Rate Equations

> **Definition 0.1** (Rate of Reaction) — The change in concentration of a reactant or product per unit time.

If more than one reactant is involved in a reaction, each can affect the rate differently. The effect of the individual reactants is described by stating an **order** with respect to each reactant. We can express the relationship between rate and the concentration mathematically.
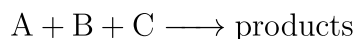
$$\text{rate } \alpha \; [A]^x$$

where x is the order of reaction with respect to A, and $[A]$ denotes the concentration of A.

There are three typical orders of reaction:

Order	Expression	If concentration doubles, rate...
zero	rate $\alpha \; [A]^0$	stays the same
first	rate $\alpha \; [A]^1$	doubles
second	rate $\alpha \; [A]^2$	quadruples

> **Remark 0.2** Notice that if a reaction is **zeroth order** with respect to a reactant A, then the concentration of A has no affect on the rate of reaction.

Consider the following reaction:

$$\text{A} + \text{B} + \text{C} \longrightarrow \text{products}$$

The rate of the reaction can be given by the expression rate $\alpha \; [A]^x[B]^y[C]^z$. This statement can be converted into a **rate equation** with rate constant k.

> **Formula 0.3** (Rate Equation)
> $$\text{rate } = k \cdot [A]^x[B]^y[C]^z$$

N/B: The order of a reactant is not necessarily the same as its **stoichiometry**[1] in the equation. The **overall order** is the sum of the individual orders. So, in the case above, the overall order is $x + y + z$. *e.g.* If we had rate $= k[B][C]^2$, then the overall order is 3.

§0.1 Rate Constants

The value and units of k can be found by rearranging the rate equation.

> **Example 0.4** Determine the order with respect to each reactant and the overall order, and hence calculate the value of the rate constant.
>
> | Experiment | $[A]/\text{mol dm}^{-3}$ | $[B]/\text{mol dm}^{-3}$ | $[C]/\text{mol dm}^{-3}$ | Rate / mol dm^{-3} s^{-1} |
> |---|---|---|---|---|
> | 1 | 1.0×10^2 | 1.0×10^2 | 1.0×10^2 | 3.0×10^4 |
> | 2 | 2.0×10^2 | 1.0×10^2 | 1.0×10^2 | 6.0×10^4 |
> | 3 | 1.0×10^2 | 2.0×10^2 | 1.0×10^2 | 3.0×10^4 |
> | 4 | 1.0×10^2 | 1.0×10^2 | 2.0×10^2 | 12.0×10^4 |

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[1]The numbers in front of species which indicate the molar ratio in a reaction equation.

Solution. Using experiments 1 and 2, when $[A]$ doubles, the rate doubles. Hence, the reaction is first order w.r.t. A.

With experiments 1 and 3, when $[B]$ doubles, the rate is unchanged. Hence, the reaction is zeroth order w.r.t. B.

Using experiments 1 and 4, when $[C]$ doubles, the rate quadruples. Hence, the reaction is second order w.r.t. C.

$$\therefore \text{ rate } = k[A]^1[B]^0[C]^2 = k[A][C]^2$$

The overall order is 3; $k = \frac{\text{rate}}{[A][C]^2} = \frac{3 \times 10^4}{10^2 \times 10^4} = \underline{0.03 \text{ mol}^{-2}\text{ dm}^6\text{ s}^{-1}}$. $\qquad\square$

Temperature has an effect on rate constants. We should recall that increasing temperature increases rate of reaction from rates.

Clearly, the larger the value of k, the faster the rate of reaction. So, increasing temperature will increase the value of k. For many reactions, the rate doubles every 10K increase in temperature; typically, doubling the rate doubles the value of k. The relationship between temperature and k is expressed mathematically by the **Arrhenius Equation**.

> **Formula 0.5** (Arrhenius equation)
> $$k = Ae^{-\frac{E_A}{RT}}$$

where A is a pre-exponential constant, E_A is the activation energy, R is the ideal gas constant and T is the absolute temperature.

By taking logs, we can rearrange the Arrhenius equation into the form '$y = mx + c$', which is more useful.

> **Formula 0.6** (Rearranged form of the Arrhenius Equation)
> $$\ln k = -\frac{E_A}{R} \cdot \frac{1}{T} + \ln A$$

We can then plot $\ln k$ against $\frac{1}{T}$ (known as **Arrhenius Plots**):

- the y-intercept is equal to $\ln A$, which can be used to find A.

- the gradient is equal to $\frac{-E_A}{R}$, which can be rearranged to find E_A.
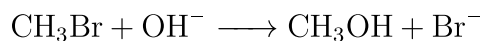
§0.2 Rate Determining Step

Reactions can occur in one step or in many steps. The series of steps that occur during a reaction is known as the **mechanism**. Steps can occur at different rates to each other.

> **Definition 0.7** (Rate-Determining Step (RDS)) — The slowest step in the mechanism of a multi-step reaction.

We can use the rate equation to infer which reactants are in the **RDS**. Reactants that do not appear in the rate equation do not influence the rate, and hence cannot be in the RDS.

We can use this to determine the RDS for the hydrolysis of bromoethane, which has rate equation: rate $= k[\text{CH}_3\text{Br}]$.

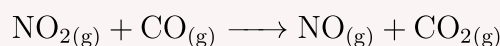$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$

- By the rate equation, only CH_3Br affects the rate, so RDS involves CH_3Br only.

    1. $CH_3Br \longrightarrow CH_3^+ + Br^-$ (slow)
    2. $CH_3^+ + OH^- \longrightarrow CH_3OH$ (fast)

- So, the rate-determining step is step 1 above since it is the only one involving CH_3Br.

The **order** of a reaction with respect to a given reagent indicates the **number of molecules** of that reagent in the RDS. Some reactions involve the formation of an **intermediate**, that is not necessarily in the overall equation or the rate equation.

> **Definition 0.8** (Intermediate) — A species that is formed in one step of a multi-step reaction and is used up in a subsequent step.

> **Example 0.9** Nitrogen dioxide NO_2 reacts with carbon monoxide CO to form nitrogen monoxide NO and carbon dioxide CO_2.
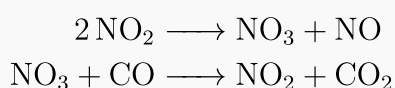>
> $$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$$
>
> The reaction is:
>
> - Second order with respect to NO_2.
> - Zeroth order with respect to CO.
>
> Propose a mechanism for this reaction.

> *Solution.* We can deduce the rate equation to be rate $= k[NO_2]^2$, so the RDS must involve $2NO_2$. In order to make the overall equation, the following mechanism works:
>
> $$2\,NO_2 \longrightarrow NO_3 + NO$$
> $$NO_3 + CO \longrightarrow NO_2 + CO_2$$
>
> $\square$