

WJEC Chemistry A-level

3.5: Chemical Kinetics

Detailed Notes

Welsh Specification

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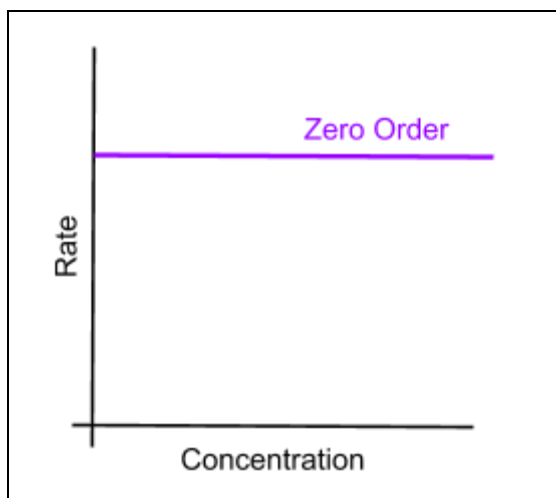


Orders of Reaction

Reactions have an **order** with respect to the different species present. This explains how different species can have more of an effect on the reaction than others. The **orders of reaction** you will need to consider range from **zero to second order**. Depending on the order of reaction of a reactant, changing the concentration of the reactant can have different effects on the whole reaction.

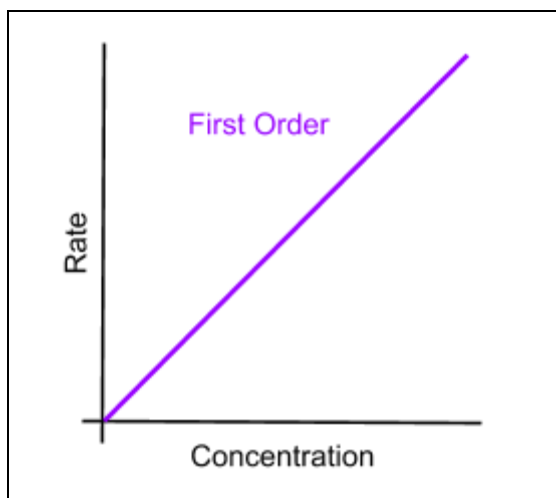
Zero Order - The concentration of this species has **no impact on rate**.

- Shown graphically as a **horizontal** line:



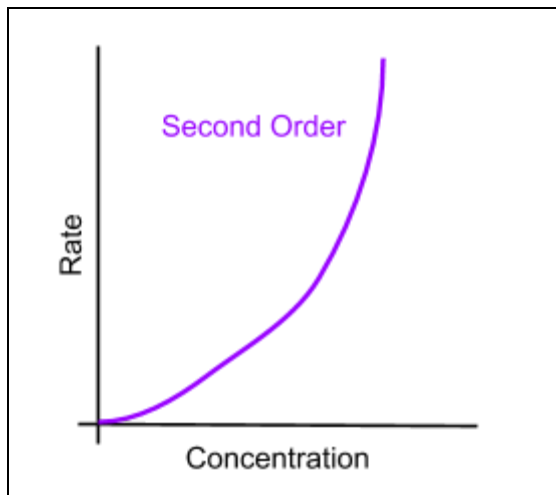
First Order - The concentration of the species and rate are **directly proportional**.

- Doubling concentration doubles the rate.



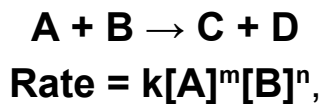


- Second Order** - The rate is proportional to the **concentration squared**.
- Doubling the concentration will increase the rate by four.



General Rate Equations

Rate of a reaction uses the orders of reaction to show how the **concentration** of reactants affect the rate of reaction. It depends on the concentrations of the reactants and a **rate constant**.



where m and n are the orders of the reaction with respect to reactant A and reactant B.

If [A] is **doubled** but the **rate stays** the same, then the **order** with respect to A is **0**.

If [A] is **doubled** and the **rate also doubles**, then the **order** with respect to A is **1**.

If [A] is **doubled** and the rate changes to be **four times faster**, then the **order** with respect to A is **2**.

The total order of reaction for this chemical reaction can be found from the general rate equation as the **sum of the separate orders**:

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

Rate Constant (k)

The rate constant for a reaction is **constant** when the reaction **temperature is constant**. It can be found by rearranging the rate equation for that reaction:

$$k = \text{Rate} / ([\text{A}]^m[\text{B}]^n)$$

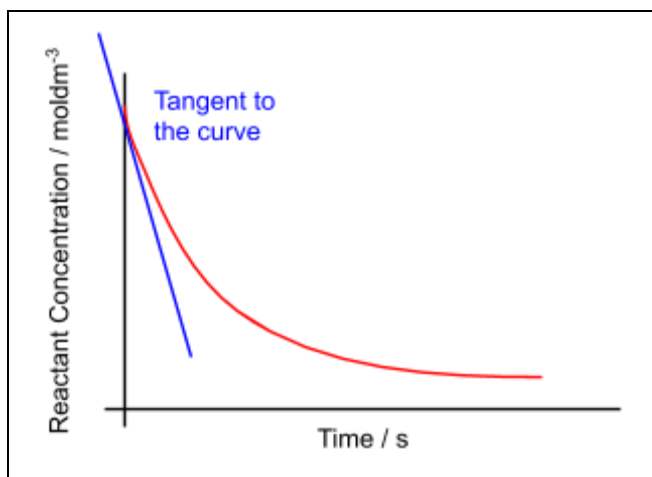




The rate constant has **varying units** depending on the number of species and their orders of reaction. This can be found by substituting the units into the equation and cancelling.

Determining Rate Equations

Rate equations can be determined experimentally by **monitoring the concentration** of a reaction mixture over time. The concentration-time graph produced can be used to find the rate by drawing a **tangent to the curve at t=0**.



The tangent is drawn at the starting point as it is the only time in the reaction where the exact **concentration is known**. This method is then repeated at **varying concentrations** to get a set of data for concentration and rate of reaction. A graph of rate against concentration can then be plotted to determine the **order of reaction** of the reactant.

Initial Rate experiments

The orders of reaction can also be determined using **experimental data** relating to **initial rates**. The data values of initial rates with varying concentrations of reactants can be collected by following the process described above. An example is shown below:

Experiment	[A] (mol dm ⁻³)	[B] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
1	0.10	0.10	0.0015
2	0.20	0.10	0.0060
3	0.20	0.20	0.0120

Between experiments 1 and 2, the concentration of A doubles ([B] stays constant) and the rate quadruples. The reaction is **second order with respect to A**.

Between experiments 2 and 3, the concentration of B doubles ([A] remains the same) and the rate doubles. The reaction is **first order with respect to B**.





From these results, the **rate equation** is: **rate = k[A]²[B]**

The rate equation can be used to **calculate the rate constant**:

- Substitute in experiment 1 values into the rate equation: $0.0015 = k \times 0.102 \times 0.10$.
- Rearrange to find k: $k = 0.0015 \div 0.001 = 1.5$.
- Work out units: $k = \text{mol dm}^{-3} \text{ s}^{-1} \div (\text{mol dm}^{-3})^3 = \text{mol}^2 \text{ dm}^{-6} \text{ s}^{-1}$.

Therefore, **k = 1.5 mol² dm⁻⁶ s⁻¹**.

Rate Determining Step

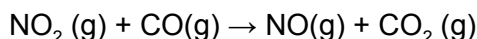
Not all stages of a reaction occur at the same rate, but the **overall rate** is determined by the **slowest step** of the reaction - the rate determining step. The **rate determining step** must include reactants which have an impact on the rate of reaction when their concentrations are changed. **Zero order reactants** have no influence on the rate of a reaction so they cannot be included in the rate-determining step.

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.

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**.

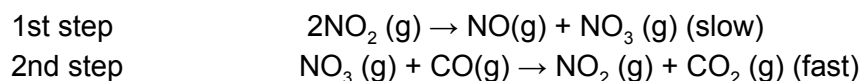
Example mechanism:

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



The rate equation for this reaction is: **rate = k[NO₂]²**

From the rate equation, the reaction is zero order with respect to CO and second order with respect to NO₂. Two molecules of NO₂ are in the rate determining step:



Clearly the 1st step is the rate determining step.





The Arrhenius Equation

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

$$K = Ae^{\frac{-E_a}{RT}}$$

$$\ln|K| = \ln|A| - \frac{E_a}{RT}$$

The Arrhenius equation is very useful 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 **$\ln A$** .

Example:

