

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.

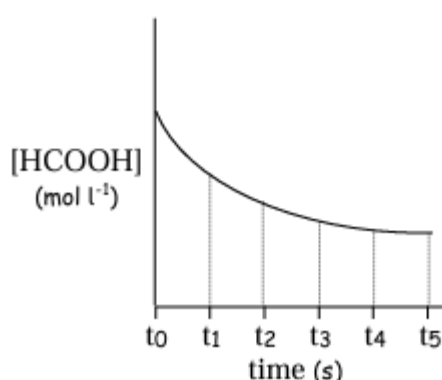
Reaction kinetics gives information on the pathways of a chemical reaction

- 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:  $\text{HCOOH} \longrightarrow \text{CO} + \text{H}_2\text{O}$

Rate can be determined by following:

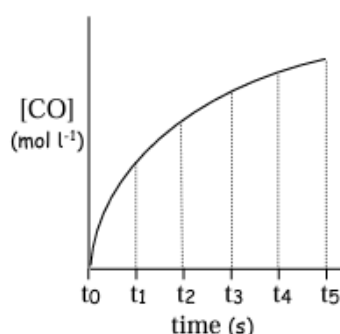
a) decrease in the concentration of HCOOH



NB: negative sign as [HCOOH] is decreasing

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

b) increase in concentration of CO



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

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  $\Delta t$  approaches zero, it becomes  $dt$

$$\begin{array}{l} \text{Instantaneous} \\ \text{Reaction} \\ \text{Rate} \end{array} = \frac{-d[\text{HCOOH}]}{dt}$$

or

$$\begin{array}{l} \text{Instantaneous} \\ \text{Reaction} \\ \text{Rate} \end{array} = \frac{d[\text{CO}]}{dt}$$

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:



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

#### The Rate Law

$$\text{Rate} \propto [A][B]$$

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

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
$\text{rate} \propto [A]^0$	0
$\text{rate} \propto [A]^1$	1
$\text{rate} \propto [A]^2$	2
$\text{rate} \propto [A]^1[B]^1$	2
$\text{rate} \propto [A]^1[B]^2$	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)



$$\text{rate} \propto [\text{H}_2\text{O}_2][\text{HI}] \text{ (discovered by experiment)}$$

order of reaction = 2 despite there being 3 reactant molecules  
(1x  $\text{H}_2\text{O}_2$  and 2x  $\text{HI}$ )

## 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 <sup>-1</sup>	[B] / mol l <sup>-1</sup>	[C] / mol l <sup>-1</sup>	Initial rate of D formed / mol l <sup>-1</sup> s <sup>-1</sup>
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] <sup>1</sup>
1+3	[B] x2	no change in rate	[B] <sup>0</sup>
1+4	[C] x2	rate x4	[C] <sup>2</sup>

Conclusions

$$\text{Rate} \propto [A]^1 [B]^0 [C]^2$$

$$\therefore \text{Rate} \propto [A] [C]^2$$

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

$$\text{Overall Order} = 1 + 0 + 2 = 3$$

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

$$\begin{aligned}\text{Rate} &= k [A] [C]^2 \\ 2.0 &= k \times [1.0] \times [1.0]^2 \\ k &= \frac{2.0 \text{ mol l}^{-1} \text{ s}^{-1}}{1 \times 1^2 \text{ mol}^3 \text{ l}^{-3}} \\ &= 2.0 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}\end{aligned}$$

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

For the reaction:  $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$

Results of Experiments:

Experiment	Initial Concentration/ $\text{mol l}^{-1}$		Initial rate of $\text{NO}_2$ formed / $\text{mol l}^{-1} \text{ s}^{-1}$
	[NO]	[O <sub>2</sub> ]	
1	$2.0 \times 10^{-5}$	$4.0 \times 10^{-5}$	$1.4 \times 10^{-10}$
2	$2.0 \times 10^{-5}$	$8.0 \times 10^{-5}$	$2.8 \times 10^{-10}$
3	$4.0 \times 10^{-5}$	$4.0 \times 10^{-5}$	$5.6 \times 10^{-10}$

Analysis of Results

Experiments Compared	Change in Conditions	Effect of Change on Rate	Order of Reactant
1+2	[O <sub>2</sub> ] x2	rate x2	[O <sub>2</sub> ] <sup>1</sup>
1+3	[NO] x2	rate x4	[NO] <sup>2</sup>

Conclusions:  $\text{Rate} \propto [\text{NO}]^2 [\text{O}_2] \therefore \text{overall order} = 2+1 = 3$

Reaction is 1<sup>st</sup> Order with respect to [NO] & 2<sup>nd</sup> Order with respect to [O<sub>2</sub>]

$$\begin{aligned}\text{Rate} &= k \times [\text{NO}]^2 \times [\text{O}_2] \\ 1.4 \times 10^{-10} &= k \times [2.0 \times 10^{-5}]^2 \times [4.0 \times 10^{-5}] \\ k &= \frac{1.4 \times 10^{-10} \text{ mol l}^{-1} \text{ s}^{-1}}{[2.0 \times 10^{-5}]^2 \times [4.0 \times 10^{-5}] \text{ mol}^3 \text{ l}^{-3}} \\ &= 8.75 \times 10^3 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}\end{aligned}$$

### 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:



$$\text{Rate} = k [\text{H}_2\text{O}_2] [\text{HI}] \quad (\text{order of both reactants} = 1)$$

- Rate controlled by a step where one molecule of  $\text{H}_2\text{O}_2$  reacts with one molecule of HI
- Step 1  $\text{H}_2\text{O}_2 + \text{HI} \longrightarrow \text{X}$  (slow: Rate Determining Step)
- Step 2  $\text{X} + \text{HI} \longrightarrow \text{product}$  (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:



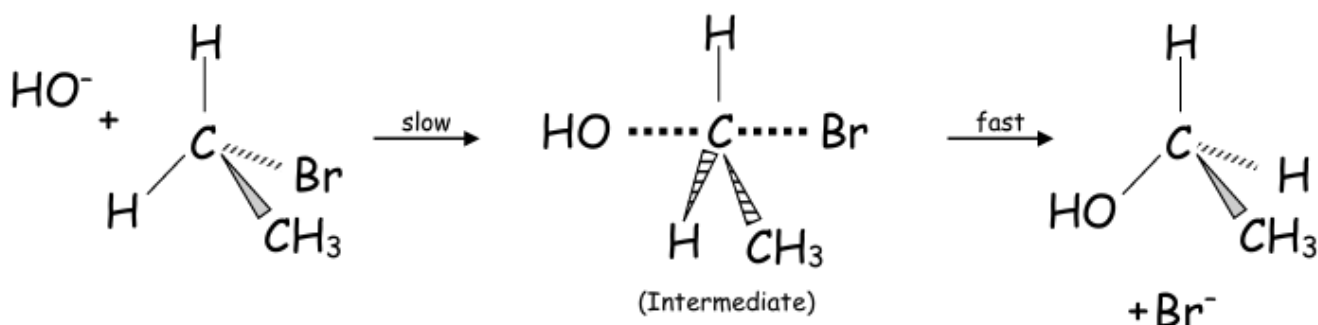
Where HOI is an intermediate formed with a transient lifetime.

Example 2: Hydrolysis of a primary halogenalkane



$$\text{Rate} = k [\text{CH}_3\text{CH}_2\text{Br}] [\text{OH}^-]$$

- both reactants are 1<sup>st</sup> 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<sup>-</sup> ion attacks the back of the molecule to displace the bromine atom to form a bromide Br<sup>-</sup> ion.
  - This mechanism is known as a S<sub>N</sub>2 process in Unit 3



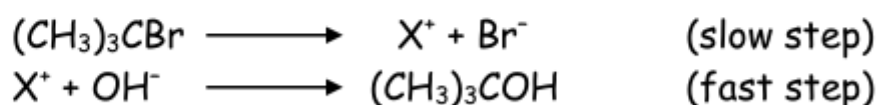
Example 3: Hydrolysis of a Tertiary Halogenalkane



$$\text{rate} = k [(\text{CH}_3)_3\text{CBr}]$$

∴ [(CH<sub>3</sub>)<sub>3</sub>CBr] is 1<sup>st</sup> order, [OH<sup>-</sup>] is zero order

- Rate determining step does not involve the OH<sup>-</sup> ion



where X is the (CH<sub>3</sub>)<sub>3</sub>C<sup>+</sup> ion - the carbo cation

### Questions:

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

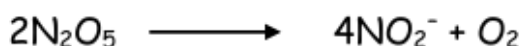


Rate measurements on four different reaction mixtures gave the following data:

Experiment	$[\text{H}^+]$ /mol l <sup>-1</sup>	$[\text{Br}^-]$ /mol l <sup>-1</sup>	$[\text{BrO}_3^-]$ /mol l <sup>-1</sup>	Relative rate / mol l <sup>-1</sup> s <sup>-1</sup>
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

- What is the rate expression for the reaction?
- What is the order of the reaction with respect to each of the reactants?
- What is the overall order of the reaction?
- 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:



$[\text{N}_2\text{O}_5]$ (mol l <sup>-1</sup> )	Rate (mol l <sup>-1</sup> s <sup>-1</sup> )
2.20	$2.25 \times 10^{-5}$
2.00	$2.10 \times 10^{-5}$
1.52	$1.58 \times 10^{-5}$
0.93	$0.96 \times 10^{-5}$

- Draw a graph of the rate against  $[\text{N}_2\text{O}_5]$
- Calculate the value of the rate constant.