CHEMICAL KINETICS

Introduction
Chemical kinetics is concerned with the dynamics of chemical reactions such as the way reactions take place and the rate (speed) of the process.

Collision theory
- particles must **COLLIDE** before a reaction can take place
- not all collisions lead to a reaction
- reactants must possess at least a minimum amount of energy - **ACTIVATION ENERGY**
  + particles must approach each other in a certain relative orientation - **STERIC EFFECT**

Rate increase

**to increase the rate** one needs, according to collision theory, to have ...

- more frequent collisions - increase particle speed or have more particles present
- more successful collisions - give particles more energy or lower the activation energy

- increase surface area
- increase temperature
- use a light source (certain reactions only)
- add a catalyst
- increase pressure (gaseous reactions only)
- increase concentration

SURFACE AREA
- increasing surface area leads to more chances of a collision
- catalysts (e.g. in catalytic converters) are used in a finely divided form for this reason
  + in many organic reactions you have two liquid layers, one aqueous and the other non-aqueous. Shaking the mixture improves the reaction rate as an emulsion is often formed and the area of boundary layers is increased and more collisions can take place.

Q.1 What is the surface area of a cube of side 1cm?

*If you cut the cube in half, what is the new surface area?*
TEMPERATURE

Effect  
• increasing the temperature increases the rate of a reaction  
• particles get more energy so they can overcome the energy barrier  
• particle speeds increase so collisions are more frequent

Distribution of molecular velocities and energies

Introduction  Because of the many collisions taking place, there is a spread of molecular velocities and energies. This has been demonstrated by an experiment. It indicated that ...

- no particles have zero velocity  
- some have very low and some have very high velocities  
- most have intermediate velocities.

Q.2  Superimpose the curves you get at a higher \( T_2 \) and a lower \( T_1 \) temperature.

Significance  \( E_a \) corresponds to the Activation Energy. The area under the curve beyond this value is proportional to the number of particles with energy greater than this limiting value.

Increasing the temperature alters the distribution;

- get a shift to higher energies/velocities  
- curve gets broader and flatter due to the greater spread of values  
- area under the curve stays constant as it corresponds to the total number of particles
Explanation

- increasing the temperature gives more particles with energy greater than $E_a$
- more reactants are able to overcome the energy barrier associated and form products
- a small rise in temperature can lead to a large increase in rate

The Effect of Temperature on the Rate of a Reaction

- as a reaction takes place the energy of the system rises to a maximum, then falls
- if energy falls to below the original value = overall release of energy = exothermic
- if energy falls to above the original value = overall absorption of energy = endothermic

Light

- shining a suitable light source onto some reactants increases the rate of reaction
- the light - often U.V. - provides energy to break bonds and initiate a reaction
- the greater the intensity of the light, the greater the effect

Examples

- the reaction between methane and chlorine - see organic notes on alkanes
- the reaction between hydrogen and chlorine

Equation

$$\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g)$$

Bond enthalpies

H-H ............. 436 kJ mol$^{-1}$ Cl-Cl ............. 242 kJ mol$^{-1}$

Mechanism

- $\text{Cl}_2 \rightarrow 2\text{Cl}^-$ initiation
- $\text{H}_2 + \text{Cl}^- \rightarrow \text{HCl} + \text{H}^-$ propagation
- $\text{H}^+ + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}^-$
- $2\text{Cl}^- \rightarrow \text{Cl}_2$ termination
- $2\text{H}^+ \rightarrow \text{H}_2$
- $\text{H}^+ + \text{Cl}^- \rightarrow \text{HCl}$
CATALYSTS

Operation

• work by providing an alternative reaction pathway with a lower Activation Energy

Lowering $E_a$ results in there being a greater area under the curve showing that more molecules have energies in excess of the Activation Energy

• decreasing the Activation Energy means that more particles will have sufficient energy to overcome the energy barrier and react

• using catalysts avoids the need to supply extra heat - safer and cheaper

• catalysts remain chemically unchanged at the end of the reaction.

Types

Homogeneous Catalysts
same phase as reactants

Heterogeneous Catalysts
different phase to reactants

Uses

• widely used in industry especially where an increase in temperature would result in a lower yield due to a shift in equilibrium (e.g. Haber and Contact Processes)

• CATALYSTS DO NOT AFFECT THE POSITION OF ANY EQUILIBRIUM but they do affect the rate at which equilibrium is attained.

• a lot is spent on research into more effective catalysts as the savings can be dramatic

• catalysts need to be changed regularly as they get ‘poisoned’ by other chemicals

• catalysts are used in a finely divided state to increase the surface area
HETEROGENEOUS CATALYSIS

Catalyst is in a **different phase to the reactants**

* e.g. a solid catalyst in a gaseous reaction

**Action**

- takes place at **active sites** on the **surface** of a solid
- **gases are adsorbed onto the surface**
- form weak bonds between gas and metal atoms

Catalysis is thought to work in **three stages** as follows ...

**Adsorption**

- formation of bonds with surface weakens bonds in gas molecules makes a subsequent reaction easier

**Reaction**

- adsorbed gases may be held on the surface increases chances of favourable collisions

**Desorption**

- the products are then released from the active sites

\[
\text{HARD Hetero} = \text{Adsorption} + \text{Reaction} + \text{Desorption}
\]

The **strength of adsorption is critical** ...

- Too weak little adsorption - molecules will not bond to surface
- Too strong molecules are held tightly and remain on the surface thus blocking reactive sites and preventing further reaction
- Just right reactants are attracted yet products can leave to open up the active sites

**Rate**

Catalysis of gaseous reactions can lead to an increase in rate in several ways ...

- one species is adsorbed onto the surface and is more likely to undergo a collision
- one species is held in a favourable position for reaction to occur
- adsorption onto the surface allows bonds to break and fragments react quicker
- two reactants are adsorbed alongside each other give a greater concentration

**Format**

- used in a **finely divided** form increases the surface area provides more collision sites.
- mounted in a **support** medium maximises surface area and reduces costs.

**Examples of catalysts**

- **Metals**  
  Ni, Pt hydrogenation reactions
  Fe Haber Process
- **Oxides**  
  Al₂O₃ dehydration reactions
  V₂O₅ Contact Process
**POLLUTANT GASES FROM INTERNAL COMBUSTION ENGINES**

### Carbon monoxide  CO

**Origin**  
- incomplete combustion of hydrocarbons in petrol because not enough oxygen was present

**Effect**  
- poisonous
- combines with haemoglobin in blood
- prevents oxygen being carried

### Oxides of nitrogen  NOx - NO, N₂O and NO₂

**Origin**  
- combination of atmospheric nitrogen and oxygen under high temperature conditions

**Effect**  
- aids formation of **photochemical smog** which is irritating to eyes, nose and throat
- aids formation of **low level ozone** which affects plant growth and is irritating to eyes, nose and throat
  
  i) sunlight breaks down NO₂  \[ \text{NO}_2 \rightarrow \text{NO} + \text{O} \]
  
  ii) ozone is produced  \[ \text{O} + \text{O}_2 \rightarrow \text{O}_3 \]

### Hydrocarbons  CₓHᵧ

**Origin**  
- hydrocarbons that have not undergone combustion

**Effect**  
- toxic and carcinogenic (cause cancer)

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**EQUATIONS FOR POLLUTION FORMATION**

- Nitrogen combines with oxygen  \[ \text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g) \]
- Nitrogen monoxide is oxidised  \[ 2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g) \]
- Incomplete hydrocarbon combustion  \[ \text{C}_8\text{H}_{18}(g) + 8\frac{1}{2}\text{O}_2(g) \rightarrow 8\text{CO}(g) + 9\text{H}_2\text{O}(l) \]

**EQUATIONS FOR POLLUTION REMOVAL**

- Oxidation of carbon monoxide  \[ 2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g) \]
- Removal of NO and CO  \[ 2\text{CO}(g) + 2\text{NO}(g) \rightarrow \text{N}_2(g) + 2\text{CO}_2(g) \]
- Aiding complete H/C combustion  \[ \text{C}_8\text{H}_{18}(g) + 12\frac{1}{2}\text{O}_2(g) \rightarrow 8\text{CO}_2(g) + 9\text{H}_2\text{O}(l) \]
HOMOGENEOUS CATALYSIS
Catalyst and reactants are in the same phase

- reaction proceeds through an intermediate species with lower energy
- there is usually more than one reaction step
- transition metal ions are often involved - oxidation state changes during the reaction

Examples

Acids  e.g. hydrolysis of esters

Gases  OZONE in the atmosphere breaks down naturally as follows ...

\[
\text{O}_3 \rightarrow \text{O}^+ + \text{O}_2
\]

However it breaks down more easily in the presence of chlorofluorcarbons (CFC's).

There is a series of complex reactions but the basic process is :-

- CFC’s break down in the presence of UV light to form chlorine radicals
  \[
  \text{CCl}_2\text{F}_2 \rightarrow \text{Cl}^+ + \cdot\text{CClF}_2
  \]
- chlorine radicals then react with ozone
  \[
  \text{O}_3 + \text{Cl}^+ \rightarrow \text{ClO}^+ + \text{O}_2
  \]
- chlorine radicals are regenerated
  \[
  \text{ClO}^+ + \text{O} \rightarrow \text{O}_2 + \text{Cl}^+
  \]

Overall, chlorine radicals are not used up so a small amount of CFC’s can destroy thousands of ozone molecules before they take part in a termination stage.

Pressure

- increasing the pressure makes gas particles get closer together
- this increases the frequency of collisions so the reaction rate increases
- many industrial processes occur at high pressure to increase the rate but it also can affect the position of equilibrium - see Chemical Equilibrium

The greater the pressure, the more frequent the collisions
**CONCENTRATION**

*Introduction*  
Increasing concentration = more frequent collisions = increased rate of reaction

However: increasing the concentration of some reactants can have a greater effect than increasing others.

*Rate*  
Reactions start off at their fastest and get slower as the concentration of reactants drops.

In a reaction such as \( A + 2B \rightarrow C \), the concentrations might change as shown:

- the steeper the curve the faster the rate of the reaction
- reactions start off quickly because of the greater likelihood of collisions
- reactions slow down with time because there are fewer reactants to collide

**Reactants (A and B)**  
Concentration decreases with time

**Products (C)**  
Concentration increases with time

\[ \text{refers to the concentration in mol dm}^{-3} \]

- the rate of change of concentration is found from the slope or gradient of the curve
- the slope at the start of the reaction will give the INITIAL RATE
- the slope gets less (showing the rate is slowing down) as the reaction proceeds

**Experimental Investigation**  
- the variation in concentration of a reactant or product is followed with time
- the method depends on the reaction type and the properties of the reactants/products

*E.g.*  
- Extracting a sample from the reaction mixture and analysing it by titration.
- Using a colorimeter or UV / visible spectrophotometer.
- Measuring the volume of gas evolved.
- Measuring the change in conductivity.

More details of these and other methods can be found in suitable text-books.
**THE RATE EQUATION**

**Format**
- is an equation that links the rate of reaction to the concentration of reactants
- can only be found by doing actual experiments
- cannot be found by just looking at the equation

the equation... \[ \text{A} + \text{B} \rightarrow \text{C} + \text{D} \]

might have a rate equation like this \[ r = k \left[ \text{A} \right] \left[ \text{B} \right]^2 \]

where
- \( r \) rate of reaction units: conc. / time, usually mol dm\(^{-3}\) s\(^{-1}\)
- \( k \) rate constant units: depend on the rate equation
- \( [\text{]} \) concentration units: mol dm\(^{-3}\)

**Interpretation**
The above rate equation tells you that the rate of reaction is...
- proportional to the concentration of reactant A, doubling \([\text{A}]\) - will double rate
- proportional to the square of the concentration of B, doubling \([\text{B}]\) - will quadruple rate

**Order of reaction**

**Individual order**
The power to which a concentration is raised in the rate equation

**Overall order**
The sum of all the individual orders in the rate equation.

e.g. in the rate equation \[ r = k \left[ \text{A} \right] \left[ \text{B} \right]^2 \]

- the order with respect to A is 1 (1st Order)
- the order with respect to B is 2 (2nd Order)

and
- the overall order is 3 (3rd Order)

**Value(s)**
- orders need not be whole numbers
- orders can be zero if the rate is unaffected by how much of a substance is present

**Remember**
The rate equation is derived from experimental evidence not by looking at an equation.

- species appearing in the stoichiometric equation sometimes aren’t in the rate equation
- similarly substances not in the stoichiometric equation can appear in the rate equation

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**Q.3** State the overall order, and the individual orders, for the following?
- \( a) \text{ rate } = k [\text{C}]^3 [\text{D}] \)
- \( b) \text{ rate } = k [\text{A}] [\text{B}]^{\frac{1}{3}} \)

**Q.4** What substances appear in the rate, but not in the stoichiometric, equation?
Experimental determination of order

Method 1 1. Plot a concentration/time graph and calculate the rate (gradient) at points on the curve.

When the concentration is 2.0 mol dm\(^{-3}\)
the gradient = \(-3.2 \text{ mol dm}^{-3}\)

44 minutes

Notice how the gradient gets less as the reaction proceeds. This shows that the rate of reaction is getting less.

The gradient is negative because the concentration is decreasing

rate = \(-7.3 \times 10^{-2} \text{ mol dm}^{-3} \text{ min}^{-1}\)

CONCENTRATION v. TIME GRAPHS

WHAT TO LOOK FOR

A ZERO ORDER
a straight line with constant slope

B FIRST ORDER
downwardly sloping curve with a constant half life

C SECOND ORDER
steeper downwardly sloping curve which levels out quicker
Method 1
2. Plot another graph of rate (y axis) versus the concentration (x axis)

A ZERO ORDER
a straight line horizontal to the x axis
rate is independent of concentration

B FIRST ORDER
a straight line with a constant slope
rate is proportional to concentration
GRADIENT = RATE CONSTANT (k)

C SECOND ORDER
an upwardly sloping curve
plotting rate v. conc² gives a straight line

Method 2
The initial rates method.
Do a series of experiments (at the same temperature) at different concentrations of a reactant but keeping all others constant.

• Plot a series of concentration / time graphs
• Calculate the initial rate (slope of curve at start) for each reaction.
• Plot each initial rate (y axis) against the concentration used (x axis)
• From the graph, calculate the relationship between concentration and rate
• Hence deduce the rate equation - see the graph at the top of the page
• To find order directly, logarithmic plots are required.
Half-life \((t_{1/2})\)

One of the characteristics of a FIRST ORDER REACTION is that it has a **constant half life** which is independent of the concentration. It is very similar to radioactive decay.

**Definition**
The time taken for the concentration of a reactant to drop to half of its original value.

the time taken to drop...
- from 1 to 1/2 = one half life
- 1/2 to 1/4 = one half life
- 1/4 to 1/8 = one half life

A useful relationship

\[
k \times t_{1/2} = \log_e 2 \\
= 0.693 \\
t_{1/2} = \text{the half life}
\]

**TO CALCULATE THE RATE CONSTANT \((k)\)**

**FOR A FIRST ORDER REACTION**

\[
k = \frac{0.693}{t_{1/2}}
\]

**Q.5**

In the reaction, \(A + B \rightarrow X + Y\), the concentration of \(A\) was found to vary as shown in the table. It was later found that the order with respect to (wrt) \(B\) was 0.

- plot a graph of \([A]\) v. time
- calculate the time it takes for \([A]\) to go from...
  - 1.30 to 0.65
  - 1.00 to 0.50
  - 0.50 to 0.25 (all in units mol dm\(^{-3}\))
- deduce from the graph that the order wrt \(A\) is 1
- calculate the value of the rate constant, \(k\)

<table>
<thead>
<tr>
<th>Time / s</th>
<th>([A] / \text{mol dm}^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.30</td>
</tr>
<tr>
<td>20</td>
<td>1.05</td>
</tr>
<tr>
<td>40</td>
<td>0.85</td>
</tr>
<tr>
<td>60</td>
<td>0.68</td>
</tr>
<tr>
<td>80</td>
<td>0.55</td>
</tr>
<tr>
<td>100</td>
<td>0.45</td>
</tr>
<tr>
<td>120</td>
<td>0.36</td>
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<tr>
<td>140</td>
<td>0.29</td>
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<tr>
<td>160</td>
<td>0.24</td>
</tr>
<tr>
<td>180</td>
<td>0.19</td>
</tr>
<tr>
<td>200</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Rate constant (k)

**Value**
- The value of the rate constant is **affected by temperature**
- **Increasing the temperature increases the value of the rate constant**
- If k increases, so does the rate
- An increase of 10°C **approximately** doubles the rate of a reaction

**Units**

The units of k depend on the overall order of reaction.

* e.g. if the rate equation is of the form \( \text{rate} = k [A]^2 \) the units of k will be \( \text{dm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \)

Divide the rate (conc per time) by as many concentrations as appear in the rate equation.

<table>
<thead>
<tr>
<th>Overall Order</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>units of k</td>
<td>mol dm(^3) sec(^{-1})</td>
<td>sec(^{-1})</td>
<td>dm(^3) mol(^{-1}) sec(^{-1})</td>
<td>dm(^6) mol(^{-2}) sec(^{-1})</td>
</tr>
</tbody>
</table>

* example in the rate equation \( r = k [A] \) k will have units of sec\(^{-1}\)
* example in the rate equation \( r = k [A] [B]^2 \) k will have units of dm\(^6\) mol\(^{-2}\) sec\(^{-1}\)

**Q.6** Derive suitable units for the rate constant k in the following rate equations.

\[ r = k[C]^3[D] \]
\[ r = k[Z]^2 \]
\[ r = k[A][B] \]
\[ r = k[A][B]^{\frac{1}{2}} \]

**Q.7** Using the data, construct the rate equation for the reaction between nitric oxide and oxygen. What is the value and the units of the rate constant (k) ?

<table>
<thead>
<tr>
<th>Expt</th>
<th>Initial [NO] / mol dm(^3)</th>
<th>Initial [O(_2)] / mol dm(^3)</th>
<th>Initial rate / mol dm(^3) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>2</td>
<td>56</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>3</td>
<td>?</td>
</tr>
</tbody>
</table>

*Hint* Compare Expts. 2 and 3 to find the order with respect to O\(_2\).
*Compare Expts. 1 and 3 to find the order with respect to NO*
Rate determining step

- many reactions consist of a series of separate stages
- each of these stages has its own rate and hence its own rate constant
- the overall rate of a multi-step process is governed by the slowest step
  - rather like a production line where the output can be held up by a slow worker
- the slowest step is known as the rate determining step.

Example - The hydrolysis of haloalkanes

Haloalkanes (RX) are hydrolysed by aqueous hydroxide ion

\[ RX + OH^- \rightarrow ROH + X^- \]

There are two possible mechanisms

Mech 1
- one step reaction
- requires both species to collide
- rate is affected by both reactants
  \[ \text{rate} = k[RX][OH^-] \]
- second order overall

Mech 2
- two step reaction
  (i) \[ RX \rightarrow R^+ + X^- \]
  (ii) \[ R^+ + OH^- \rightarrow ROH \]
- step (i) is slower as it involves bonds breaking and will thus be the rate determining step
- rate depends only on [RX]
  \[ \text{rate} = k[RX] \]
- first order overall

Mechanism 2 is very common with tertiary (3°) haloalkanes whereas primary (1°) and secondary (2°) haloalkanes usually undergo hydrolysis via a second order process.

Example 1 Iodine reacts with propanone...

\[ \text{CH}_3\text{COCH}_3 + I_2 \rightarrow \text{CH}_3\text{COCH}_2I + HI \]

The rate equation for the reaction is

\[ \text{rate} = k[\text{CH}_3\text{COCH}_3][H^+] \]

- Why is \([H^+]\) in the rate equation? the reaction is catalysed by acid
- Why is \([I_2]\) not in the rate equation? the reaction has more than one step and the slowest step doesn’t involve iodine

The rate determining step must therefore involve propanone and acid.

Investigation of the rate equation gives an idea of whether, or not, a reaction takes place in a series of steps.
**Example 2**  
The reaction \( \text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2\text{I}^- \longrightarrow \text{I}_2 + 4\text{H}_2\text{O} \) takes place in 3 steps

*Step 1* \( \text{H}_2\text{O}_2 + \text{I}^- \longrightarrow \text{IO}^- + \text{H}_2\text{O} \) \[\text{slow}\]

*Step 2* \( \text{IO}^- + \text{H}_3\text{O}^+ \longrightarrow \text{HIO} + \text{H}_2\text{O} \) \[\text{fast}\]

*Step 3* \( \text{HIO} + \text{H}_3\text{O}^+ + \text{I}^- \longrightarrow \text{I}_2 + 2\text{H}_2\text{O} \) \[\text{fast}\]

*The rate determining step is STEP 1 as it is the slowest*

**Example 3**  
The reaction \( 2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2 \) takes place in 3 steps

*Step 1* \( \text{N}_2\text{O}_5 \longrightarrow \text{NO}_2 + \text{NO}_3 \) \[\text{slow}\]

*Step 2* \( \text{NO}_2 + \text{NO}_3 \longrightarrow \text{NO} + \text{NO}_2 + \text{O}_2 \) \[\text{fast}\]

*Step 3* \( \text{NO} + \text{NO}_3 \longrightarrow 2\text{NO}_2 \) \[\text{fast}\]

*The rate determining step is STEP 1 as it is the slowest*

*The rate equation for the reaction is*  
\[ \text{rate} = k [\text{N}_2\text{O}_5] \]

**Molecularity**  
The number of individual particles of the reacting species taking part in the rate determining step of a reaction

*e.g.  A + 2B \( \longrightarrow \) C + D  molecularity is 3 - one A and two B's need to collide

A \( \longrightarrow \) 2B  has a molecularity of 1 - only one A is involved

**Autocatalysis**  
A small number of reactions appear to speed up, rather than slow down, for a time. This is because one of the products is acting as a catalyst and as more product is formed the reaction gets faster. One of the best known examples is the catalytic properties of Mn\(^{2+}\)\(_\text{(aq)}\) on the decomposition of MnO\(_4^-\)\(_\text{(aq)}\). You will notice it in a titration of KMnO\(_4\) with either hydrogen peroxide or ethanedioic (oxalic) acid.