Kinetics

Reaction kinetics gives information on the pathways of a chemical reaction

- Relates to the effect of the concentration on the reaction rate
- Rate is usually expressed as the change of concentration per unit time

Rate is independent of the size of the reaction sample analysed.

<u>The Rate Law</u>

$$\text{Rate} \quad \alpha \quad [A]\,[B]$$

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

Where k is the rate constant.
n is the order of the reaction with respect to A
m is the order of the reaction with respect to B

Values of order of reaction (n+m) refer to actual numbers of particles involved in a single step controlling the overall rate of reaction.

These values are ***not*** the stoichiometric coefficients from a balanced chemical equation (i.e. not the numbers in front of the chemical formulae)

$$H_2O_2 + 2HI \longrightarrow 2H_2O + I_2$$

rate α $[H_2O_2]\,[HI]$ (discovered by experiment)

The overall order of the reaction is the sum of the powers of the concentrations (i.e. n+m)

Rate Law Equation	Order of Reaction
rate α $[A]^0$	0
rate α $[A]^1$	1
rate α $[A]^2$	2
rate α $[A]^1[B]^1$	2
rate α $[A]^1[B]^2$	3

Order of Reactions

Determining the Rate Constants & Order of Reaction

Rate constant determined by series of experiments

Zero order—does not affect reaction rate

First order—doubles reaction rate

Second order—quadruples reaction rate

Rate Determining Step

Chemical reactions proceed in a series of sequential stages

- Slowest step is called the **rate determining step**
- Overall rate of reaction determined by the slowest step
- Experimentally determined rate equations and order of reactions can give information about the mechanism of the reaction

Example

$$H_2O_2 + 2HI \longrightarrow 2H_2O + I_2$$

- Step 1 $\quad H_2O_2 + HI \longrightarrow X$ (slow: Rate Determining Step)
- Step 2 $\quad X + HI \longrightarrow$ product (faster step)

where X is an intermediate formed during the reaction

Rate controlled by a step where one molecule of H_2O_2 reacts with *one* molecule of HI

Rate = k $[H_2O_2]$ [HI] (order of both reactants =1)

- Kinetics of reaction give no direct information about the nature of the intermediate chemical X or the total number of steps involved
- Further information is deduced by other means, for example spectroscopy

Order of Reactions

Units for Rate constant

Order goes UP ⬆️ → L power UP ⬆️ → mol power DOWN ⬇️

🟡 0th order
➡️ $(mol\ L^{-1})\ s^{-1}$

🟢 1st order
➡️ s^{-1}

🔵 2nd order
➡️ $L\ mol^{-1}\ s^{-1}$

🟣 3rd order
➡️ $L^{2}\ mol^{-2}\ s^{-1}$

🟠 4th order
➡️ $L^{3}\ mol^{-3}\ s^{-1}$

🔴 5th order
➡️ $L^{4}\ mol^{-4}\ s^{-1}$

Kinetics - Rate Equation & Rate Constant

Example 1: Calculate the rate constant and the order of each reactant

For the reaction: $A + B + C \longrightarrow D$

Results of Experiments:

Experiment	[A] / mol l^{-1}	[B] / mol l^{-1}	[C] / mol l^{-1}	Initial rate of D formed / mol l^{-1} s^{-1}
1	1.0	1.0	1.0	2.0
2	2.0	1.0	1.0	4.0
3	1.0	2.0	1.0	2.0
4	1.0	1.0	2.0	8.0

1st Order with respect to [A]
Zero Order with respect to [B]
2nd Order with respect to [C]

Overall Order = 1 + 0 + 2 = 3

$$\text{Rate} \quad \alpha \quad [A]^1 \; [C]^2$$

To calculate the rate constant, substitute in values from experiment 1:

$$\text{Rate} = k\,[A]\,[C]^2$$

$$2.0 = k \times [1.0] \times [1.0]^2$$

$$k = \frac{2.0 \text{ mol } l^{-1} s^{-1}}{1 \times 1^2 \text{ mol}^3\, l^{-3}}$$

$$= 2.0 \quad l^2 \text{ mol}^{-2} \text{ s}^{-1}$$

Kinetics - Rate Equation & Rate Constant

Example 2: Calculate the rate constant and the order of both reactants

For the reaction: $2NO + O_2 \longrightarrow 2NO_2$

Results of Experiments:

Experiment	Initial Concentration/ mol l^{-1}		Initial rate of NO_2 formed / mol l^{-1} s^{-1}
	[NO]	[O_2]	
1	2.0×10^{-5}	4.0×10^{-5}	1.4×10^{-10}
2	2.0×10^{-5}	8.0×10^{-5}	2.8×10^{-10}
3	4.0×10^{-5}	4.0×10^{-5}	5.6×10^{-10}

Reaction is 1st Order with respect to [NO] & 2nd Order with respect to [O_2]

$$\text{Rate} \quad \alpha \quad [NO]^2\,[O_2]$$

$$\therefore \text{ overall order} = 2+1 = 3$$

To calculate the rate constant, substitute in values from experiment

$$\text{Rate} = k \times [NO]^2 \times [O_2]$$

$$1.4 \times 10^{-10} = k \times [2.0 \times 10^{-5}]^2 \times [4.0 \times 10^{-5}]$$

$$k = \frac{1.4 \times 10^{-10} \ \text{mol } l^{-1} s^{-1}}{[2.0 \times 10^{-5}]^2 \times [4.0 \times 10^{-5}] \ \text{mol}^3 \, l^{-3}}$$

$$= 8.75 \times 10^{3} \quad l^2 \, \text{mol}^{-2} \, s^{-1}$$

Kinetics - Zero Order

Zero Order Reactants

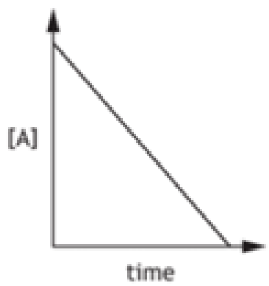
Concentration of reactant has no effect on reaction rate. Not involved in R.D.S (slow step).

This reactant is zero order

$[C_4H_9Br]$ (mol l^{-1})	$[OH^-]$ (mol l^{-1})	*Initial rate* (mol l^{-1} s^{-1})
0·25	0·10	$3{\cdot}3 \times 10^{-6}$
0·50	0·10	$3{\cdot}3 \times 10^{-6}$

Time graph

- zero order



Rate graph

- zero order