1.6 Kinetics

Kinetics is the study of the speed of chemical reactions

- Factors affecting the rate of reaction include
    - Temperature
    - Concentration of reactants
    - Particle size/surface area
    - Presence of a catalyst
- Activation energy must be overcome to react
- Activated complex formed as reaction proceeds.

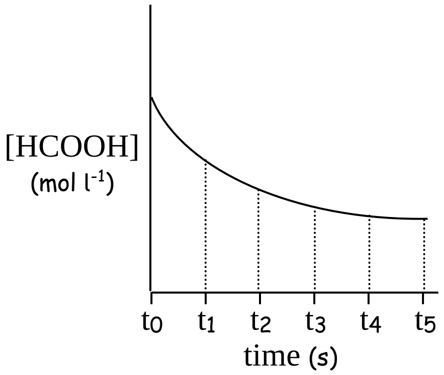
Reaction kinetics gives information on the pathways of a chemical reaction

- 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.

For example: $HCOOH \longrightarrow CO + H_2O$

Rate can be determined by following:

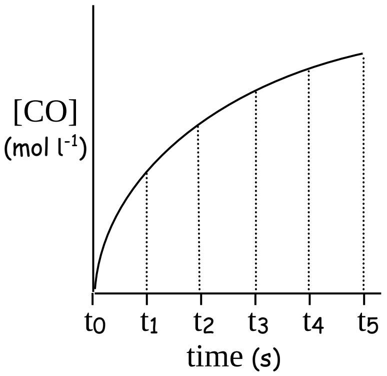
a) decrease in the concentration of HCOOH



NB: negative sign as [HCOOH] is decreasing

$$\text{Average Reaction Rate} = \frac{-\left([HCOOH]_2 - [HCOOH]_1\right)}{t_2 - t_1}$$

b) increase in concentration of CO



$$\text{Average Reaction Rate} = \frac{+\left([CO]_2 - [CO]_1\right)}{t_2 - t_1}$$

In both graphs, reaction rate decreases as the reaction proceeds.

- Reaction rate decreases as gradient of line approaches zero (horizontal)
- The shorter the time interval, the more accurate the measurement of instantaneous rate
- As Δt approaches zero, it becomes dt

$$\text{Instanteous Reaction Rate} = \frac{-\,d\,[HCOOH]}{dt} \quad \text{or} \quad \text{Instanteous Reaction Rate} = \frac{d\,[CO]}{dt}$$

The rate, at particular time t, is given by the gradient of the tangent to the curve at time t.

- At $t=0$, rate has its maximum value
- It is usual to determine initial rate of reaction and use this value to determine other kinetic values

2.9.1 Reaction Rates and Concentration

Consider the following reaction:

$$A + B \xrightarrow{\quad} \text{products}$$

- Rate of forward reaction depends on [A] & [B] at that particular time.

The Rate Law

$$\text{Rate} \; \alpha \; [A][B]$$

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

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

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

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

- The controlling rate step is called the *rate determining step.*
- These values are ***not*** the stoichiometric coefficients from a balanced chemical equation (i.e. not the numbers in front of the chemical formulae)

e.g. $H_2O_2 + 2HI \xrightarrow{\quad} 2H_2O + I_2$

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

order of reaction = 2 despite there being 3 reactant molecules
(1x H_2O_2 and 2x HI)

Determining the Rate Constants & Order of Reaction

- Rate constant determined by series of experiments
  - Initial concentration of reactants are changed between experiments

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

Analysis of Results

Experiments Compared	Change in Conditions	Effect of Change on Rate	Order of Reactant
1+2	[A] x2	rate x2	$[A]^1$
1+3	[B] x2	no change in rate	$[B]^0$
1+4	[C] x2	rate x4	$[C]^2$

Conclusions

$$\text{Rate} \;\alpha\; [A]^1\,[B]^0\,[C]^2$$

$$\therefore \text{Rate} \;\alpha\; [A]\,[C]^2$$

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

Overall Order = 1 + 0 + 2 = 3

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

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

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

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

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

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}

Analysis of Results

Experiments Compared	Change in Conditions	Effect of Change on Rate	Order of Reactant
1+2	$[O_2]$ x2	rate x2	$[O_2]^1$
1+3	[NO] x2	rate x4	$[NO]^2$

Conclusions: Rate α $[NO]^2\,[O_2]$ $\therefore$ overall order = 2+1 =3

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

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

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

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

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

2.9.2 Kinetics and Reaction Mechanism

Chemical kinetics can follow the *bottle-neck* principle

- A large crowd leaving a car park after a concert can take a long time to leave as they have to queue to exit the car park though a narrow exit.

Chemical reactions proceed in a series of sequential stages

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

Example 1: $H_2O_2 + 2HI \longrightarrow 2H_2O + I_2$

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

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

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

where X is an intermediate formed during the reaction

- 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

Actual Mechanism:

- $H_2O_2 + HI \longrightarrow H_2O + HOI$
- $HOI + HI \longrightarrow H_2O + I_2$

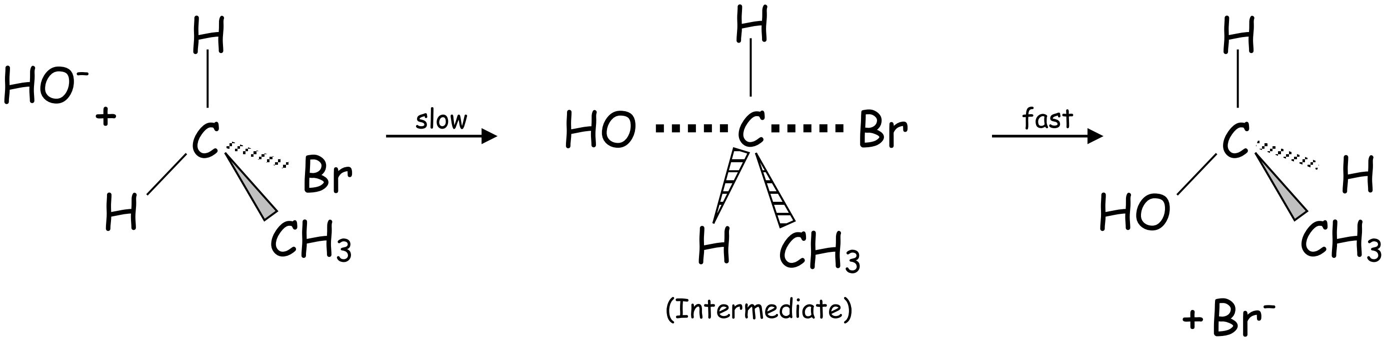
Where HOI is an intermediate formed with a transient lifetime.

Example 2: Hydrolysis of a primary halogenalkane

$CH_3CH_2Br + OH^- \longrightarrow CH_3CH_2OH + Br^-$

Rate = k $[CH_3CH_2Br][OH^-]$

- both reactants are 1st order reactants
- both reactants are involved in the rate determining step
  - rate determining step is in fact the only step in this reaction mechanism
  - OH^- ion attacks the back of the molecule to displace the bromine atom to form a bromide Br^- ion.
  - This mechanism is known as a S_N2 process in Unit 3



Example 3: Hydrolysis of a Tertiary Halogenalkane

$(CH_3)_3CBr + OH^- \longrightarrow (CH_3)_3COH + Br^-$

rate = k $[(CH_3)_3CBr]$

$\therefore$ $[(CH_3)_3CBr]$ is 1st order, $[OH^-]$ is zero order

- Rate determining step does not involve the OH^- ion

$(CH_3)_3CBr \longrightarrow X^+ + Br^-$ (slow step)
$X^+ + OH^- \longrightarrow (CH_3)_3COH$ (fast step)

where X is the $(CH_3)_3C^+$ ion – the carbocation

Questions:

1. Bromide ions and bromate ions react in acid solution to give bromine according to the equation:

$$6H^+ + 5\,Br^- + BrO_3^- \longrightarrow 3Br_2 + 3H_2O$$

Rate measurements on four different reaction mixtures gave the following data:

Experiment	$[H^+]$ /mol l^{-1}	$[Br^-]$ /mol l^{-1}	$[BrO_3^-]$ /mol l^{-1}	Relative rate / mol l^{-1} s^{-1}
1	0.45	0.375	0.075	1
2	0.45	0.75	0.075	2
3	0.9	0.375	0.075	4
4	0.45	0.375	0.15	4

a) What is the rate expression for the reaction?
b) What is the order of the reaction with respect to each of the reactants?
c) What is the overall order of the reaction?
d) Explain why the rate equation and the overall equation are different.

2. The reaction rates for the following reaction at various starting concentrations are given in the table below:

$$2N_2O_5 \longrightarrow 4NO_2^- + O_2$$

$[N_2O_5]$ (mol l^{-1})	Rate (mol l^{-1} s^{-1})
2.20	2.25×10^{-5}
2.00	2.10×10^{-5}
1.52	1.58×10^{-5}
0.93	0.96×10^{-5}

a) Draw a graph of the rate against $[N_2O_5]$
b) Calculate the value of the rate constant.