

OCR (B) Chemistry A-level

Storyline 6: The Chemical Industry Detailed Notes

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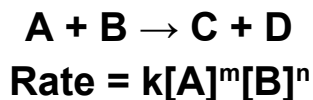




Kinetics

Rates and Rate Equations

The rate of a reaction shows how fast **reactants are converted into products**. The rate of reaction 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 each 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.

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

The **units** for rate of reaction are **mol dm⁻³s⁻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.

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

The rate constant, **k**, can be calculated by **rearranging the rate equation** for that reaction. **k** 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**.

Rate Graphs and Orders

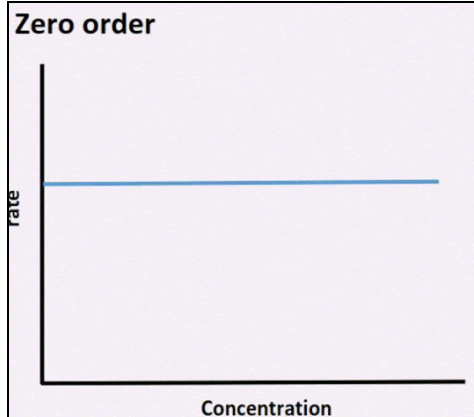
The orders of reaction (that you need to know about at A-level) range from **zero to second order**. This means that changing the concentration of reactants can have different effects on the whole reaction:





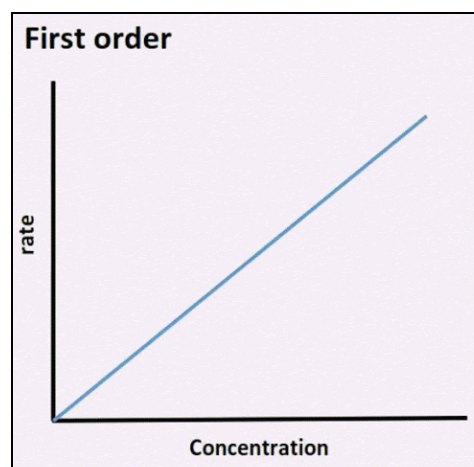
Zero Order

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



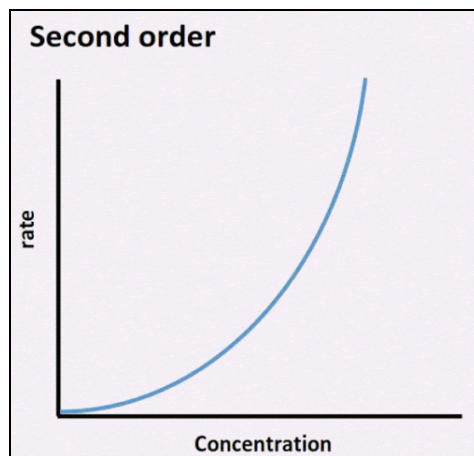
First Order

- 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



Images courtesy of dereksavvy-chemist.blogspot.com





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**:

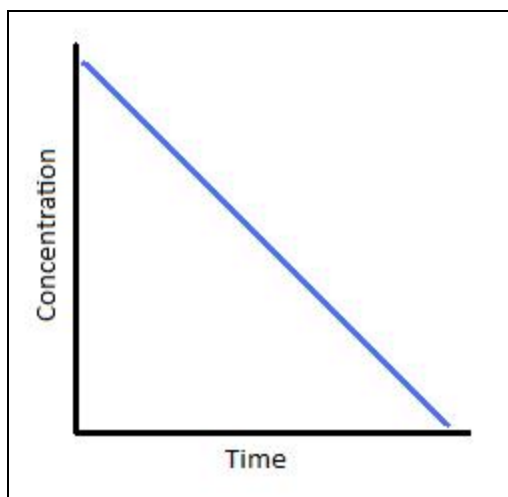


Image courtesy of chem.libretexts.org

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

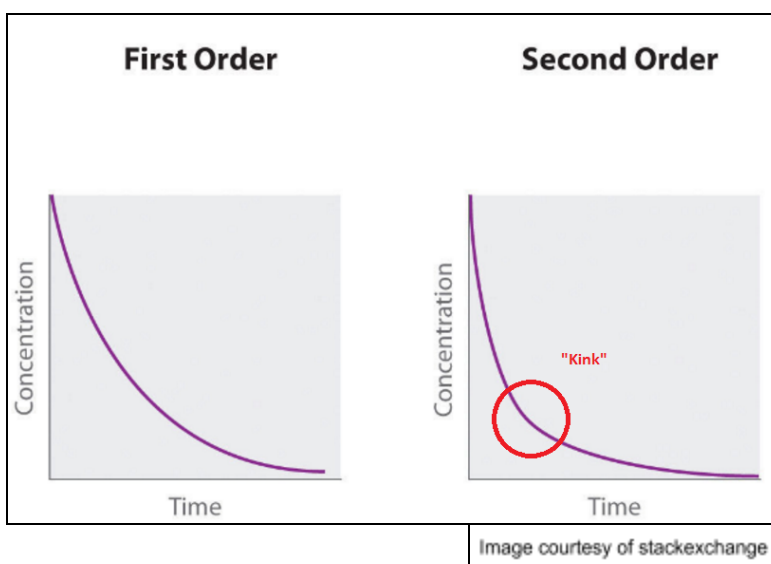


Image courtesy of stackexchange



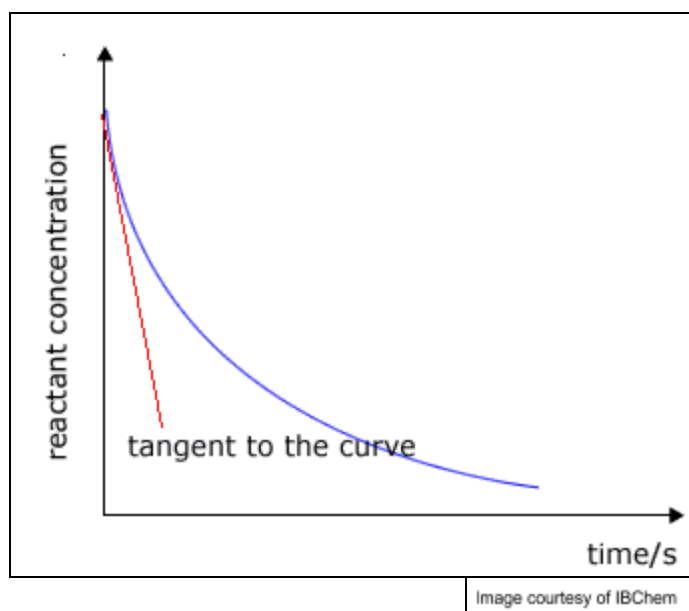


On a **concentration-time graph**, the rate of reaction is equal to the gradient of the curve at a given point. Therefore, the graph can be used to find the **rate** at a certain time by drawing a **tangent** to the curve at this given time and calculating the **gradient** of the tangent.

$$\text{Gradient} = (\text{change in } y) \div (\text{change in } x)$$

Drawing a **tangent** to the curve when **time = 0** finds the **initial rate** of reaction. The tangent at any other position finds the rate of reaction at that moment in time. The units of rate calculated in this way are generally **mol dm⁻³s⁻¹**.

Example:



Suitable **physical quantities** to **monitor** which reflect the rate of reaction include concentration, gas volume, and mass.

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** (2²).





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.

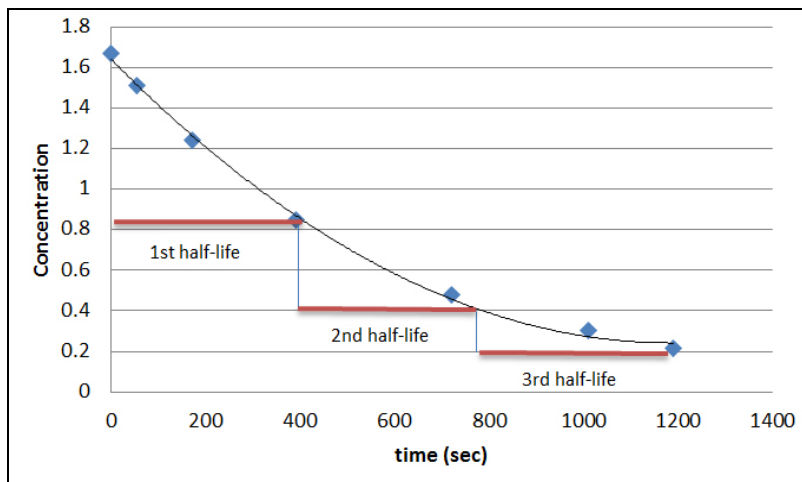
First Order Reaction

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: Half life of a first order reactant

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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.

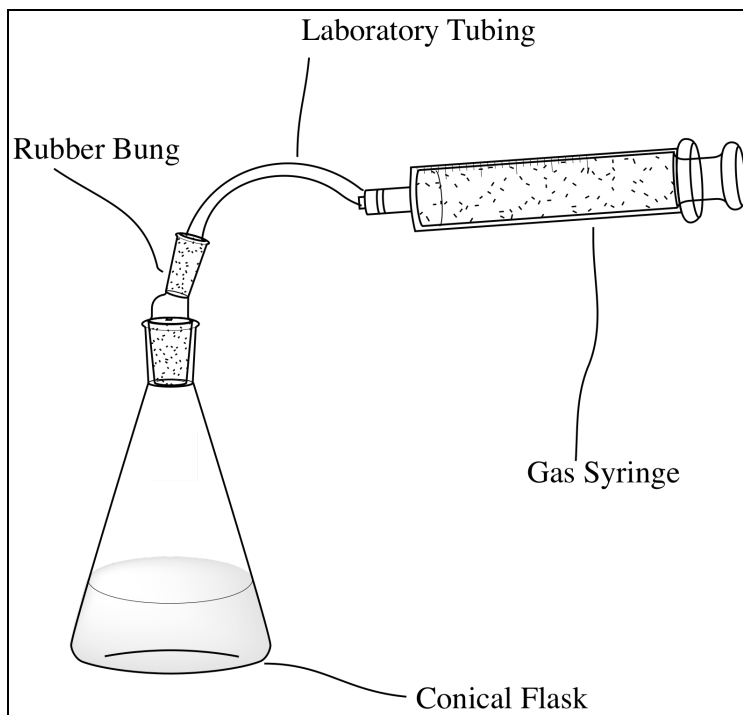
Volume of Gas Evolved

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:



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:

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

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

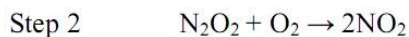


Image courtesy of The Student Room



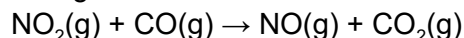


In this question, step 2 would be the rate determining step as all the reactants of this step are in the rate equation given at the start.

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.

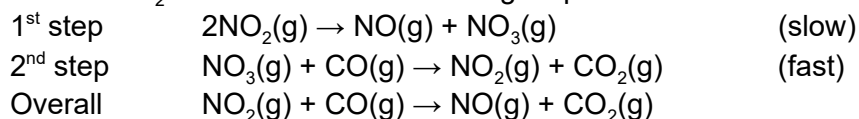
Example mechanism:

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 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**:

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

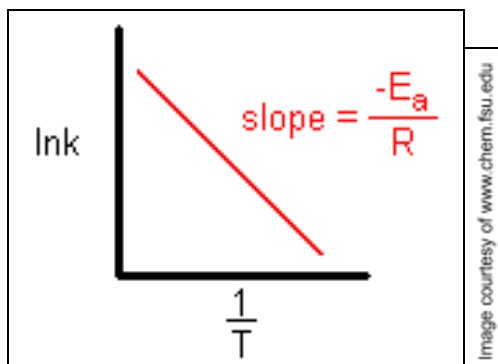
Where:

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

Image courtesy of StevePayer

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 $\ln(A)$:





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.

Equilibrium

Factors Affecting K_c

The value of K_c is not **affected by concentration or pressure change** or by the use of a **catalyst**. However, it is 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) **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) **increases**.

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



Compromise between Rate of Reaction and Product Yield

Changing the conditions of reaction can **shift** the **position** of the equilibrium to favour the production of either the **products** or the **reactants**, as described above. However, a condition change which produces a **higher proportion of the product** may also **reduce the rate of the reaction**. The rate of reaction is increased by increases in temperature, pressure or concentration.

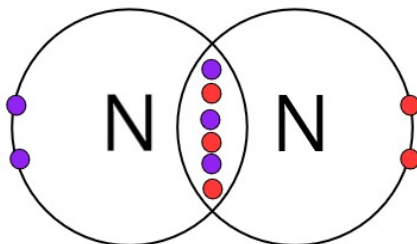
For example, **decreasing the temperature** of a reaction with a **forward endothermic reaction** would **increase** the product **yield**, but **decrease** the **rate** of reaction.

In the industry, when a factor increases the product yield but decreases the rate of a reaction, a **compromise** must be made. If the product yield was the only thing taken into account, the rate of reaction would occur **so slowly** that the product is not actually made at a useful rate. Therefore, reaction conditions are selected to give both a **relatively good product yield** and a **relatively fast rate of reaction**. You must also consider safety and economics when determining the conditions used in industrial reactions.

Inorganic Chemistry and the Periodic Table

Nitrogen

Nitrogen, N_2 , has a **low reactivity** due to its bonding.



A nitrogen molecule, shown above, has a **triple covalent bond** between **two nitrogen atoms**. Chemical reactions normally involve **breaking bonds** so that new bonds can be formed. Therefore, nitrogen is **very unreactive** as a large amount of energy is required to break the **strong** triple covalent bond.

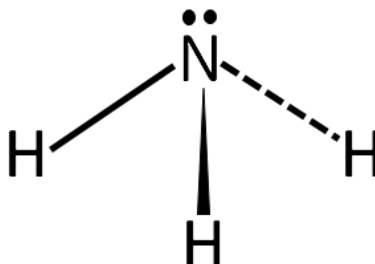
Nitrogen molecules are also **unreactive** since the bonds in nitrogen molecules are **nonpolar** and are **not easily polarisable**. This means **electrophiles** and **nucleophiles** are not attracted to nitrogen molecules, making the molecules less likely to be involved in reactions.





Ammonia

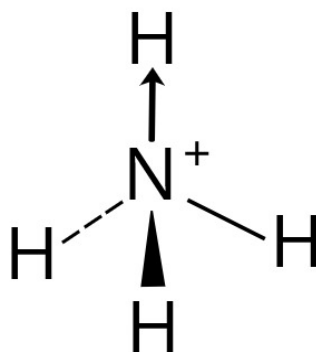
Ammonia has three hydrogen atoms which are **covalently bonded** to a nitrogen atom, this leaves a **lone pair of electrons**. The bonding shape is pyramidal with a bond angle of 107 degrees. Ammonia is a nucleophile due to the lone pair of electrons on the nitrogen atom.



The Ammonium Ion

Ammonium ions have three hydrogens covalently bonded to the nitrogen and one dative covalent/coordinate bond to a fourth hydrogen. Once bonded, these four bonds are indistinguishable. Ammonium ions are often produced during **acid-base reactions**.

The ammonium ion has a **tetrahedral** shape. The structure of the ion is shown below (the arrow represents the coordinate/dative covalent bond):



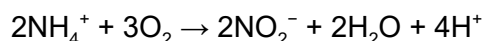
Oxides of Nitrogen

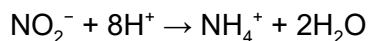
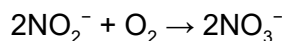
Oxides of nitrogen, such as **nitrogen monoxide**, can be formed as a result of **combustion reactions in car engines**. Nitrogen oxides are also produced **naturally** by the occurrence of **lightning**.

The three common **oxides of nitrogen** and their appearances are:

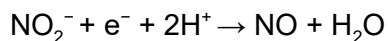
- N₂O, nitrous oxide - a sweet-smelling colourless gas
- NO, nitric oxide - a colourless gas
- NO₂, nitrogen dioxide - a **brown** gas

Nitrate (V) ions, nitrate (III) ions and ammonium ions are **interconvertible** by the following reactions:

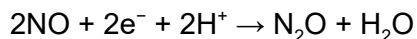




Nitrite ions can also be **reduced** to nitric acid by the following reaction:



Nitric oxide can also be **reduced** to nitrous oxide by the following reaction:



Tests for Nitrogen Compounds

Test for **nitrate(V) ions**: warm the sample with Devarda's alloy and NaOH, test the gas released with damp red litmus paper. If the paper turns blue this confirms the presence of nitrate(V) ions.

Test for **ammonium ions**: warm a sample with NaOH, test the gas released with damp red litmus paper. If the paper turns blue this confirms the presence of ammonium ions.

In both cases, **ammonia is evolved**. This gas is basic, so turns damp red litmus paper blue.

Sustainability

When carrying out a reaction in industry many factors must be taken into account. For example, costs and sources of **raw materials**, **energy** costs, costs associated with the **plant** and **byproducts**. The **benefits** to society of the product of the reaction must be balanced with the **risks and hazards** associated with it.

