Edexcel Chemistry A-level

Topic 16: Kinetics II

Detailed Notes

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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:

$$\mathbf{A + B \rightarrow C}$$

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

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.

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

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. This can be found by **substituting the units** into the rearranged equation and **cancelling**.

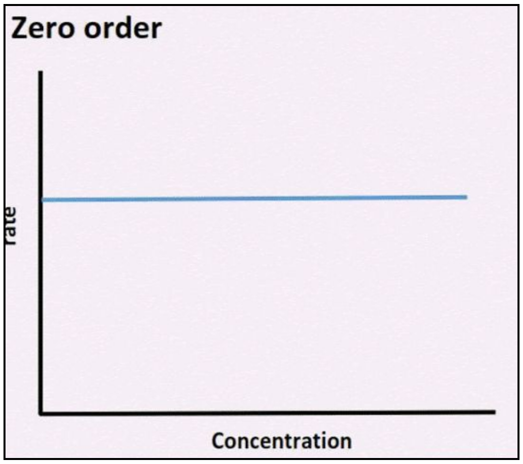
$$k = \frac{\text{Rate}}{[A]^m[B]^n}$$

Orders of Reaction

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

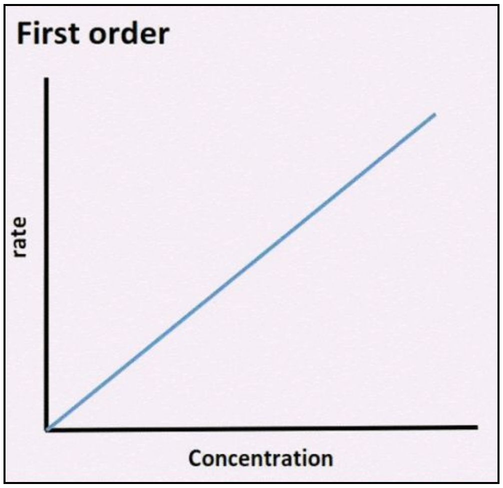
Zero Order

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



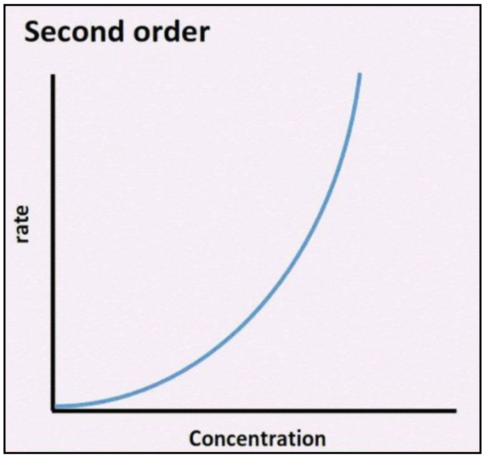
First Order

- 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 **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.

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

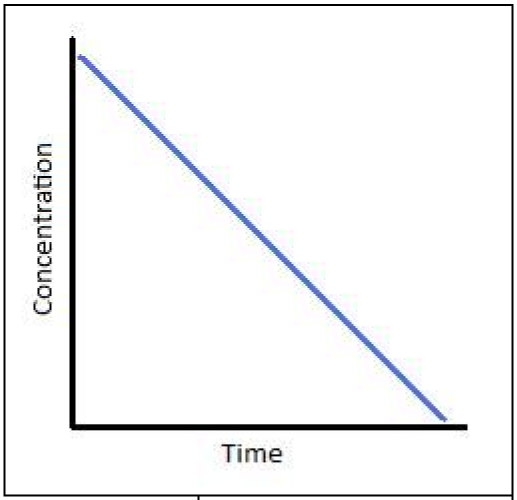
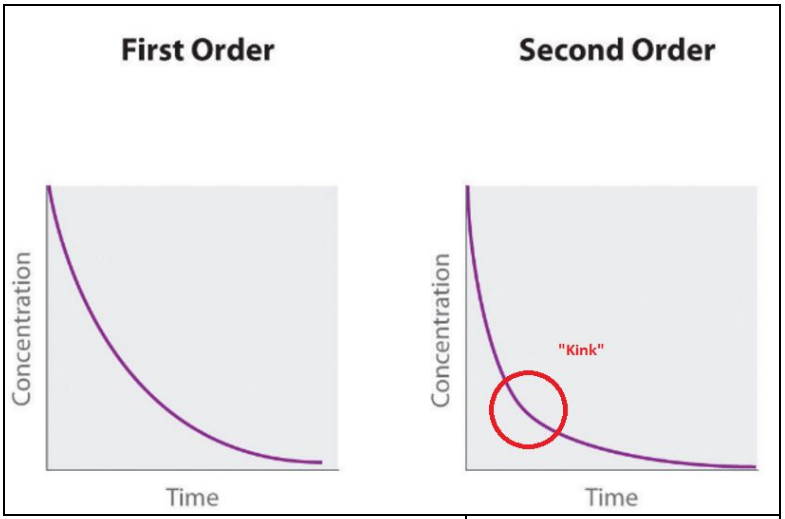


Image courtesy of chem.libretexts.org

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



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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^{-3})	Initial [B] (mol dm^{-3})	Initial [C] (mol dm^{-3})	Initial rate (mol dm^{-3} s^{-1})
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]^2**

Half-life

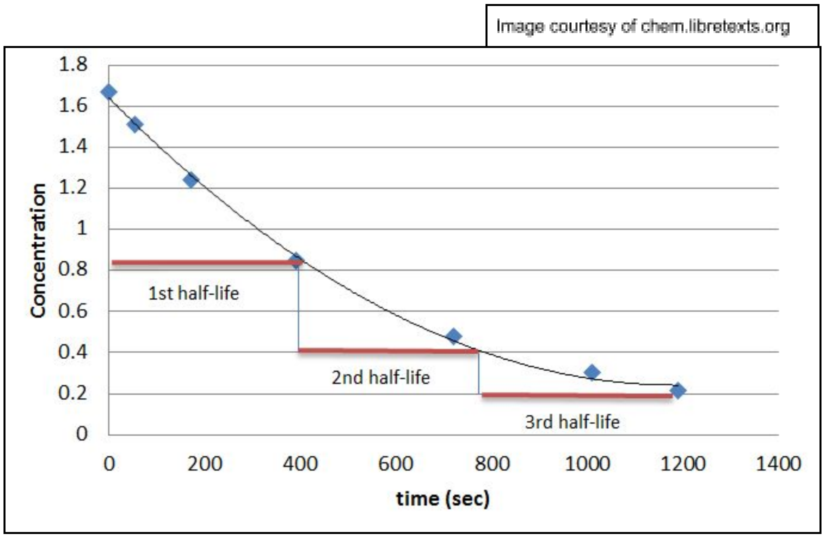
Half-life ($t_{1/2}$): The time taken for the initial concentration of the reactants to decrease by half.

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:



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**. Varying the concentration of reactants and their effects on the rate can also be used to find reactant orders and the overall order of reaction.

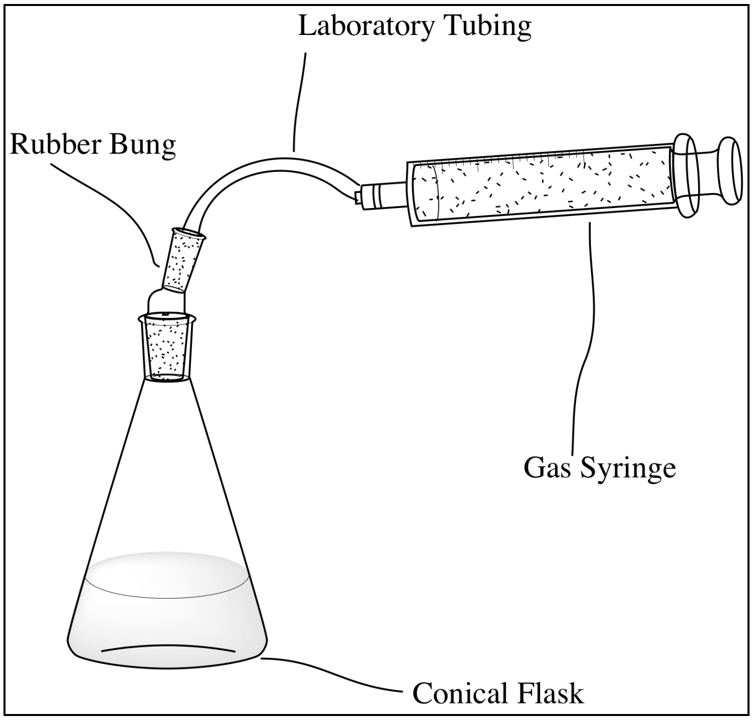
Mass Change

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 set-up:



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.

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$$

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**.

The 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. Therefore, the rate equation contains all the species involved in the stages **up to and including the rate determining step**.

This means that 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:

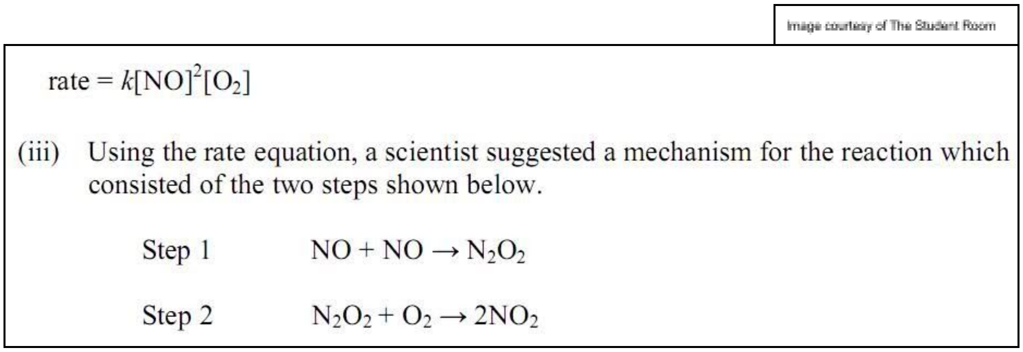


Image courtesy of The Student Room

rate = $k[NO]^2[O_2]$

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

Step 1 $NO + NO \rightarrow N_2O_2$

Step 2 $N_2O_2 + O_2 \rightarrow 2NO_2$

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. 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:

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

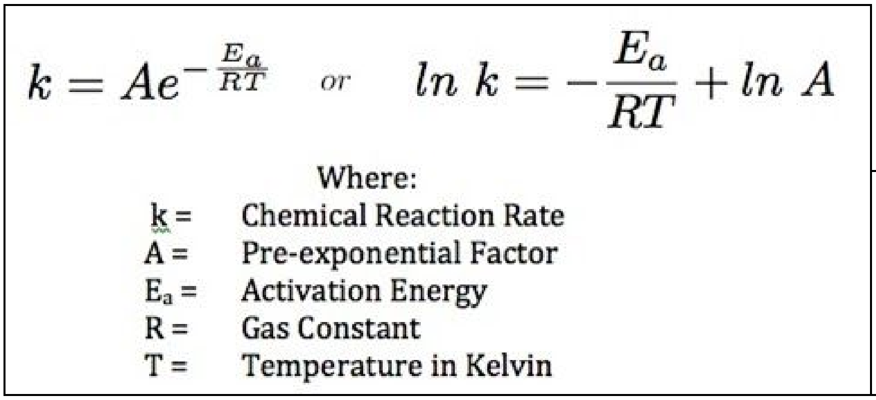
The rate equation for this reaction is: rate = $k[NO_2]^2$

- From the rate equation, the reaction is zero order with respect to CO(g) and second order with respect to $NO_2(g)$.
- 2 molecules of NO_2 are in the rate-determining step

1st step	$2NO_2(g) \rightarrow NO(g) + NO_3(g)$	(slow)
2nd step	$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$	(fast)
Overall	$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$	

The Arrhenius Equation

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



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

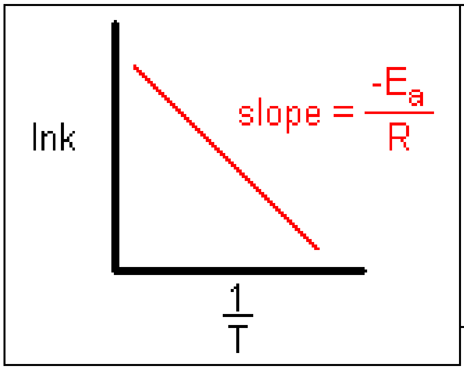
Where:

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 **negative and constant** and the y-intercept is ln(A):

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



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S_N1 and S_N2 of Halogenoalkanes

S_N1 and **S_N2** are types of nucleophilic substitution reactions. The S_N1 mechanism occurs in **two steps** whereas the S_N2 reaction occurs in **one**.

Mechanisms

In S_N1 reactions, the **leaving group (X) leaves first** and then in the second step the nucleophile attacks the **carbocation** formed. The first step which forms the carbocation intermediate is the rate determining step so the rate equation for S_N1 reactions includes the concentration of the **halogenoalkane only**.

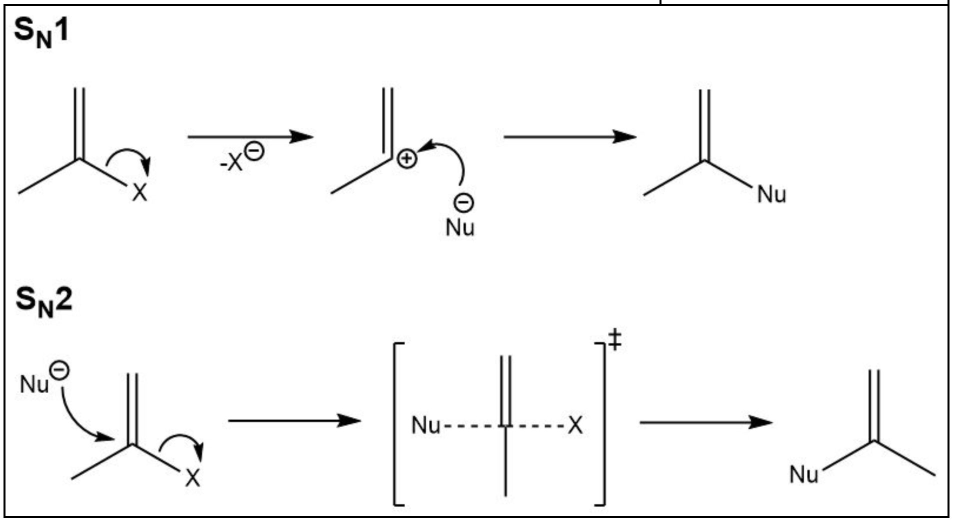
Rate = k [Halogenoalkane]

In S_N2 reactions, the **leaving group (X) leaves while the nucleophile attacks the molecule**. Because these steps occur simultaneously and this is the only step in the mechanism, this is the rate determining step. Therefore, the rate equation includes **both** the concentration of the **halogenoalkane** and the concentration of the **nucleophile**.

Rate = k [Halogenoalkane] [Nu:]

Example:

Image courtesy of Stack Exchange



Reaction Rates

The rate of S_N1 reactions depends on the **stability** of the **carbocation intermediate**. Therefore, **tertiary halogenoalkanes** react the **fastest** in S_N1 reactions since tertiary halogenoalkanes are the most stable. The rate of S_N2 reactions depends on how easily the nucleophile can **access** the carbon attached to the leaving group (X). Therefore, **primary halogenoalkanes** react the **fastest** in S_N2 reactions since there are smaller groups surrounding carbon attached to the leaving group.