16. Kinetics II

The rate of reaction is defined as the **change in concentration** of a substance **in unit time**

Its usual unit is mol dm$^{-3}$s$^{-1}$

When a graph of concentration of reactant is plotted vs time, the **gradient** of the curve is the rate of reaction.

The **initial rate** is the rate at the start of the reaction where it is fastest.

Reaction rates can be calculated from graphs of concentration of reactants or products.

**Techniques to investigate rates of reaction**

There are several different methods for measuring reactions rates. Some reactions can be measured in several ways:

- **Measurement of the change in volume of a gas**
  This works if there is a change in the number of moles of gas in the reaction. Using a gas syringe is a common way of following this.
  
  $$\text{(CH}_3\text{)}_2\text{C=CH}_2(\text{g}) + \text{H}_2\text{I}(\text{g}) \rightarrow \text{(CH}_3\text{)}_3\text{Cl}(\text{g})$$
  
  $$\text{HCOOH(aq)} + \text{Br}_2(\text{aq}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{Br}^-(\text{aq}) + \text{CO}_2(\text{g})$$

**Measurement of change of mass**

This works if there is a gas produced which is allowed to escape. Works better with heavy gases such as CO$_2$.

$$\text{HCOOH(aq)} + \text{Br}_2(\text{aq}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{Br}^-(\text{aq}) + \text{CO}_2(\text{g})$$

**Titration samples of reaction mixture with acid, alkali, sodium thiosulphate etc**

Small samples are removed from the reaction mixture, quenched (which stops the reaction) and the titrated with a suitable reagent.

- HCOOCH$_3$(aq) + NaOH(aq) → HCOONa(aq) + CH$_3$OH(aq)  
  The NaOH could be titrated with an acid
- BrO$_3^-$ (aq) + 5Br$^-$ (aq) + 6H$^+$ (aq) → 3Br$_2$(aq) + 3H$_2$O(l)  
  The H$^+$ could be titrated with an alkali
- CH$_3$COCH$_3$(aq) + I$_2$(aq) → CH$_3$COCH$_2$I(aq) + H$^+$ (aq) + I$^-$ (aq)  
  The I$_2$ could be titrated with sodium thiosulphate

**Colorimetry.**

If one of the reactants or products is coloured then colorimetry can be used to measure the change in colour of the reacting mixtures.

$$\text{H}_2\text{O}_2(\text{aq}) + 2\text{I}^- (\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow 2\text{H}_2\text{O}(l) + \text{I}_2(\text{aq})$$

The I$_2$ produced is a brown solution.

**Measuring change in electrical conductivity**

Can be used if there is a change in the number of ions in the reaction mixture.

$$\text{HCOOH(aq)} + \text{Br}_2(\text{aq}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{Br}^-(\text{aq}) + \text{CO}_2(\text{g})$$

**Measurement of optical activity.**

If there is a change in the optical activity through the reaction this could be followed in a polarimeter.

$$\text{CH}_3\text{CHBrCH}_3 (l) + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{CH(OH)CH}_3 (l) + \text{Br}^-(\text{aq})$$

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Rate Equations
The rate equation relates mathematically the rate of reaction to the concentration of the reactants.

For the following reaction, \( aA + bB \rightarrow \) products, the generalised rate equation is: \( r = k[A]^m[B]^n \)

- \( r \) is used as symbol for rate
- The unit of \( r \) is usually \( \text{mol dm}^{-3}\text{s}^{-1} \)
- \( m, n \) are called reaction orders
- Orders are usually integers 0, 1, 2
- 0 means the reaction is zero order with respect to that reactant
- 1 means first order
- 2 means second order
- NOTE: the orders have nothing to do with the stoichiometric coefficients in the balanced equation. They are worked out experimentally

Calculating orders from initial rate data

For zero order: the concentration of A has no effect on the rate of reaction \( r = k[A]^0 = k \)

For first order: the rate of reaction is directly proportional to the concentration of A \( r = k[A]^1 \)

For second order: the rate of reaction is proportional to the concentration of A squared \( r = k[A]^2 \)

Graphs of initial rate against concentration show the different orders. The initial rate may have been calculated from taking gradients from concentration/time graphs

Continuous rate experiments

For a rate concentration graph to show the order of a particular reactant the concentration of that reactant must be varied whilst the concentrations of the other reactants should be kept constant.

Continuous rate data
This is data from one experiment where the concentration of one substance is followed throughout the experiment.

For this method to work the concentrations of the reactants not being followed must be in large excess in the experiment so their concentrations stay virtually constant and do not affect rate.

This data is processed by plotting the data and calculating successive half-lives.

The half-life of a first-order reaction is independent of the concentration and is constant
The rate constant (k)

1. The units of k depend on the overall order of reaction. It must be worked out from the rate equation.
2. The value of k is independent of concentration and time. It is constant at a fixed temperature.
3. The value of k refers to a specific temperature and it increases if we increase temperature.

Example (first order overall)

Rate = $k[A][B]^0$  \( m = 1 \) and \( n = 0 \)
- reaction is first order in A and zero order in B
- overall order = \( 1 + 0 = 1 \)
- usually written: Rate = $k[A]$

Calculating units of k

1. Rearrange rate equation to give k as subject
2. Insert units and cancel

\[
k = \frac{\text{Rate}}{[A]} \quad k = \frac{\text{mol dm}^{-3}s^{-1}}{\text{mol dm}^{-3}}
\]

Unit of k = s^{-1}

Example: Write the rate equation for the reaction between A and B where A is 1st order and B is 2nd order.

\[ r = k[A][B]^2 \quad \text{overall order is 3} \]

Calculate the unit of k

1. Rearrange rate equation to give k as subject
2. Insert units and cancel
3. Simplify fraction

\[
k = \frac{\text{Rate}}{[A][B]^2} \quad k = \frac{\text{mol dm}^{-3}s^{-1}}{\text{mol dm}^{-3} \cdot (\text{mol dm}^{-3})^2}
\]

Unit of k = mol^{-2} dm^6 s^{-1}
Working out orders from experimental initial rate data

The initial rate is the rate at the start of the reaction, where it is fastest. It is often obtained by taking the gradient of the conc vs time graph.

Normally to work out the rate equation we do a series of experiments where the initial concentrations of reactants are changed (one at a time) and measure the initial rate each time. This data is normally presented in a table.

**Example:** work out the rate equation for the following reaction, \( A + B + 2C \rightarrow D + 2E \), using the initial rate data in the table.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>([A]) mol dm(^{-3})</th>
<th>([B]) mol dm(^{-3})</th>
<th>([C]) mol dm(^{-3})</th>
<th>Rate mol dm(^{-3}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.5</td>
<td>0.25</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.5</td>
<td>0.25</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>1.0</td>
<td>0.25</td>
<td>0.4</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>0.5</td>
<td>0.5</td>
<td>0.1</td>
</tr>
</tbody>
</table>

In order to calculate the order for a particular reactant it is easiest to compare two experiments where *only that reactant* is being changed.

If conc is doubled and rate stays the same: order = 0
If conc is doubled and rate doubles: order = 1
If conc is doubled and rate quadruples: order = 2

For reactant A compare between experiments **1 and 2**
For reactant A as the concentration **doubles** (B and C staying constant) so does the rate. Therefore the order with respect to reactant **A is first order**

For reactant B compare between experiments **1 and 3**:  
As the concentration of B **doubles** (A and C staying constant) the rate **quadruples**.  
Therefore the order with respect to **B is 2nd order**

For reactant C compare between experiments **1 and 4**:  
As the concentration of C **doubles** (A and B staying constant) the rate **stays the same**.  
Therefore the order with respect to C is zero order

The overall rate equation is \( r = k [A][B]^2 \)  
The reaction is 3\(^{rd}\) order overall and the unit of the rate constant = mol\(^{-2}\)dm\(^6\)s\(^{-1}\)
Working out orders when two reactant concentrations are changed simultaneously

In most questions it is possible to compare between two experiments where only one reactant has its initial concentration changed. If, however, both reactants are changed then the effect of both individual changes on concentration are multiplied together to give the effect on rate.

- In a reaction where the rate equation is \( r = k [A] [B]^2 \)
  - If the \([A]\) is \(x2\) that rate would \(x2\)
  - If the \([B]\) is \(x3\) that rate would \(x3^2=x9\)
  - If these changes happened at the same time then the rate would \(x2x9=x18\)

Example
work out the rate equation for the reaction, between X and Y, using the initial rate data in the table

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial concentration of X/ mol dm(^{-3})</th>
<th>Initial concentration of Y/ mol dm(^{-3})</th>
<th>Initial rate/ mol dm(^{-3}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>0.1</td>
<td>(0.15 \times 10^{-6})</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.1</td>
<td>(0.30 \times 10^{-6})</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.2</td>
<td>(2.40 \times 10^{-6})</td>
</tr>
</tbody>
</table>

For reactant X compare between experiments 1 and 2
For reactant X as the concentration doubles (Y staying constant) so does the rate. Therefore the order with respect to reactant X is **first order**

Comparing between experiments 2 and 3:
Both X and Y **double** and the rate goes up by \(8\)
We know X is first order so that will have doubled rate
The effect of Y, therefore, on rate is to have quadrupled it.
Y must be **second order**

Calculating a value for k using initial rate data

Using the above example, choose any one of the experiments and put the values into the rate equation that has been rearranged to give k. Using experiment 3:

\[
r = k [X] [Y]^2 \rightarrow k = \frac{r}{[X] [Y]^2} \]

\[
k = \frac{2.40 \times 10^{-6}}{0.2 \times 0.2^2} = 3.0 \times 10^{-4} \text{mol}^2\text{dm}^6\text{s}^{-1}
\]

Remember k is the same for all experiments done at the same temperature.
Increasing the temperature increases the value of the rate constant k
Increasing the temperature increases the value of the rate constant $k$.

**Increasing temperature increases the rate constant $k$.**

The relationship is given by the Arrhenius equation

\[ k = Ae^{-\frac{E_A}{RT}} \]

where $A$ is the Arrhenius constant, $R$ is the gas constant, and $E_A$ is activation energy.

**Using the Arrhenius equation (equations will be given in the exam)**

\[ k = Ae^{-\frac{E_A}{RT}} \]

The Arrhenius equation is usually rearranged to (You don’t need to know how)

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

You should be able to do rearrangements and substitute values into both these equations.

**Units**

- Temperature uses the unit $K$
- $R = 8.31 \text{ J mol}^{-1}\text{K}^{-1}$
- Activation energy will need to be in $J \text{ mol}^{-1}$ to match the units of $R$
- The unit of the Arrhenius constant $A$ will be the same as the unit of the rate constant $k$

**Example**

A reaction carried out at $30^\circ C$ has a value of $k = 4.26 \times 10^{-8} \text{ s}^{-1}$

The activation energy $E_A = 95.8 \text{ kJ mol}^{-1}$

The gas constant $R = 8.31 \text{ J K}^{-1}\text{ mol}^{-1}$

Calculate a value for the Arrhenius constant, $A$, for the reaction.

Using Equation

\[ k = Ae^{-\frac{E_A}{RT}} \]

Rearrange to

\[ A = \frac{k}{e^{-\frac{E_A}{RT}}} = \frac{4.26 \times 10^{-8}}{e^{-95800/(8.31 \times 308)}} = \frac{4.26 \times 10^{-8}}{e^{37.4}} = \frac{4.26 \times 10^{-8}}{5.55 \times 10^{-17}} = 7.67 \times 10^8 \text{ s}^{-1} \]

**Example**

A reaction carried out at $25^\circ C$ has a value of $k = 3.3 \times 10^{-3} \text{ mol}^{-1}\text{ dm}^3\text{ s}^{-1}$

$\ln A = 17.1$

The gas constant $R = 8.31 \text{ J K}^{-1}\text{ mol}^{-1}$

Calculate a value for the activation energy in $\text{kJ mol}^{-1}$

Using Equation

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

Rearrange to

\[ E_A = (\ln A - \ln k) \times RT = (17.1 - 5.71) \times 8.31 \times 298 \]

\[ = 56486 \text{ J mol}^{-1} \]

\[ = 56.5 \text{ kJ mol}^{-1} \]
Calculating the activation energy graphically from experimental data

Using the rearranged version
\[ \ln k = \ln A - \frac{E_A}{RT} \]

\( k \) is proportional to the rate of reaction so \( \ln k \) can be replaced by \( \ln(\text{rate}) \)

From plotting a graph of \( \ln(\text{rate}) \) or \( \ln k \) against \( 1/T \) the activation energy can be calculated from measuring the gradient of the line.

\text{Example}

<table>
<thead>
<tr>
<th>Temperature ( T ) (K)</th>
<th>( 1/T )</th>
<th>time ( t ) (s)</th>
<th>( 1/t )</th>
<th>( \ln (1/t) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>297.3</td>
<td>0.003364</td>
<td>53</td>
<td>0.018868</td>
<td>-3.9703</td>
</tr>
<tr>
<td>310.6</td>
<td>0.00322</td>
<td>24</td>
<td>0.041667</td>
<td>-3.1781</td>
</tr>
<tr>
<td>317.2</td>
<td>0.003153</td>
<td>16</td>
<td>0.0625</td>
<td>-2.7726</td>
</tr>
<tr>
<td>323.9</td>
<td>0.003087</td>
<td>12</td>
<td>0.083333</td>
<td>-2.4849</td>
</tr>
<tr>
<td>335.6</td>
<td>0.00298</td>
<td>6</td>
<td>0.166667</td>
<td>-1.7918</td>
</tr>
</tbody>
</table>

\[
\text{gradient} = \frac{y_2 - y_1}{x_2 - x_1}
\]

The gradient should always be \(-\)ve

In above example gradient = -5680

\[
E_A = - \text{gradient \times R (8.31)} = -5680 \times 8.31 = 47200 \text{ J mol}^{-1}
\]

The unit of \( E_A \) using this equation will be J mol\(^{-1}\).

Convert into kJ mol\(^{-1}\) by dividing 1000

\[
E_A = 47.2 \text{ kJ mol}^{-1}
\]
Rate Equations and Mechanisms

A mechanism is a series of steps through which the reaction progresses, often forming intermediate compounds. If all the steps are added together they will add up to the overall equation for the reaction.

Each step can have a different rate of reaction. The slowest step will control the overall rate of reaction. The slowest step is called the rate-determining step.

The molecularity (number of moles of each substance) of the molecules in the slowest step will be the same as the order of reaction for each substance.

- 0 moles of A in slow step would mean A is zero order.
- 1 mole of A in the slow step would mean A is first order.

Example 1
overall reaction
A + 2B + C → D + E
Mechanism
Step 1 A + B → X + D slow
Step 2 X + C → Y fast
Step 3 Y + B → E fast

r = k [A][B][C]

C is zero order as it appears in the mechanism in a fast step after the slow step.

Example 2
overall reaction
A + 2B + C → D + E
Mechanism
Step 1 A + B → X + D fast
Step 2 X + C → Y slow
Step 3 Y + B → E fast

r = k [X][C]

The intermediate X is not one of the reactants so must be replaced with the substances that make up the intermediate in a previous step.

A + B → X + D

r = k[A][B][C]

Investigating the rate of reaction between iodine and propanone

Propanone reacts with iodine in acidic solution (the acid is a catalyst) as shown in the equation below.

\[
\text{CH}_3\text{COCH}_3(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow \text{CH}_3\text{COCH}_2\text{I}(\text{aq}) + \text{H}^+(\text{aq}) + \text{I}^-(\text{aq})
\]

This reaction can be followed by removing small samples from the reaction mixture with a volumetric pipette. The sample is then quenched by adding excess sodium hydrogen carbonate to neutralize acid catalyst which stops the reaction. Then the sample can be titrated with sodium thiosulfate using a starch catalyst.

\[
2\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})
\]

yellow/brown sol       colourless sol

This reaction is zero order with respect to \(\text{I}_2\) but 1\textsuperscript{st} order with respect to the propanone and acid catalyst.

The rate equation for the reaction is

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

If there is a zero order reactant there must be at least two steps in the mechanism because the rate determining step will not involve the zero order reactant.

The rate determining step of this reaction must therefore contain one propanone molecule and one H\(^+\) ion forming an intermediate. The iodine will be involved in a subsequent faster step.

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Example 3: \( S_N1 \) or \( S_N2 \)?

Remember the nucleophilic substitution reaction of halogenoalkanes and hydroxide ions. 
This is a one step mechanism:

\[
\text{HO:} \quad \begin{array}{c}
\text{H} \\
\text{CH}_3 \\
\text{C} \\
\text{Br}
\end{array} \quad \text{δ}^- \quad \begin{array}{c}
\text{H} \\
\text{CH}_3 \\
\text{C} \\
\text{Br}
\end{array} \quad \text{δ}^- \quad \rightarrow \quad \begin{array}{c}
\text{HO} \\
\text{CH}_3 \\
\text{C} \\
\text{Br}
\end{array} \quad \text{δ}^- \quad \begin{array}{c}
\text{H} \\
\text{CH}_3 \\
\text{C} \\
\text{OH}
\end{array} \quad + \text{:Br}^-
\]

\[
\text{CH}_3\text{CH}_2\text{Br} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{Br}^- \quad \text{slow step}
\]

The rate equation is:
\[
r = k \left[ \text{CH}_3\text{CH}_2\text{Br} \right] \left[ \text{OH}^- \right]
\]

This is called \( S_N2 \). 
Substitution, Nucleophilic, 2 molecules in rate determining step

Primary halogenoalkanes tend to react via the \( S_N2 \) mechanism.

### \( S_N1 \) nucleophilic substitution mechanism for tertiary halogenoalkanes

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{C} \quad \begin{array}{c}
\text{Br} \\
\text{CH}_3
\end{array}
\end{array} \rightarrow \begin{array}{c}
\text{H}_3\text{C} \\
\text{C} \quad \begin{array}{c}
\text{Br} \\
\text{CH}_3
\end{array}
\end{array} \quad \text{:OH}^- \rightarrow \begin{array}{c}
\text{H}_3\text{C} \\
\text{C} \\
\text{OH}
\end{array} \quad \text{CH}_3 \quad \text{CH}_3
\]

The Br first breaks away from the halogenoalkane to form a carbocation intermediate. 
The hydroxide nucleophile then attacks the positive carbon.

Overall Reaction:
\[
(\text{CH}_3)_2\text{CBr} + \text{OH}^- \rightarrow (\text{CH}_3)_2\text{COH} + \text{Br}^-
\]

Mechanism:
\[
(\text{CH}_3)_2\text{CBr} \rightarrow (\text{CH}_3)_2\text{C}^- + \text{Br}^- \quad \text{slow}
\]
\[
(\text{CH}_3)_2\text{C}^- + \text{OH}^- \rightarrow (\text{CH}_3)_2\text{COH} \quad \text{fast}
\]

The rate equation is:
\[
r = k \left[ (\text{CH}_3)_2\text{CBr} \right]
\]

This is called \( S_N1 \). 
Substitution, Nucleophilic, 1 molecule in rate determining step

Primary halogenoalkanes do not do the \( S_N1 \) mechanism because they would only form an unstable primary carbocation.

Example 4

Overall Reaction:
\[
\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)
\]

Mechanism:
Step 1: \( \text{NO}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_3 \) slow 
Step 2: \( \text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2 \) fast 
\( \text{NO}_3 \) is a reaction intermediate 
\( \text{NO}_2 \) appears twice in the slow steps so it is second order. \( \text{CO} \) does not appear in the slow step so is zero order.
\[
r = k \left[ \text{NO}_2 \right]^2
\]

Example 5

Using the rate equation rate = \( k[\text{NO}_2]^2[\text{H}_2] \) and the overall equation \( 2\text{NO}(g) + 2\text{H}_2(g) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g) \), the following three-step mechanism for the reaction was suggested. \( X \) and \( Y \) are intermediate species.

Step 1 \( \text{NO} + \text{NO} \rightarrow X \)
Step 2 \( X + \text{H}_2 \rightarrow Y \)
Step 3 \( Y + \text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \)

Which one of the three steps is the rate-determining step?

Step 2 – as \( \text{H}_2 \) appears in rate equation and combination of step 1 and 2 is the ratio that appears in the rate equation.