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 $A + 2B \rightarrow C$ 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

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

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

\[
\text{gradient} = \frac{y}{x}
\]
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
**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?

### 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 $= -7.3 \times 10^{-2}$ mol dm$^{-3}$ min$^{-1}$

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### 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 \((x \text{ axis})\)

(cont)

![Graph showing three regions: A, B, and C.]

**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.
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.

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

$$k \frac{t}{2} = \log_e 2$$

$$= 0.693$$

$$t_{1/2} = \text{the half life}$$

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

**FOR A FIRST ORDER REACTION**

$$k = \frac{0.693}{t_{1/2}}$$

**Q.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 (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>$[A]$ / 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.

* e.g. if the rate equation is \( \text{rate} = k [A]^2 \) the units of k 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 \( \text{sec}^{-1} \)
- in the rate equation \( r = k [A] [B]^2 \) \( k \) has units of \( \text{dm}^6 \text{ mol}^{-2} \text{ sec}^{-1} \)

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

\[ r = k[C]^1[D] \]
\[ r = k [Z]^2 \]
\[ r = k [A] [B] \]

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
**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...

\[ \text{CH}_3\text{COCH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{HI} \]

*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 \([\text{I}_2]\) 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 halogenoalkanes

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

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