren Sørenson.

It is related to $[H^+]$ / $[H_3O^+]$ through the expression: $pH = -log_{10}[H^+]$ / $[H_3O^+]$. A pH value below 7 is acidic, while a pH value above 7 is basic and pH 7 is neutral.

Eg. Calculate the pH of the following solutions:

1. A 0.002 mol L^{-1} solution of HC/.

```
pH = 2.7
```

2. A 0.007 mol L⁻¹ solution of H₂SO₄ (assuming complete ionisation)

```
H_2SO_{4(aq)} \rightarrow 2H^+_{(aq)} + SO_4^{2^-}_{(aq)}
Complete ionisation produces 2 x 0.007 mol L<sup>-1</sup> H<sup>+</sup> ions = 0.014 mol L<sup>-1</sup> pH = - log [0.014] = 1.85
```

3. A 0.005 mol L⁻¹ solution of NaOH.

```
NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}
Complete ionisation produces 0.005 mol L<sup>-1</sup>OH<sup>-</sup> ions [H<sup>+</sup>] = 1.00 x 10<sup>-14</sup>/0.005 = 2 x 10<sup>-12</sup> mol L<sup>-1</sup> pH = - log [2 x 10<sup>-12</sup>] = 11.70
```

4. Calculate the final pH of a solution made up by adding 5.67 g of HC*I* solid to 23.5 mL of a 3.96 ×10⁻¹ mol L⁻¹ Ba(OH)₂ solution (assume no change in volume).

```
-0.76
```

5. Calculate [H⁺] of HNO₃ solution with a pH of 1.38.

```
0.0417 mol L<sup>-1</sup>
```

6. Calculate [OH¹] and [H₃O¹] of a Mg(OH)₂ solution with a pH of 12.68.

```
[H_3O^+] = 2.09 \times 10^{-13}
[OH^-] = 4.79 \times 10^{-2}
```

pH can be measured using an indicator solution (a specific weak acid that changes colour over a range of pH), indicator paper or a pH meter (which is much more precise, if used correctly). A pH meter measures the voltage difference across two electrodes placed in the solution.

- The self-ionisation of water is an **endothermic process**. An increase in temperature will favour the endothermic (forward) reaction which would result in an increased equilibrium constant. (eg at 40 °C, $K_w = 2.916 \times 10^{-14}$).
- Similarly, at lower temperatures, the exothermic (reverse) reaction is favoured and so the equilibrium constant is reduced (eg at 10 °C, $K_w = 2.93 \times 10^{-15}$).

It is important to remember that even though pure water at temperatures above 40 °C has a pH less than 7, it is not acidic (this is because a neutral pH of 7 only applies at 25 °C). Pure water at, whatever temperature, is always neutral.

Complete Essential Chemistry Set 5

Buffers

A buffer is a solution that resists changes in its pH when small amounts of an acid or base are added. It is made up of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid. They are often prepared by adding the salt of the conjugate acid or base to the weak base or acid (respectively).

Eg Mixing 2 mol of ethanoic acid, CH₃COOH, with 2 mol sodium ethanoate NaCH₃COO and making the solution volume up to 1.00 L. This solution contains a high concentration of weak acid, CH₃COOH, and its conjugate weak base, CH₃COO⁻ (from NaCH₃COO).

The equilibrium set up is given as: $CH_3COOH_{(s)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$

If acid is added, the system adjusts (according to Le Châtelier's Principle) by shifting the equilibrium to the left. In this case, the acetate ions will react with the excess H_3O^+ to keep the overall $[H_3O^+]$ relatively constant. Similarly, if a base is added, the system adjusts by shifting the equilibrium to the right to replace the H_3O^+ which reacted with the OH^- .

In both these cases, the acid or base can be consumed without a great alteration to the $[H_3O^+]$ in the original mixture. As a result, the pH of the mixture does not alter appreciably. Of course, buffer solutions have their limits and eventually if enough acid or base is added, the pH will change significantly.

Explain buffering using Collision Theory
Using the ethanoic/ sodium ethanoate buffer system:

If **acid** is **added** to the system this increases the H^+/H_3O^+ concentration. This increases the frequency of collisions between H_3O^+ and CH_3COO^- and so increases the rate of the reverse reaction relative to the forward reaction and the equilibrium shifts left. This will consume H_3O^+ until new equilibrium is established where H_3O^+ concentration is very close to what it was originally (maintaining pH).

If **base is added** to the system this decreases the H^+/H_3O^+ concentration. This reduces the frequency of collisions between H_3O^+ and CH_3COO^- and so reduces the rate of the reverse reaction relative to the forward reaction and the equilibrium shifts right. This will increase H_3O^+ until new equilibrium is established where H_3O^+ concentration is very close to what it was originally (maintaining pH).

The buffer capacity of a solution depends on two factors:

- The relative concentrations of the weak acid (base) and its conjugate base (acid). Equal concentrations of these two offers the best buffering capacity.
- The concentration of the weak acid (base) and its conjugate base (acid). The greater the concentrations (in general) the greater the buffering capacity.

Blood has a system of buffers present in it to maintain a fairly consistent pH range between 7.35 and 7.45. This is essential to maintain the body systems functioning.

One of the buffer systems to help blood maintain this narrow pH range is the **carbonic acid** and **hydrogen carbonate ion** buffer system. Carbonic acid is the weak acid and the hydrogen carbonate ion is the weak conjugate base.

$$H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons HCO_{3(aq)} + H_3O_{(aq)}^+$$

If blood becomes too acidic, $[H_3O^+]$ becomes too high,equilibrium shifts to the left as the HCO_3^- reacts with the excess H_3O^+ . If blood becomes too basic, $[H_3O^+]$ falls too low, equilibrium shifts to the right producing more H_3O^+ .

An enzyme found in blood called carbonic anhydrase catalyses the formation of carbonic acid from carbon dioxide which ensures the equilibrium adjusts quickly to changes in $H_2CO_{3(aq)}$ or $CO_{2(aq)}$. The $H_2CO_3/HCO_3^-/CO_2$ buffer system is particularly useful because it allows the excess H_3O^+ to exit the body through the lungs as CO_2 .

Another blood buffer system is the dihydrogenphosphate and hydrogenphosphate, $H_2PO_4^{-1}/HPO_4^{2-1}$ buffer system.

Complete Essential Chemistry Set 6

Acid-Base Titrations

Acid- base titrations (also called volumetric analysis) are an analytical procedure often used to determine the concentration of a solution or the amount of a particular substance present. The concentration of one solution must be accurately known. This is called the **standard solution**. The purpose of the titration is to determine the concentration of the acid or base in the unknown solution.

Five main pieces of equipment are used in titrations:

- Pipette used to accurately deliver a known volume (aliquot) of liquid. It is rinsed with the liquid to be delivered from it prior to use.
- Burette used to accurately deliver a variable volume (titre) of liquid. It is rinsed with the liquid to be delivered from it prior to use.
- Volumetric flask used to prepare an accurately known volume of solution.
 It is rinsed with de-ionised water prior to use.
- Analytical balance used to weigh out an accurately known mass.
- Conical flask used to hold the solutions during the titration. It is rinsed with de-ionised water prior to use.

In the titration process, a carefully measured volume of one solution, called an aliquot, is added to a conical flask. A variable volume of the other solution, called the titre, is then carefully added from a burette into the conical flask until the reaction between the acid and base is complete. This theoretical point in the titration when neither acid nor base remain is called the equivalence point.

Indicators are used to determine when stoichiometrically equivalent amounts of the two reactants have reacted. This point is called the equivalence point. The point at which the indicator **changes colour** is called the end point. To be a useful indicator, the end point should match the equivalency point.

For an indicator (which is a weak acid) in solution, the following reaction takes place:

$$HInd_{(aq)} \rightleftharpoons H^+_{(aq)} + Ind^-_{(aq)}$$

The colour changes are due to the difference in the colours of HInd and Ind-.

A standard solution has an accurately known concentration. A primary standard solution is used to determine the concentration of a secondary standard solution. A primary standard solution should possess the following characteristics:

- Has a high degree of purity and a known formula.
- The reactions it is involved in are known.
- It must be stable. That is, it should not decompose in air, react with oxygen, carbon dioxide or other gases in the air
- It must not absorb water from the atmosphere. That is, it is not hygroscopic (absorbs water from the atmosphere) or deliquescent (absorbs so much water that it eventually dissolves in the water it absorbs).
- It should have a relatively high formula mass to minimize weighing errors (percentage uncertainty is minimized).

Common primary standards used in acid-base titrations include anhydrous sodium carbonate, oxalic acid ($H_2C_2O_4$) and potassium hydrogenphthalate (KHC₈H₄O₄).

When performing titrations, a practice run is always performed and at least three trials which should agree to within ± 0.3 mL (at least two of them). The practice run is never used in the calculating of the concentration.

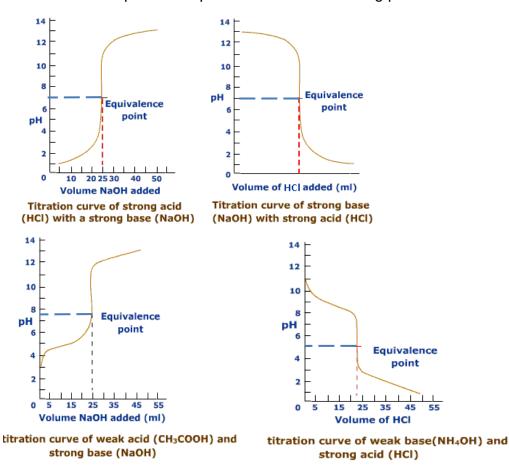
The Products of Neutralisation Reactions

Not all equivalency points of acid-base reactions will be neutral. <u>Only the reaction between a strong acid and a strong base will produce a neutral solution</u>. As such, the choice of indicator is very important. Below is a list of common indicators and their useful pH range.

Indicator	Colour in Acid	Colour in Base	pH Range
Universal indicator	Red	Purple	0.0-14.0
Methyl orange*	Red	Yellow	3.1-4.4
Bromophenol blue*	Yellow	Purple	3.0-4.6
Methyl red	Red	Yellow	4.4-6.2
Litmus	Red	Blue	4.5-8.3
Bromothymol blue	Yellow	Blue	6.0-7.6
Phenolphthalein*	Colourless	Pink	8.3-10.0
Alizarine yellow R	Yellow	Red	10.2-12.0
Bromothymol blue Phenolphthalein*	Yellow Colourless	Blue Pink	6.0-7.6 8.3-10.0

^{*}denotes more commonly used (Although Universal Indicator is never used as an acid/base titration, you must be familiar with its colours in various pH ranges i.e. red 0-2, orange 3-4, yellow 5-6, green 7, blue 8-10, violet 11-14)

During a titration, the pH does not change in a linear fashion. Below are typical titration curves for various reactions. Note that the equivalence point occurs at the turning point of the curve.



Reactions Between a Weak Acid and a Strong Base

Write an equation for the reaction between acetic acid and sodium hydroxide in aqueous solution. Which salt is produced? Are solutions of this salt acidic, basic or neutral? Which indicator should be used?

- $CH_3COOH_{(aq)} + OH^-_{(aq)} \rightarrow CH_3COO^-_{(aq)} + H_2O_{(l)}$ then
- $CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$
- Result is a basic solution. Indicator to use is phenolphthalein.

Write an equation for the reaction between hypochlorous acid (HC/O) and potassium hydroxide in aqueous solution. Which salt is produced? Are solutions of this salt acidic, basic or neutral? Which indicator should be used?

- $HC/O_{(aq)} + OH_{(aq)}^{-} \rightarrow C/O_{(aq)}^{-} + H_2O_{(l)}$ then
- $C/O^{-}_{(aq)} + H_2O_{(l)} \rightleftharpoons HC/O_{(aq)} + OH^{-}_{(aq)}$
- Result is a basic solution. Indicator to use is phenolphthalein.

Summing up, the end point of titrations between a weak acid and a strong base in aqueous solution are basic and the indicator to be used is phenolphthalein.

Reactions Between a Strong Acid and a Weak Base

Which salt is formed when an aqueous solution of ammonia is added to a hydrochloric acid solution? Are solutions of this salt acidic, basic or neutral? Which indicator should be used?

- $NH_{3(aq)} + H^{+}_{(aq)} \rightarrow NH_{4}^{+}_{(aq)}$ followed by $NH_{4}^{+}_{(aq)} + H_{2}O_{(l)} \rightleftharpoons NH_{3(aq)} + H_{3}O^{+}_{(aq)}$
- Result is an acidic solution. Indicator to use is methyl orange or bromophenol blue.

Which salt is formed when an aqueous solution of sodium hydrogencarbonate is added to nitric acid. Are solutions of this salt acidic, basic or neutral? Which indicator should be used?

- $HCO_3^-(aq) + H^+(aq) \rightarrow CO_2(g) + H_2O_{(1)}$
- followed by $CO_{2(q)} + H_2O_{(l)} \Rightarrow H_2CO_{3(aq)}$
- then $H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons HCO_{3(aq)} + H_3O^{+}_{(aq)}$
- Result is an acidic solution. Indicator to use is methyl orange or bromophenol blue.

Summing up, the end point of titrations between a strong acid and a weak base in aqueous solution are acidic and the indicator to be used is methyl orange or bromophenol blue.

Reaction Between a Weak Acid and A Weak Base

The reaction between acetic acid and ammonia can be represented by the equation:

$$OCH_3COOH_{(aq)} + NH_{3(aq)} \rightarrow CH_3COO^{-}_{(aq)} + NH_4^{+}_{(aq)}$$

The pH of solutions of salts such as ammonium acetate depend on the relative strengths of the anion as a base and the cation as an acid. Ammonium acetate solutions are very close to neutral. As such, a pH meter is definitely the more preferred choice to monitor this type of acid-base titration as the pH change around the equivalence point is too gradual.

The titration calculation

Eg 20.00 mL aliquots of hydrochloric acid solution are titrated with 9.039×10^{-2} mol L⁻1sodium carbonate solution. Several titrations were performed and the volumes of sodium carbonate solution used were 19.45 mL, 18.90 mL, 18.77 mL and 18.85 mL. What is the concentration of the hydrochloric acid in the solution?

 $C_{(HCI)} = 1.703 \times 10^{-1} \text{ mol L}^{-1}$

In a **back titration**, a known volume of an excess reactant is added to the reactant being analysed. A titration is then carried out to determine the amount of excess reactant remaining after the reaction.

Eg Magnesium oxide is not very soluble in water, and is difficult to titrate directly. Its purity can be determined by use of the back titration method. 4.06 g of impure magnesium oxide was completely dissolved in 100.0 mL of hydrochloric acid, of concentration 2.00 mol L⁻¹ (in excess). The excess acid required 19.70 mL of sodium hydroxide (0.200 mol L⁻¹) for neutralisation. Determine the percentage purity of the magnesium oxide in the original sample.

Purity MgO = 97.3%

Sometimes the solution to be analysed is too concentrated for the standard solution and would require a titre too large for the burette. In this case the solution of high concentration is **diluted**.

The following equation will be used in these calculations: $c_1V_1 = c_2V_2$ where

c₁ = original undiluted solution concentration in mol L⁻¹

 V_1 = original undiluted solution volume in litres

c₂ = new diluted solution concentration in mol L⁻¹

 V_2 = new diluted solution volume in litres

Eg. A laboratory technician needs to accurately confirm the concentration of a batch of commercial hydrochloric acid. In order to do so a 15.00 mL sample is transferred to a 2.500 L volumetric flask and made up to the mark with distilled water. 20.00 mL aliquots require on average 16.65 mL of 9.08×10^{-2} mol L⁻¹ NaOH_(aq) for equivalence. Determine the concentration of HCl_(aq) in the commercial solution.

n(NaOH) = cV
=
$$9.08 \times 10^{-2} \times 16.65 \times 10^{-3}$$

= 1.51×10^{-3} mol

$$HCI_{(aq)} + NaOH_{(aq)} \rightarrow NaCI_{(aq)} + H_2O_{(l)}$$

Thus $n(HCI) = n(NaOH) = 1.51 \times 10^{-3} \text{ mol}$

c (HCI diluted) =
$$\frac{n}{V} = \frac{1.51 \times 10^{-3}}{20.00 \times 10^{-3}} = 7.56 \times 10^{-2} \text{ mol L}^{-1}$$

$$c_1V_1 = c_2V_2$$

$$\mathbf{c_1} = \frac{c_2 V_2}{V_1} = \frac{7.56 \times 10^{-2} \times 2.50}{15.00 \times 10^{-3}} = \mathbf{12.6} \text{ mol L}^{-1} \mathbf{HCl}_{\text{(aq)}}$$

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cf: Ethanoic acid solution is added to zinc hydrogencarbonate solution

$$CH_3COOH_{(aq)} + HCO_3^{-}_{(aq)} \rightarrow CH_3COO^{-}_{(aq)} + H_2O_{(l)} + CO_{2(g)}$$

cf: Hydrochloric acid is added to solid zinc hydrogencarbonate

$$2 H^{^{+}}\,_{(aq)} + Zn \big(HCO_{3}\big)_{2(s)} \ \rightarrow \ Zn^{2+}_{(aq)} \ + 2 H_{2}O_{(I)} + 2CO_{2(g)}$$