

# OCR A Chemistry A-level

## Module 5.1: Rates, Equilibrium and pH Detailed Notes

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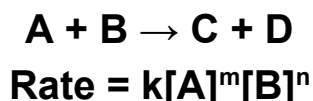


## 5.1.1 How Fast?

### Orders, Rate Equations and Rate Constants

#### Rates and Rate Equations

The rate of a reaction shows how fast reactants are converted into products. It depends on the **concentrations** of the reactants and the **rate constant**. The rate of reaction is given by the rate equation:



The constants  $m$  and  $n$  show the **order of the reaction** with respect to that species. This means that different species can have more of an effect on the rate of reaction than others. The values  $m$  and  $n$  can be 0, 1 or 2 - corresponding to **zero** order, **first** order or **second** order.

The **total order** of reaction for this chemical reaction can be found as the **sum** of the separate orders.

$$\text{Total order} = m + n$$

The **units** for rate of reaction are  $\text{mol dm}^{-3}\text{s}^{-1}$ .

#### Rate Constant (k)

The rate constant for a reaction is constant when the reaction **temperature is constant**. The rate constant relates the concentrations of the species that affect the rate of a reaction to the overall rate of reaction.

The rate constant,  $k$ , can be calculated by **rearranging the rate equation** for that reaction. It has **varying units** depending on the number of species and their orders of reaction. The units of  $k$  can be found by **substituting the relevant units** into the rearranged equation and performing **cancellations**.

$$k = \frac{\text{Rate}}{[\text{A}]^m[\text{B}]^n}$$



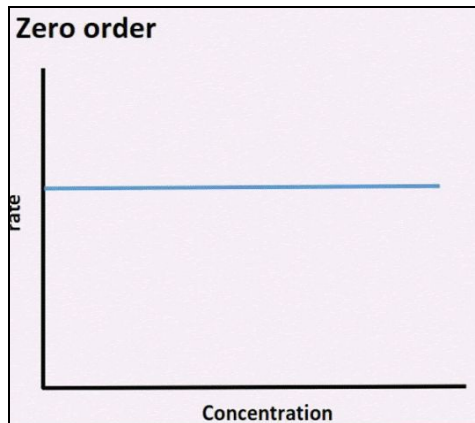


## Rate Graphs and Orders

The orders of reaction (that you need to know about at A-level) range from **zero to second order**. This means that changing the concentration of reactants can have different effects on the whole reaction:

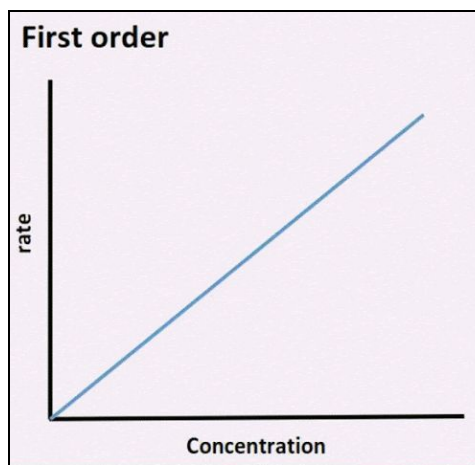
### Zero Order

- The concentration of this species has **no impact** on rate.
- Shown on a rate-concentration graph as a **horizontal** line.
- Rate =  $k$



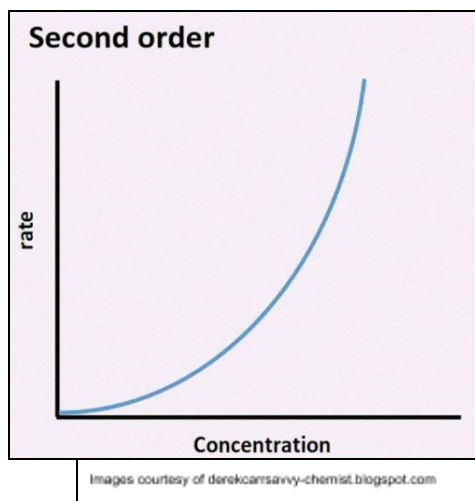
### First Order

- The concentration of the species and the rate are **directly proportional**.
- Doubling the concentration doubles the rate.
- Rate =  $k[A]$



### Second Order

- The rate is proportional to the concentration of the species **squared**.
- Doubling the concentration will increase the rate by **four times**.
- Rate =  $k[A]^2$

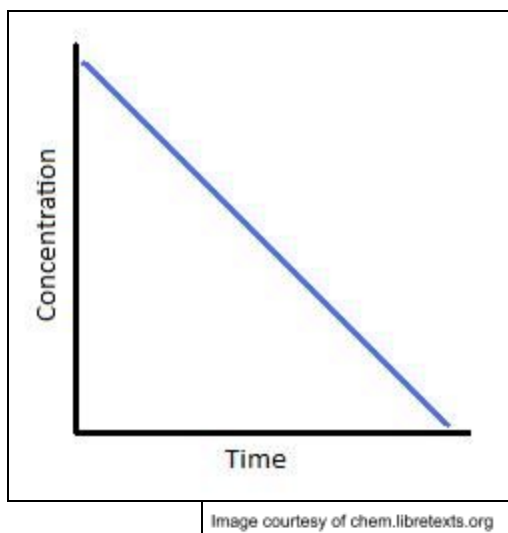




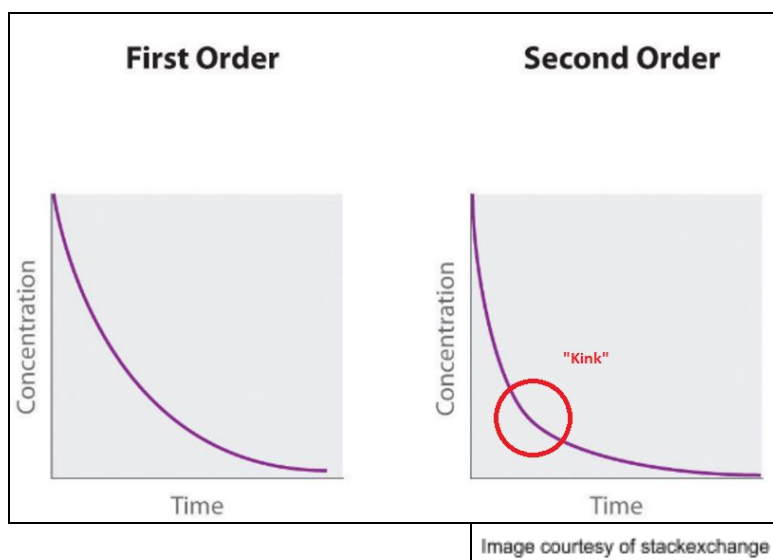
## Concentration-Time Graphs

Reaction orders can be worked out by using **rate-concentration** graphs as shown above, but they can also be determined from the shapes of **concentration-time** graphs. These graphs can be generated by **continuously monitoring** the concentration of reactants during an experiment. Calculating the gradient of these graphs gives the rate.

The concentration-time graph for a **zero order** reaction is **linear**:



The concentration-time graphs for first order and second order reactions are **curved**:





## Initial Rates

Using the initial rate of reactions is one way the order of a reaction can be determined. This involves **varying the concentrations** of reactants and measuring the **initial rate** of the reaction.

**Doubling** the concentrations of zero, first and second order reactants would have the following effects:

- **Zero order** - **No change** to the initial rate.
- **First order** - Initial rate **doubles**.
- **Second order** - Initial rate **quadruples** ( $2^2$ ).

*Example:*

Trial	Initial [A] (mol dm <sup>-3</sup> )	Initial [B] (mol dm <sup>-3</sup> )	Initial [C] (mol dm <sup>-3</sup> )	Initial rate (mol dm <sup>-3</sup> s <sup>-1</sup> )
1	10	10	10	40
2	20	10	10	80
3	10	20	10	40
4	10	10	20	160

From this data, you can deduce that:

- A is a **first** order reactant
- B is a **zero** order reactant
- C is a **second** order reactant

This would give the rate equation: **Rate = k[A][C]<sup>2</sup>**

## Half-life

**Half-life ( $t_{1/2}$ ):** The time taken for the initial concentration of the reactants to decrease by half.

The half-life can be found from a **concentration-time graph**. The overall order of a reaction affects how the length of the half-life changes over the course of a reaction.

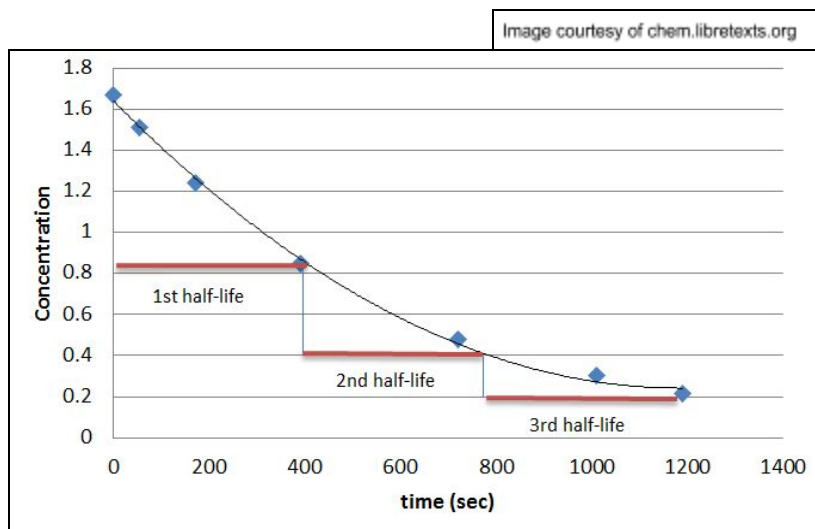
## First Order Reaction

In a first order reaction, the half-life of a reaction is **constant** throughout the reaction. So the time taken for the reactant concentration to go from 100% to 50% is the same as the time taken for the reactant concentration to go from 50% to 25%, and so on.





Example: Half life of a first order reactant



## Experimental Techniques

There are various experimental techniques that can be used to obtain **rate data** for reactions. This allows for the calculation of the **overall order** of reaction and the rate of reaction at **given times**.

The two general ways this can be investigated is by:

- Measuring the change in a **reactant** mass or concentration over time.
- Measuring the change in a **product** mass or concentration over time.

Collecting this raw data allows you to generate a **concentration-time graph**, **mass-time graph** or **volume-time graph**, which can then be used to calculate the **rate of reaction**. To find reactant orders and the overall order of reaction the concentration of reactants can be varied and their effects on the rate of reaction can be analysed.

## Mass Change

If a **gas is produced** by a reaction, then the mass of the reaction mixture will **decrease** as the reaction proceeds. Plotting a mass-time graph and drawing a **tangent** to the curve can be used to find the rate of reaction.

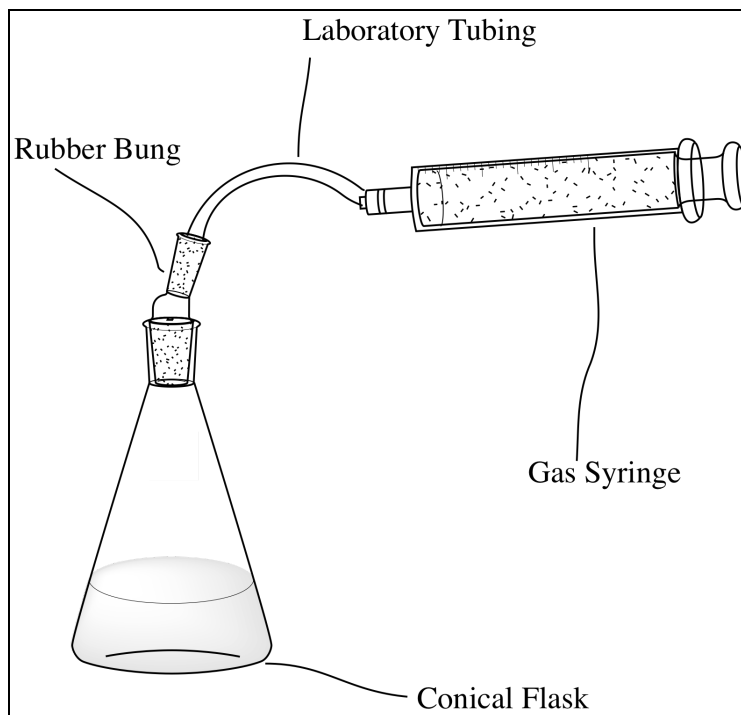
## Volume of Gas Evolved

If a **gas is produced** by a reaction, the rate of reaction can be found by **measuring the volume of gas** produced over the course of the reaction, and plotting a graph of volume evolved against time. A **gas syringe** or an **underwater** upside down measuring cylinder can be used to collect the gas.





Experiment setup:



### Titration

Small samples of a reaction mixture can be **removed** at **regular intervals** throughout a reaction. These samples can then be **titrated** to determine the **concentration** of a given reactant or product at that time. A concentration-time graph can then be plotted.

### Colorimetry

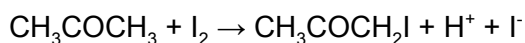
Colorimetry can be used to determine the rate of reaction for a reaction that involves the **formation or depletion** of a **coloured species**. A colorimeter is a device that measures the amount of light that is **absorbed** by a solution. The amount of light absorbed by the solution is proportional to the **concentration** of the coloured species.

In a colorimetry experiment, a **calibration curve** is often generated. This involves using a **colorimeter** to measure the absorbance of solutions of **known concentrations**, from which a calibration curve is plotted.

Then, throughout the experiment, the absorbance of samples from the reaction mixture can be measured and the **calibration curve** used to convert the absorbance readings into concentration values. A **concentration-time** graph can then be plotted.

### **Example: Iodination of propanone**

The acid catalysed reaction of propanone and iodine can be monitored using colorimetry.





The initial solution is **brown** in colour due to the **iodine** present. As the iodine is used up in the reaction, the colour of the solution changes from **brown** to **orange**, to **yellow** and finally to **colourless**. The concentration of iodine can be found by continually taking samples of the reaction mixture and measuring the absorbance using a **colorimeter**.

## Rate Determining Step

Not all stages of a reaction occur at the same rate, but the overall rate is **determined by the slowest step** of the reaction, also known as the **rate determining step**. Therefore, the rate equation contains all the species involved in the stages **up to and including the rate determining step**.

The rate determining step can be identified from a reaction sequence by looking at which steps include the species in the rate equation. The rate determining step can also be used to **predict the mechanism** for the reaction.

*Example:*

Image courtesy of The Student Room

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

(iii) Using the rate equation, a scientist suggested a mechanism for the reaction which consisted of the two steps shown below.

Step 1       $\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O}_2$

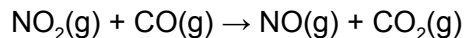
Step 2       $\text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{NO}_2$

***In this question, step 2 would be the rate determining step as all the reactants of this step are in the rate equation given at the start.***

When constructing a reaction mechanism, the **powers in the rate equation** indicate the number of molecules of each substance involved in the slowest step and any steps before this. Any **intermediates** generated in the slowest step must be reactants in another step as they are **not present** in the balanced overall equation.

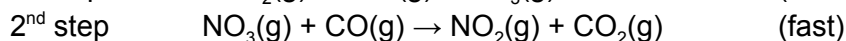
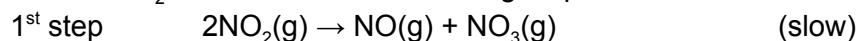
*Example mechanism:*

Nitrogen dioxide and carbon monoxide react to form nitrogen monoxide and carbon dioxide:



The rate equation for this reaction is:  $\text{rate} = k[\text{NO}_2]^2$

- From the rate equation, the reaction is zero order with respect to  $\text{CO}(\text{g})$  and second order with respect to  $\text{NO}_2(\text{g})$ .
- 2 molecules of  $\text{NO}_2$  are in the rate-determining step







## Effect of Temperature on Rate Constants

As the temperature increases, the rate constant increases and the rate of reaction increases.

### The Arrhenius Equation

The Arrhenius equation shows how the rate constant,  $k$ , and temperature,  $T$ , are related **exponentially**:

$$k = Ae^{-\frac{E_a}{RT}} \quad \text{or} \quad \ln k = -\frac{E_a}{RT} + \ln A$$

Where:

- $k$  = Chemical Reaction Rate
- $A$  = Pre-exponential Factor
- $E_a$  = Activation Energy
- $R$  = Gas Constant
- $T$  = Temperature in Kelvin

Image courtesy of SlidePlayer

It is a very useful equation and the **logged form** can be used in the form ' $y = mx + c$ ' to show the relationship graphically. On a graph of  $\ln(k)$  against  $1/T$ , the gradient is  $-E_a/R$  which is **negative and constant**, and the y-intercept is  $\ln(A)$ :

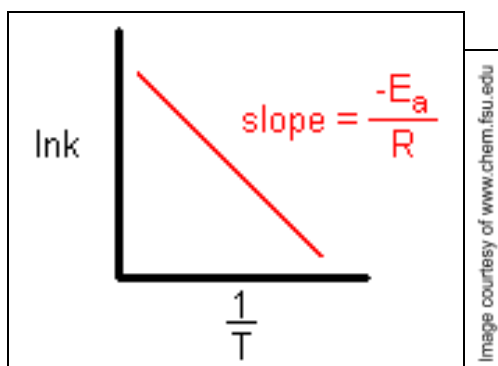


Image courtesy of www.chem.fsu.edu

The above relationship shows how the **activation energy** for a reaction (the minimum energy required for two particles to react) can be found **graphically** using experimental methods and data.





## 5.1.2 How Far?

### Equilibrium

#### Mole Fractions and Partial Pressure

A **mole fraction** shows the proportion that a molecule accounts for of the total moles present. It is calculated by dividing moles of substance A by the total moles present.

Within a gaseous system, each gas has a **partial pressure**. The partial pressures add up to give the total system pressure. The partial pressure of a substance is found using the **mole fraction** of that substance and the **total pressure of the system**.

$$\text{Partial Pressure of A} = \frac{\text{Moles of A}}{\text{Total Moles}} \times \text{Total Pressure}$$

Partial pressure of A would be shown as (**P<sub>A</sub>**).

*Example:*

Image courtesy of SlidePlayer

A mixture of gases contains 0.51 mol N<sub>2</sub>, 0.28 mol H<sub>2</sub>, and 0.52 mol NH<sub>3</sub>. If the total pressure of the mixture is 2.35 atm, what is the partial pressure of H<sub>2</sub>?

$$\begin{aligned} \text{Total moles in the system} &= 0.51 + 0.28 + 0.52 \\ &= 1.31 \text{ moles} \end{aligned}$$

$$\begin{aligned} \text{Mole fraction of H}_2 &= 0.28 / 1.31 \\ &= 0.21 \end{aligned}$$

$$\begin{aligned} (P_{H_2}) &= 0.21 \times 2.35 \\ &= 0.50 \text{ atm} \end{aligned}$$

Partial pressures are commonly measured in **Pascals** but are occasionally measured in atmospheres.

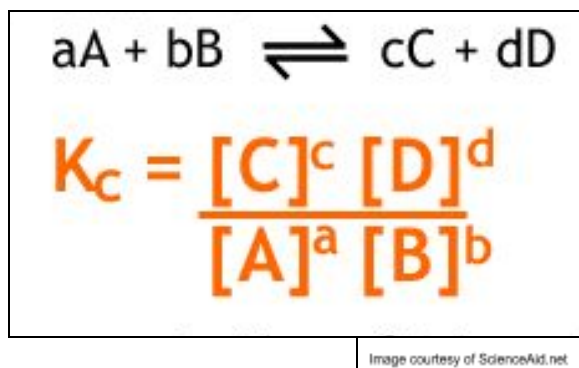




## Calculating K<sub>c</sub>

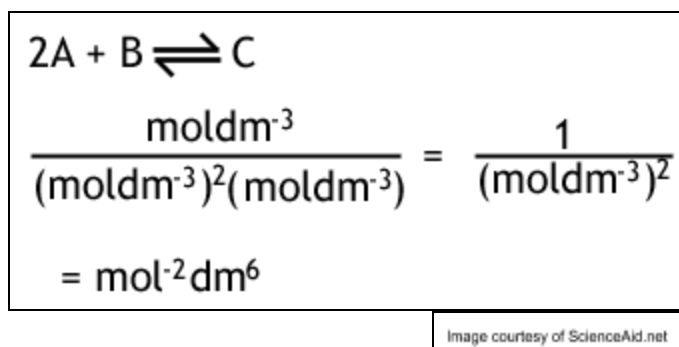
K<sub>c</sub> is the equilibrium constant of a reversible reaction. K<sub>c</sub> is equal to the **concentration of the products divided by the concentration of the reactants** at equilibrium. The concentration terms are **raised to a power** of the same value as the number of moles of that substance.

*Example: The K<sub>c</sub> expression*



The equilibrium constant has **varying units**, depending on the chemical reaction. The units can be calculated by **substituting the concentration units into the K<sub>c</sub> expression**. Some of these units will then cancel, giving the overall units of K<sub>c</sub> for that reaction.

*Example: Finding the units of K<sub>c</sub>*



## Homogeneous and Heterogeneous

The equilibrium constant, K<sub>c</sub>, can be found for both **homogeneous** and **heterogeneous** reactions. Homogeneous reactions are reactions in which the reactants and products are in the same **phase**, whereas heterogeneous reactions are reactions in which some of the reactants and/or products are in different phases to each other.

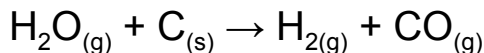
For **homogeneous** reactions, K<sub>c</sub> is calculated as shown **above**.

The **difference** when calculating K<sub>c</sub> for **heterogeneous** reactions is that any terms representing a **solid** are **not included** in the calculation.





Example:



The solid carbon is not included in the equation for  $K_c$ :

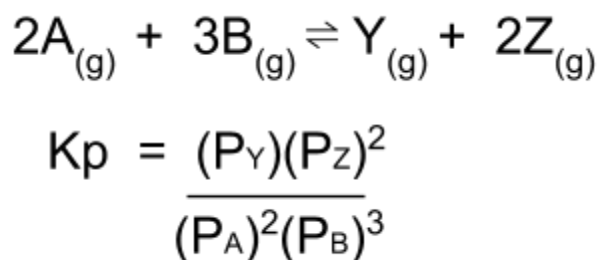
$$K_c = \frac{[\text{H}_2][\text{CO}]}{[\text{H}_2\text{O}]}$$

### Gaseous Equilibrium Constant ( $K_p$ )

$K_p$  is the equilibrium constant used for **gaseous equilibria**.  $K_p$  is calculated from gaseous reactants and products. If all reactants and products are in the **gaseous state**, the system is said to be **homogeneous**.

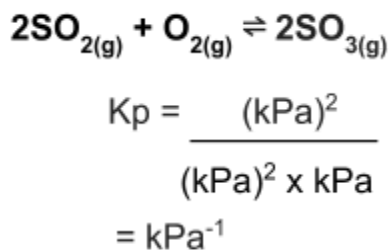
### Calculating $K_p$

Partial pressures allow the value of  $K_p$  for a gaseous equilibrium to be found.  $K_p$  is equal to the product of the **partial pressures of products** over the product of the **partial pressure of reactants**. It is similar to  $K_c$  in that any variation in moles **raises the partial pressure to a power** of equal quantity to the number of moles.



The gaseous equilibrium constant has **varying units**, depending on the chemical reaction. The units can be calculated by **substituting the partial pressure units into the  $K_p$  expression**. Some of these units will then cancel, giving the overall units of  $K_p$  for that reaction.

Example: Finding the units for  $K_p$





## Homogeneous and Heterogeneous

Similarly to  $K_c$ , the gaseous equilibrium constant,  $K_p$ , can be found for both **homogeneous** and **heterogeneous** reactions.

For **homogeneous** reactions,  $K_p$  is calculated as shown **above**.

The **difference** when calculating  $K_p$  for **heterogeneous** reactions is that any terms representing a **solid** are **not included** in the calculation.



The solid  $\text{CaCO}_3$  and  $\text{CaO}$  are not included in the equation for  $K_p$ : 
$$K_p = (P_{\text{CO}_2})$$

## Factors Affecting $K_c$ and $K_p$

The values of  $K_c$  and  $K_p$  are **not affected by concentration or pressure change** or by the use of a **catalyst**. However, they are affected by changing the reaction **temperature**.

**Concentration** and **pressure** changes and the addition of a **catalyst** affect the **rate** of the reaction (the kinetics) but not the **position** of the equilibrium. They only affect how fast the system reaches equilibrium, hence they have **no impact** on the equilibrium constant.

**Temperature**, on the other hand, does change the **position** of the equilibrium, resulting in different concentrations of reactants and products.

If the forward reaction is **exothermic**, an increase in temperature will decrease the rate of the forward reaction because the equilibrium shifts to the **left** to oppose the change and favour the reverse endothermic reaction. This will decrease the concentrations of products and increase the concentrations of reactants, and therefore the equilibrium constant ( $K_c$  or  $K_p$ ) **decreases**.

If the forward reaction is **endothermic**, an increase in temperature will increase the rate of the forward reaction because the equilibrium shifts to the **right** to oppose the change. This will increase the concentrations of products and decrease the concentrations of reactants, and therefore the equilibrium constant ( $K_c$  or  $K_p$ ) **increases**.

Similar arguments can be made for the effect of **decreasing** the temperature.





## 5.1.3 Acids, Bases and Buffers

### Brønsted–Lowry Acids and Bases

Acid-base equilibria involve the **transfer of protons** between substances. Therefore, substances can be classified as acids or bases depending on their interaction with protons.

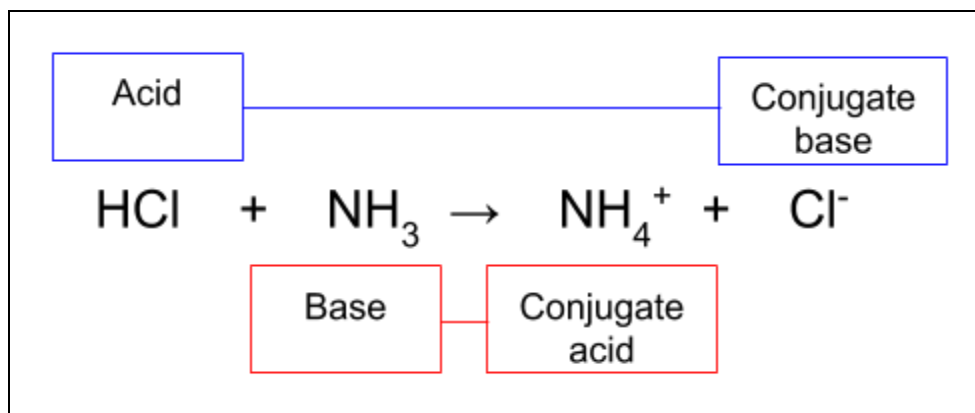
A Brønsted-Lowry **acid** is a **proton donor**. For example, ammonium ions ( $\text{NH}_4^+$ ).

A Brønsted-Lowry **base** is a **proton acceptor**. For example, hydroxide ions ( $\text{OH}^-$ ).

### Brønsted–Lowry conjugate acid-base pairs

A **conjugate acid** is the species formed when a **base accepts a proton**. A **conjugate base** is the species formed when an **acid donates a proton**. Conjugate acids and conjugate bases form conjugate acid-base pairs.

*Example:*

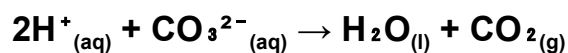


### Ionic Equations

An ionic equation shows the **reacting ions** in a chemical equation. **Spectator ions** are ions that do not change in the reaction and are left out of the ionic equation. It is important to **balance** elements and charge in ionic equations.

In the reactions of acids with carbonates, metal oxides, and alkalis,  $\text{H}^+$  is the reacting ion.

*Example:*



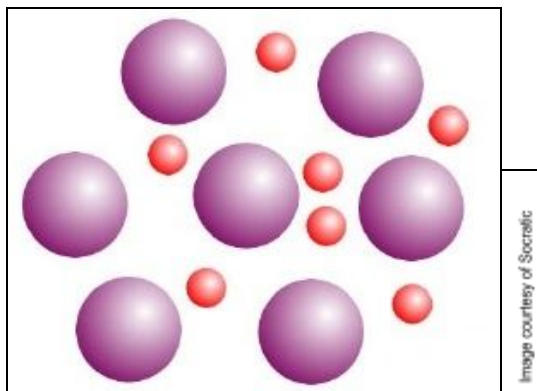


## Acid and Base Strength

Acid strength doesn't refer to the concentration of a solution. A **strong acid** is defined as being:

**An acid that completely dissociates into its ions when in solution.**

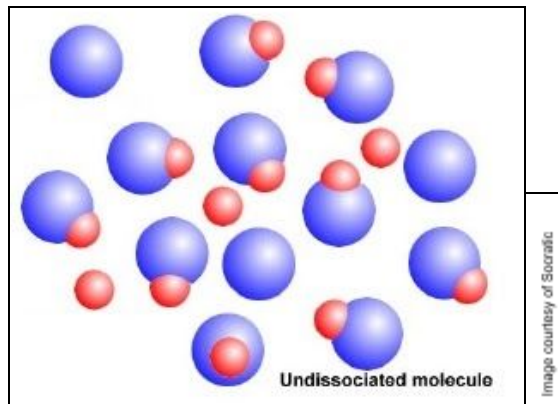
*Example:*



In comparison, a **weak acid** is defined as being:

**An acid that only slightly dissociates into its ions when in solution.**

*Example:*



The same definitions are true for **strong** and **weak bases**.

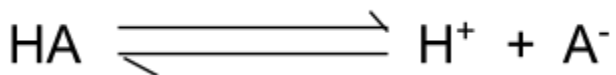
Strong acids have pH between 0-1 and weak acids have pH between 3-7. Strong bases have pH between 12-14 and weak bases have pH between 7-11.

## The Acid Dissociation Constant

Weak acids and bases only **slightly dissociate** in solution to form an **equilibrium** mixture.

Therefore, the reaction has an acid dissociation constant, **K<sub>a</sub>**.





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

The constant  $K_a$  can be found using **pKa**:

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

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

The value  $\text{p}K_a$  is a logarithmic acid dissociation constant, representing how acidic something is. A **low value** of  $\text{p}K_a$ , or equivalently a large  $K_a$ , indicates a **strong acid**.

## pH and $[\text{H}^+_{(\text{aq})}]$

### Determining pH

pH is a measure of **acidity and alkalinity**. It is a **logarithmic** scale from 0 to 14 that gives the concentration of  **$\text{H}^+$  ions** in a solution. 0 is an **acidic** solution with a high concentration of  $\text{H}^+$  ions whereas 14 is a **basic** solution with a low concentration of  $\text{H}^+$  ions.

pH is a specific example of  $\text{p}K_a$  for when  $\text{H}^+$  ions are present. It can be calculated using the **concentration of hydrogen ions**,  $[\text{H}^+]$ , as follows:

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

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

This equation also allows the concentration of  $\text{H}^+$  ions to be determined if the pH is known. When using these equations above, the concentration of  $\text{H}^+$  ions is given in  **$\text{mol dm}^{-3}$** .

This concentration of  $\text{H}^+$  ions is equivalent to the **concentration of a strong acid** as it **completely dissociates** to ions in solution.







## Diluting Acids

If you dilute a strong acid **10 times** its pH will increase by **one unit**, because pH is a **logarithmic scale**. Diluting it **100 times** and **1000 times** would, therefore, increase the pH by **two units** and **three units**, respectively.

Weak acids do not behave in the same way. Weak acids are **not fully dissociated in solution**, so diluting them causes the **equilibrium to shift** to oppose the change. This means a **10x dilution** of a weak acid would increase the pH by **less than one unit**.

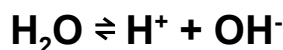
## Ionic Product of Water

Water **slightly dissociates** to form hydroxide and hydrogen ions in an equilibrium with its own equilibrium constant, **K<sub>w</sub>**.



At **25°C**, room temperature, K<sub>w</sub> has a constant value of **1.0 x 10<sup>-14</sup>**. However, as temperature changes, **this value changes**.

The **forward** reaction in the equilibrium of water is **endothermic** and is therefore favoured when the temperature of the water is increased. As a result, as temperature increases, **more H<sup>+</sup> ions** are produced meaning the water becomes **more acidic**.



In the same way that pK<sub>a</sub> can be calculated from K<sub>a</sub>, **pK<sub>w</sub>** can be calculated from **K<sub>w</sub>**.

$$pK_w = -\log_{10} K_w$$

$$K_w = 10^{-pK_w}$$

The pH of a **strong base** can be calculated using pK<sub>w</sub> or K<sub>w</sub>. For a **strong base**, the concentration of OH<sup>-</sup> will be the **same** as the concentration of the base.

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

$$\text{Rearrange } K_w \text{ to find } [H^+]: [H^+] = \frac{K_w}{[OH^-]}$$

Use  $K_w = 10^{-14}$  and the concentration of the base to find  $[H^+]$ .

$$\text{Finally, calculate pH using: } pH = -\log_{10}[H^+]$$





## Calculations

The relationships of  $K_a$ ,  $pK_a$  and  $[H^+]$  can be used to find the **pH of weak acids and bases**. Depending on the reaction and the relative concentrations, a different method may have to be used:

HA in excess - Use  $[HA]$  and  $[A^-]$  along with  $K_a$  to find  $[H^+]$ , then pH.

$A^-$  in excess - Use  $K_w$  to find  $[H^+]$ , then pH.

HA =  $A^-$  - In this case,  $pK_a$  is equal to pH, therefore find  $pK_a$ .

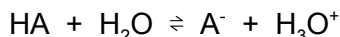
## Calculating the $K_a$ of Weak Acids

Weak acids only **partially dissociate** in solution. Therefore, the **equilibrium** of a weak acid has to be taken into account.

1. The initial concentrations, change in concentrations and equilibrium concentrations of the reactants and products have to be found.
2. The concentration of  $H^+$  ions can then be found using the pH given.
3. This value can be used to find the actual equilibrium concentrations.
4. Finally, these values can be substituted into the expression for  $K_a$ .

*Example:*

A weak acid, HA, with a concentration of 0.25 M has a pH of 3.5. What is its  $K_a$ ?



We assume that 'x' mol of HA dissociates to  $A^-$  and  $H_3O^+$ .

	HA	$A^-$	$H_3O^+$
<b>Initial</b>	0.25	0	0
<b>Change</b>	-x	+x	+x
<b>End</b>	0.25 - x	x	x

Using the pH value given, the  $[H^+]$  (= x) can be calculated:

$$[H_3O^+] = [H^+] = 10^{-pH}$$

$$[H^+] = 10^{-3.5} = 3.16 \times 10^{-4} \text{ M}$$

$$x = 3.16 \times 10^{-4} \text{ M}$$





Substituting into the expression for  $K_a$  and using the equilibrium concentrations:

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(x)(x)}{(0.25-x)}$$

We can now substitute in the value of  $x$  calculated earlier:  $x = 3.16 \times 10^{-4} \text{ M}$

$$K_a = \frac{(3.16 \times 10^{-4})^2}{(0.25 - (3.16 \times 10^{-4}))}$$

$$K_a = 3.99 \times 10^{-7}$$

### Approximations

For weak acid calculations, the following approximations are made:

$$[HA]_{\text{equilibrium}} \sim [HA]_{\text{undissociated}}$$

$$\text{i.e. } [HA] \gg [H^+]$$

$$[HA]_{\text{equilibrium}} \sim [A^-]_{\text{equilibrium}}$$

$$\text{i.e. negligible dissociation of } H_2O$$

These approximations are limited to calculations for weak acids. For stronger weak acids, the approximations breakdown because the first assumption may no longer be valid.

## Buffers: Action, Uses and Calculations

### Buffer Action

A buffer solution is a system that **minimises pH changes** on addition of small amounts of an acid or a base. It is formed from a **weak acid and its salt** or an excess of a **weak acid and a strong alkali**. This produces a mixture containing  **$H^+$  ions** and a large **reservoir of  $OH^-$  ions** which helps to resist any change in pH. Therefore, a buffer solution is defined as:

**A solution which is able to resist changes in pH when small volumes of acid or base are added.**





The large reservoir of OH<sup>-</sup> ions allows the **ratio of acid to base** in the mixture to be kept almost **constant**.

Consider the following buffer solution:  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$

The **OH<sup>-</sup> concentration** will **increase** if a small amount of base is added, making the solution more basic. The extra OH<sup>-</sup> ions will react with the NH<sub>4</sub><sup>+</sup> ions, to form the **original reactants**. Therefore, the equilibrium will shift to the left to remove the OH<sup>-</sup> ions and stop the pH from changing largely.

### Buffer Calculations

Buffer calculations are long calculations that use acid-base calculations. There are two types:

- Acid + Base** - Find the number of moles of each species.
- Calculate their concentration when at equilibrium using the total volume.
  - Use Ka to find [H<sup>+</sup>] and therefore pH.

- Acid + Salt** - Find the moles of the salt.
- Use Ka to find pH.

*Example:*

A buffer solution contains 0.35 mol dm<sup>-3</sup> methanoic acid and 0.67 mol dm<sup>-3</sup> sodium methanoate. For methanoic acid, Ka = 1.6 x 10<sup>-4</sup> mol dm<sup>-3</sup>. Find the pH of this buffer.

We **assume** that the **sodium methanoate completely dissociates** so that the equilibrium concentration of HCOO<sup>-</sup> is the same as the initial concentration of HCOO<sup>-</sup>Na<sup>+</sup>. Similarly, HCOOH only slightly dissociates so we assume that the **equilibrium concentration** is equal to the **initial concentration**.

1. First, find the expression for Ka for methanoic acid



$$K_a = \frac{[\text{H}^+] \times [\text{HCOO}^-]}{[\text{HCOOH}]}$$

2. Rearrange the expression to find [H<sup>+</sup>]

$$[\text{H}^+] = \frac{K_a \times [\text{HCOOH}]}{[\text{HCOO}^-]}$$

$$[\text{H}^+] = 1.6 \times 10^{-4} \times (0.35/0.67) = 8.4 \times 10^{-5}$$

3. Convert [H<sup>+</sup>] to pH

$$\text{pH} = -\log_{10}(8.4 \times 10^{-5}) = 4.08$$





## Adding Small Volumes

The pH of a buffer solution doesn't change much but will change in the **order of 0.1 or 0.01 units of pH** when a **small volume** of acid or base is added.

Adding small amounts of **acid ( $H^+$ ) increases the concentration** of the acid in the buffer solution, meaning the overall solution will get slightly **more acidic**.

Adding small amounts of **base ( $OH^-$ ) decreases the concentration** of acid in the buffer solution, meaning the overall solution will get slightly **more basic**.

## Uses of Buffers

Buffer solutions are common in **nature** in order to keep systems regulated. This is important as **enzymes** or reactions in living organisms often require a **specific pH**, which can be maintained using a buffer solution.

Another important buffer in nature is found in the human circulatory system. The **pH of human blood** is maintained in a buffer between **carbonic acid and hydrogencarbonate ions**. These ions **neutralise any acidic substances** that enter the bloodstream, converting them to carbonic acid and water. This buffer is present in blood plasma, maintaining a pH between 7.35 and 7.45.

## Neutralisation

### Enthalpy Change of Neutralisation

When **strong** acids and bases react together they will produce **very similar enthalpies of neutralisation**. This is because the solutions completely dissociate, so the same, simple acid-base reaction occurs between  **$H^+$  and  $OH^-$  ions** to produce water in each case. The other dissociated ions present are simply **spectator ions** and do not affect the reaction.

However, in reactions of **weak** acids and bases, the ions only slightly dissociate so **other enthalpy changes** also occur within the solution. As a result, the enthalpies of neutralisation can **vary** quite a lot.

### Titration Curves

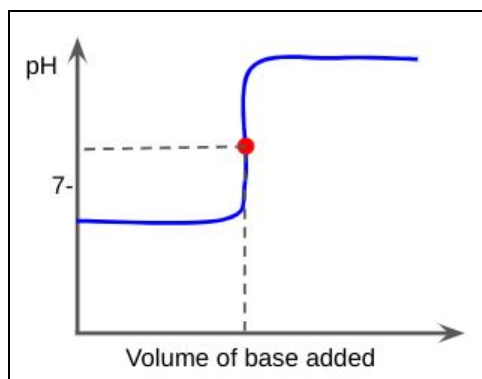
A pH titration curve shows how the pH of a solution **changes** during an **acid-base reaction**. When an acid and base react, a **neutralisation point** is reached, identified as a large **vertical section** of the pH curve, through the neutralisation/equivalence point.

To obtain a pH titration curve, alkali is slowly added to an acid (or vice versa) and the pH is regularly measured with a **pH probe**. The **smaller** the added volumes, the **more accurate** the curve produced.



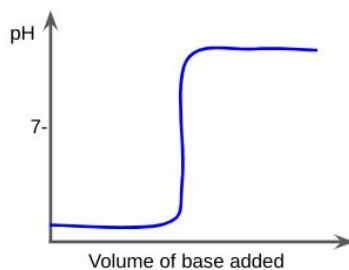


Example: The red dot indicates the equivalence point

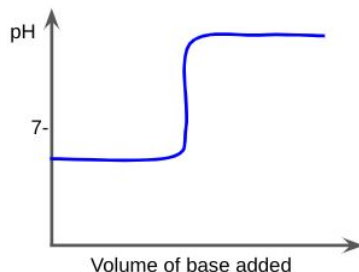


For a strong acid - strong base reaction, the neutralisation point occurs around **pH 7**. Other combinations of strong and weak acids and bases results in a **different neutralisation point**:

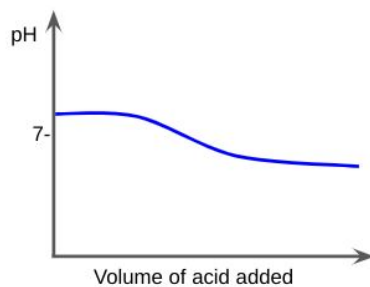
- Strong Acid + Strong Base = pH 7



- Strong Acid + Weak Base = < pH 7 (more acidic)
- Weak Acid + Strong Base = > pH 7 (more basic)



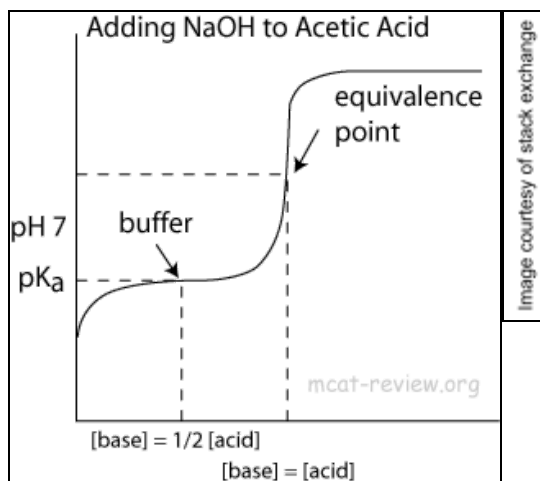
- Weak Acid + Weak Base = normally pH 7 but hard to determine





## Calculating $K_a$ from Titration Curves

The vertical region of a titration curve is the **equivalence point**. At **half the equivalence point** the **pH is equal to  $pK_a$** , by definition.



**Therefore, by reading the pH at half the equivalence point,  $K_a$  can be easily calculated from  $pK_a$ .**

## Indicators

Specific chemical indicators have to be used for specific reactions as they can **only indicate a pH change within a certain range**.

The two most common indicators used at A-level are **methyl orange** and **phenolphthalein**:

Methyl Orange - used for reactions with a **more acidic** neutralisation point.  
- red in acids and turns **yellow** at the neutralisation point.

Phenolphthalein - used for reaction with a **more basic** neutralisation point.  
- pink in alkalis and turns **colourless** at the neutralisation point.

Indicator	pH at colour change	Colour in acid	Colour in base
Methyl orange	3-5	Red	Yellow
Phenolphthalein	8-10	Colourless	Pink
Litmus	5-8	Red	Blue

It is important that, depending on the strength of the titration reactants, the **correct indicator is selected** so that the colour change occurs at neutralisation. The pH at colour change must fall within the vertical section on the titration curve.

Indicators are **weak acids** themselves, so only a few drops are used otherwise they could affect the overall pH. They should be considered as HA. The colour change occurs due to an equilibrium **shift between the HA and  $A^-$  forms** of the indicator.

