CHEMICAL KINETICS

Reminder The following methods can be used to increase the rate of a reaction.

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

*How they affect the rate has been studied in earlier work with special reference to Collision Theory.*

CONCENTRATION

Introduction Increasing concentration = more frequent collisions = increased rate

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

Rate Reactions start off at their fastest then slow as the reactant concentration drops.

*eg In the reaction A + 2B → 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

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

- the rate of change of concentration is found from the slope or gradient
- the slope at the start will give give the INITIAL RATE
- the slope gets less (showing the rate is slowing down) as the reaction proceeds
Investigation • the variation in concentration of a reactant or product is followed with time
  • method depends on the reaction type and the properties of 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 or a change in conductivity

THE RATE EQUATION

Format • links the rate of reaction to the concentration of reactants
  • can only be found by doing actual experiments, not by looking at the equation

the equation… \[ A + 2B + X \rightarrow C + D \]

might have a rate equation like this \[ r = k [A][B]^2 \]

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

Interpretation The above rate equation tells you that the rate of reaction is...
  • proportional to the conc of reactant A doubling \([A]\) - will double rate
  • proportional to the square of the conc of B doubling \([B]\) - will quadruple rate
  • not proportional to the conc of X altering \([X]\) - no effect on 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.

\[ r = k [A][B]^2 \]

• 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 substance is present

Remember The rate equation is derived from experimental evidence not by from an equation.
• species in the stoichiometric equation sometimes aren’t in the rate equation
• substances not in the stoichiometric equation can appear in the rate equation
Experimental determination of order

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

   When the concentration is 2.0 mol dm$^{-3}$
   the gradient =  - 3.2  mol dm$^{-3}$
   44 minutes

   The gradient is negative because
   the concentration is decreasing

   rate = -7.3 x 10$^{-2}$ mol dm$^{-3}$ min$^{-1}$

Q.1  State the overall order, and the individual orders, for the following ?

a)  rate = $k[C]^3[D]$

b)  rate = $k [Z]$

Q.2  What substances appear in the rate, but not in the stoichiometric, equation ?

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; levels out quicker
Method 1

2. Plot another graph of rate \((y\text{ axis})\) versus the concentration \((x\text{ axis})\)

\[\text{A} \quad \text{ZERO ORDER}\]
a straight line horizontal to the x axis
rate is independent of concentration

\[\text{B} \quad \text{FIRST ORDER}\]
a straight line with a constant slope
rate is proportional to concentration
\[
\text{GRADIENT} = \text{RATE CONSTANT } (k)
\]

\[\text{C} \quad \text{SECOND ORDER}\]
an upwardly sloping curve; plotting rate \(v.\) conc\(^2\) 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 \((y\text{ axis})\) against the concentration used \((x\text{ axis})\)
- 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.

Find the initial rate (gradient of the tangent) at time = zero
Half-life \((t_{\frac{1}{2}})\)

A characteristic 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.

\[
\text{the time taken to drop...}
\]

\[
\text{from } 1 \ \text{to } \frac{1}{2} = \text{one half life}
\]

\[
\frac{1}{2} \ \text{to } \frac{1}{4} = \text{one half life}
\]

\[
\frac{1}{4} \ \text{to } \frac{1}{8} = \text{one half life}
\]

A useful relationship

\[
k \ t_{\frac{1}{2}} = \log_e 2
\]

\[
= 0.693
\]

\[
t_{\frac{1}{2}} = \text{the half life}
\]

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

FOR A FIRST ORDER REACTION

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

**Q.3**

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 \(B\) 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>
</tr>
<tr>
<td>140</td>
<td>0.29</td>
</tr>
<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.

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

Calculation
Divide rate (conc per time) by as many concentrations that are 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 $r = k [A]$ $k$ has units of sec$^{-1}$
- in the rate equation $r = k [A] [B]^2$ $k$ has units of dm$^6$ mol$^2$ sec$^{-1}$

Q.4 Derive suitable units for the rate constant $k$ in the following rate equations.

\[ r = k[C]^3[D] \]

\[ r = k [Z]^2 \]

\[ r = k [A] [B] \]

Q.5 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
The Arrhenius equation

**Rate Equation**
- A typical rate equation may like this \( r = k [A] [B]^2 \)
- It shows how rate is affected by the concentrations of reactants \([A]\) and \([B]\)
- The rate constant \((k)\) shows how other variables affect the rate
- A **change of temperature** or the addition of **catalyst** affects the value of \(k\)
- It is expressed mathematically using the **Arrhenius equation**

\[
k = A e^{-\left(\frac{E_a}{R T}\right)}
\]

**Arrhenius equation**
- Represents the fraction of the molecules in a gas which have energies equal to or greater than the activation energy at a stated temperature
- Includes factors like the frequency of collisions and their orientation. It varies slightly with temperature, although not much and is taken as constant across small temperature ranges.

**k** rate constant units depend on overall order

**T** temperature \(K\) \((K = ^\circ C + 273)\)

**R** gas constant \(8.13 \text{ J K}^{-1} \text{ mol}^{-1}\)

**E_a** activation energy \(\text{J mol}^{-1}\)

**e** constant \(2.71828\)

**A** pre-exponential factor (frequency factor) no units

**Calculations**
- Values of \(A\) and \(E_a\) are obtained from the Arrhenius equation by the relationship

\[
k = -\frac{E_a}{RT} + \ln A
\]

\(\ln\) is a logarithmic term (\(\log_e\) NOT \(\log_{10}\))
(it can be obtained from a calculator)

**Graphical method**
- Convert and re-arrange the equation into the straight line formula \(y = mx + c\)

\[
\ln k = \left(\frac{E_a}{R}\right) \frac{1}{T} + \ln A
\]

\[
y = m x + c
\]

- **y axis** plot \(\ln k\)
- **x axis** plot \(\frac{1}{T}\)
- **Gradient (m)** gives \(-\left(\frac{E_a}{R}\right)\)
- **y intercept (c)** gives \(\ln A\)

**Gradient (m) = \(y/c\)**
Rate determining step

Explanation • 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
  • investigation of the rate equation gives an idea of whether, or not, a reaction takes place in a series of steps

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

• Why is \([\text{H}^+]\) 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.

Example 2 The reaction \( \text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2\text{I}^- \rightarrow \text{I}_2 + 4\text{H}_2\text{O} \) takes place in 3 steps

Step 1 \( \text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{IO}^- + \text{H}_2\text{O} \) slow

Step 2 \( \text{IO}^- + \text{H}_3\text{O}^+ \rightarrow \text{HIO} + \text{H}_2\text{O} \) fast

Step 3 \( \text{HIO} + \text{H}_3\text{O}^+ + \text{I}^- \rightarrow \text{I}_2 + 2\text{H}_2\text{O} \) fast

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

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

Step 1 \( \text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3 \) (occurs twice) slow

Step 2 \( \text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2 \) fast

Step 3 \( \text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2 \) fast

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

The rate equation for the reaction is \( \text{rate} = k [\text{N}_2\text{O}_5] \)
The hydrolysis of haloalkanes

Introduction
Haloalkanes (RX) are hydrolysed by aqueous hydroxide ions:

\[ RX + OH^- (aq) \rightarrow ROH + X^- \]

There are two possible mechanisms

**Mech. 1**
- one step reaction
- requires both species to collide
- rate is affected by both reactants
- second order overall

\[ \text{rate} = k[RX][OH^-] \]

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

\[ \text{rate} = k[RX] \]

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

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

- e.g. \[ A + 2B \rightarrow C + D \]  - molecularity is 3 - one A and two B’s need to collide
- \[ A \rightarrow 2B \]  - however has a molecularity of 1 - only one A is involved