**3.1.9 Rate equations**

**AS Link:**

**3.1.5 - Kinetics**

**Review of kinetics**

**Collision theory** states:

* particles must **collide** before a reaction can take place (not all collisions lead to a reaction)
* reactants must possess a minimum amount of energy – **activation energy**

**Main factors affecting the rate of a reaction:**

* Temperature
* Concentration
* Pressure
* Surface area
* Catalyst

To **increase the rate** of reaction there needs to be more **frequent** **successful** collisions:

* give particles more energy to increase particle speed
* have more particles present
* lower the activation energy

**Maxwell-Boltzmann distribution**

By plotting energy against number of particles with that energy the **spread of energies** can be clearly seen.

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| 3 | It has these features: |
| 4  5  2  1 | 1. The **area** under the curve represents the **total number of molecules** in the sample. 2. Curve starts at **0,0** because **no particles** have **zero energy.** 3. Peak shows that **most particles** have **most** **probable** **intermediate** **energy** (Emp). 4. **Average** **energy**, Ē **not** **same** as **most probable** energy this is the maximum point of the curve. 5. **Few** have very **high energy** (no upper limit), the curve approaches zero **asymptotically** at high temperatures (it never meets axis). |

**Activation energy**

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| For a reaction to start there **must be sufficient energy to start breaking bonds**. The area under the graph to the **right of the activation energy line** represents the number of **particles** **with sufficient energy** to react i.e. the number of molecules **with energy that is equal to or greater than the activation energy**.  ***Sheet: Kinetics review questions*** |  |

**The rate of chemical reactions**

***Definition***: The rate of a chemical reaction is the **change in amount** of reactant or product per unit **time.**

This is usually measure of the change in concentration so the units will be **mol dm-3 s-1**

N.B. slow reactions expressed as per min or hr

Looking at a typical reaction: A + 2B →C

The concentrations of A and B decrease as C increases with time. Measuring these gives a graph:

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To measure the reaction rate you need to be able to measure the **concentration** of one of the **reactants or products over time,** wherethe former decrease and the latter increases. The **temperature** must be kept **constant** because **rate varies with temperature**. The method used depends on the substance and the speed of the reaction.

In this example for every A that reacts there are 2 of B (as shown in the equation), so B decreases twice as fast as A. So you must state whether you are following A, B or C.

**It’s usual to measure the product, because it increases with time**.

Measuring the amount of a reactant or product at regular time intervals is called **continuous monitoring**. The method used depends on the reactants used and products made.

For example:

* **gas volume** in a gas syringe or in a measuring cylinder by displacement of water
* **loss of mass** as a gas is produced by placing the reaction mixture on a balance
* **pH** **change** using a pH meter
* **colour change** using a colorimeter to measure the absorbance of the solution.

***Starter: 1.3 – Measuring reaction rate in the lab Q1&3***

***Application: CGP46 PQ1-4***

***Fact recall: CGP46 Q1-4***

The rate of reaction at any instant

The **rate** at a **particular point in time** is often needed rather than the rate over a period of time. By **plotting** the amount of **reactant** or **product** **against time** for a reaction will produce enable the **change in concentration** at a **point in time** to be determined.

**rate = change in *y* = change in concentration**

**change in *x* time**

**Example – CGP47**

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| The graph shows the data collected from an experiment where the decomposition of X was monitored over time. Work out the rate of the reaction. |  |

To find the rate of this reaction the gradient of the line must be calculated, since it is a straight line the gradient is the same at all points on the line.

To calculate the gradient pick two points on the line that are easy to read, it’s best to pick points which pass exactly through the corners of a grid.

Calculate the gradient:

Change in y = 0.14-0.50 = -0.36 mol dm-3

Change in x = 15-2.5 = 12.5 mins

Put the values in the equation: rate = change in *y* = -0.36 = -0.029 mol dm-3 min-1

change in *x* 12.5

The gradient is negative but this can be ignored when giving the rate

The rate of reaction is **0.029 mol dm-3 min-1**

**Example CGP48**

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| If the graph is a **curve** then to find the **rate of change** at a particular **point in time** a **tangent** is **drawn** to determine the **gradient**.  A tangent is a line that touches a curve and has the same gradient as the curve at that point.  The graph shows how the concentration changes over time.  Calculate the rate at 3 minutes. |  |

Place a ruler at the 3 minutes point on the curve so that you can see the whole of the curve and the space between the ruler and the curve is equal on both sides of the point.

Draw a line to make the tangent, extending it across the graph.

Calculate the gradient:

Change in y = 0.46-0.22 = 0.24 mol dm-3

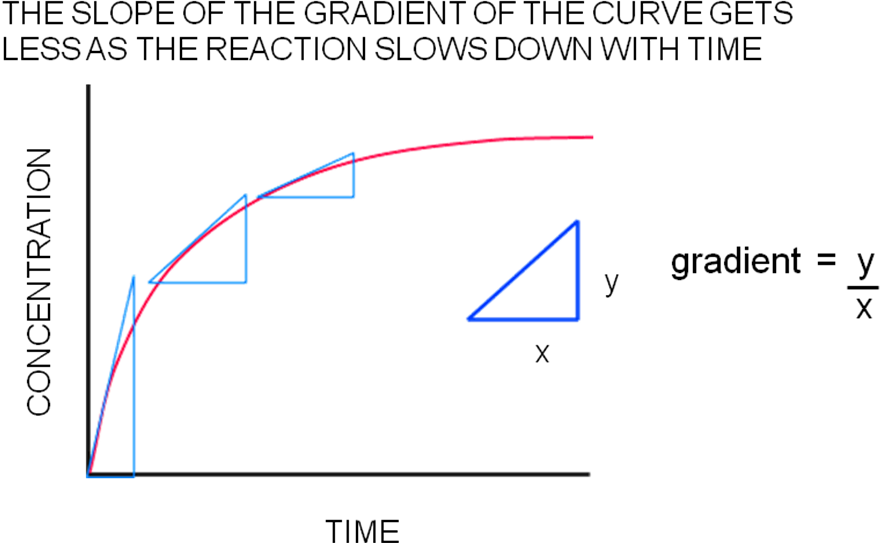
Change in x = 5.0-1.4 = 3.6 mins

Put the values in the equation: rate = change in *y* = 0.24 = 0.067 mol dm-3 min-1

change in *x* 3.6

The rate of reaction at 3 minutes is **0.067 mol dm-3 min-1**

The **rate of a reaction changes with time** so drawing multiple tangent will allow the rate at different points in time to be calculated.



***Task: How can you work out the initial rate?***

Draw a tangent on the slope at start of reaction

***Starter: 1.2 – Calculating reaction rate***

***Application: CGP49 PQ1-3***

***Required practical 7b***: Measuring the rate of reaction by a continuous monitoring method:

The reaction between magnesium and hydrochloric acid (changing concentration)

**The rate expression or equation**

The **rate** of a reaction **depends** on the **concentrations** of **some or all of the species** in the reaction vessel i.e. the **reactants** and **catalysts**. They **don’t** necessarily **all make a contribution** to how fast the reaction goes. The **rate** and the **concentrations** **cannot** be **predicted from** the overall **chemical equation**.

A + 2B →C [ ] represents concentration

The concentration of A shown by [A] may have more of an effect than the concentration of B [B] or [A] may have no effect on the rate and only [B] matters. Equally a species that doesn’t appear in the equation may affect the rate e.g. a catalyst.

**Experimentation** shows how each species contributes to the rate. This gives rise to the **rate expression**.

**rate [A] [B]**

The **rate expression shows the contributions** of the species **that do affect the rate**. It describes **how the rate of the reaction at a particular temperature depends on the concentration of a species** involved in a reaction. It is possible that one or more species may appear in the chemical equation but not in the rate expression. The rate is ‘proportional’ to …

In this case both **[A] and [B] have an equal effect on the rate**, so **doubling** either **[A] or [B]** would **double** the **rate** of the reaction, **doubling** concentration of **both** would **quadruple the rate**.

Here’s another example:

rate [A] [B]2



In this case **doubling [A] would double the rate** and **doubling [B] would quadruple** the rate.

So the **rate expression** can be written as:

rate [A]m [B]n



Where the indices ***m* and *n*** show the **extent** to which each species **affect the rate** of the reaction.

Remember a species not in the chemical equation may appear in the rate expression.

The rate constant, k

The **rate expression can become the rate equation** if the proportionality sign is replace with an **equal sign** and a **constant is introduced** called the **rate constant** or velocity constant.

*k* is **different for every reaction** and **varies with temperature**, so **temperature** must be **stated**.

**Units** for rate always **mol dm-3 s-1**

**Units** **vary for *k*** – dependent on overall order of reaction

rate = *k* [A]m [B]n

[ ] represents concentration

*m* and *n* are the orders of the reaction with respect to the species affecting the rate

*k* is the rate constant

The **bigger** the **value of *k***, the **faster the reaction**.

Reaction orders

rate = *k* [A]m [B]n

The indices ***m*** and ***n*** are usually an **integral** whole numbers, most commonly **0, 1 or 2** and are called the **orders of reaction** with respect to A and B.

They can **never be inferred from the coefficients** (number of moles) in the **stoichiometric** equation (balanced chemical equation showing ratio of moles), they are **always deduced experimentally**.

For the rate equation above ***m*** shows how the **concentration of A** affects the rate and ***n*** how the **concentration of B** affects the rate.

So:

* If **[A] changes and rate stay the same**, the order of reaction with respect to A is **zero order**, A will not feature in the rate equation.
* If the **rate is proportional to [A]**, the order of reaction with respect to A is **first** order - doubling [A] doubles the rate or tripling [A] triples the rate.
* If the **rate is proportional to [A]2**, the order of reaction with respect to A is **second** order - doubling [A] the rate will be 22 = 4 times faster, tripling [A] the rate will be

32 = 9 times faster.

The **order of the reaction**, with respect to one of the species, is **shown by the power** of each and the **overall order** of the reaction is the **sum of the orders** of all the species.

***Definition***: The overall **order of reaction** is the sum of the powers of the concentration terms in the rate equation.

**Example**

Rate = k [A] 1st order with respect to A

overall reaction is 1st order

Rate = k [A][B] 1st order with respect to A

1st order with respect to B

overall reaction is 2nd order

overall reaction is 1st order

**Example CGP50**

The rate equation for the reaction is rate = *k*[NO]2[H2]

2H2 + 2NO → 2H2O + N2

Determine the order of the reaction with respect to H2 and NO, then work out the overall order of the reaction

Second order with respect to NO

First order with respect to H2

Third order overall

***Task: If the rate of the reaction is shown by the following rate equation work out the order of the reaction with respect to A and B, then work out the overall order of the reaction***

If rate = *k* [A]2[B]2

A = second order i.e. second order with respect to A

B = second order i.e. second order with respect to B

Overall = fourth order i.e. fourth order overall

***Sheet: Introduction to orders***

Writing rate equations

If the order of reaction of each reagent affecting the rate is given then a rate equation can be written for a reaction.

**Example CGP51**

The chemical equation below shows the acid-catalysed reaction between propanone and iodine.

H+

CH3COCH3 + I2 → CH3COCH2I + H+ + I-

1. The reaction is first order with respect to propanone, first order with respect to the acid catalyst and zero order with respect to iodine. Write the rate equation.

rate = *k*[CH3COCH3]1[H+]1[I2]0

But [X]1 is usually written [X] and [X]0 equals one so it’s left out.

This gives rate = *k*[CH3COCH3][H+]

The rate is proportional to the concentration of propanone and the acid catalyst.

If the concentrations of each reagent are known and the value for the rate constant then the rate of the reaction at a particular temperature can be determined.

**Example CGP51**

1. The chemical equation above at a certain temperature, k was found to be 520 mol-1   
   dm3 s-1 when [CH3COCH3] = [I2] = [H+] = 1.5 x 10-3 mol dm-3. Calculate the rate at this temperature.

rate = *k*[CH3COCH3][H+] = 520 x (1.5 x 10-3) x (1.5 x 10-3) = 1.17 x 10-3

The units are ~~mol~~~~-1~~ ~~dm~~~~3~~ s-1 x ~~mol dm~~~~-3~~ x mol dm-3 = mol dm-3 s-1

**Rate = 1.17 x 10-3 mol dm-3 s-1**

Value of the rate constant, *k*

Remember once the **rate equations has been determined** the **value** of the **rate constant** can be **calculated** if the **rate** and **concentration are known**. The rate equation can be used to work out the rate constant, *k*, but the **units for *k* vary** **depending on the overall order** of the reaction so they must be **worked out** each time and stated.

**Example CGP52**

The reaction below is second order with respect to NO and zero order with respect to CO and O2.

NO + CO + O2 → NO2 + CO2

At a certain temperature the rate is 1.76 x 10-3 mol dm-3 s-1, when [NO] = [CO] = [O2]

concentration NO 2.00 x 10-3 mol dm-3.   
Find the value of the rate constant at this temperature.

The rate equation: rate = *k*[NO]2

So: 1.76 x 10-3 = *k* (2.00 x 10-3)2

Re-arrange: *k* = 1.76 x 10-3 = 440

(2.00 x 10-3)2

Units for *k*: ~~mol dm~~~~-3~~ s-1 = mol-1 dm3 s-1

(~~mol dm~~~~-3~~) (mol dm-3)

Answer: **440 mol-1 dm3 s-1**

***Task: Find the value and units for k***

rate = *k* [A]2 [B]1

[A] = 2.0 x 10-3 mol dm-3

[B] = 1.0 x 10-3 mol dm-3

Initial rate = 28.0 x 10-4 mol dm-3 s-1

You **need to know the [A] and [B]** and **order of the reaction** with respect to A and B.

So 28.0 x 10-4 = *k* (2.0 x 10-3)2 x 1.0 x 10-3

28 x 10-4 = *k* x 4.0 x 10-9

*k* = 28.0/4 x 105 = 7.0 x 105

Units: mol dm-3 s-1 = *k* (mol dm-3)2 x mol dm-3

~~mol dm~~~~-3~~ s-1 = *k* (mol dm-3)2 x ~~mol dm~~~~-3~~ mol-2 dm6 s-1

Therefore: ***k* = 7.0 x 105 mol-2 dm6 s-1**

Units for *k*

**Zero-order**: rate = *k*

**units = mol dm-3 s-1**

**First-order**: rate = *k* [A] so *k* = rate

[A]

insert units *k* = mol dm-3 s-1 cancels  ~~mol dm~~~~-3~~ **s-1**

mol dm-3  ~~mol dm~~~~-3~~

**units = s-1**

**Second-order**: rate = *k* [A] [B] so *k* = rate

[A] [B]

insert units *k* = mol dm-3 s-1 cancels ~~mol dm~~~~-3~~ **s-1**

(mol dm-3) (mol dm-3) (~~mol dm~~~~-3~~) (**mol dm-3**)

**units = mol-1 dm3 s-1**

***Task: Work out units for rate constant for third & fourth-order reactions***

**Third-order**: rate = *k* [A] [B] [C] so *k* = rate

[A] [B] [C]

insert units *k* = ~~mol dm~~~~-3~~ s-1

(~~mol dm~~~~-3~~~~)~~ (mol dm-3) (mol dm-3)

**units = mol-2 dm6 s-1**

**Fourth-order**: rate = *k* [A] [B] [C] [D] so *k* = rate

[A] [B] [C] [D]

insert units *k* = ~~mol dm~~~~-3~~ s-1

(~~mol dm~~~~-3~~) (mol dm-3) (mol dm-3) (mol dm-3)

**units = mol-3 dm9 s-1**

There is a **simple pattern to the units** of the rate constant and the order of the reaction based on the rate equation, but it’s best to **work them out each time**.

rate = *k* [A]m [B]n or **rate = *k* x (concentration) *n+m***

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| **Order of reaction**  **= n + m** | **Rate equation**  **rate = *k* x (concentration) *n+m*** | **Units of the**  **rate constant** |
| 0 | rate = *k* x (concentration) *0* | mol dm-3 s-1 |
| 1 | rate = *k* x (concentration) *1* | s-1 |
| 2 | rate = *k* x (concentration) *2* | mol-1 dm3 s-1 |
| 3 | rate = *k* x (concentration) *3* | mol-2 dm6 s-1 |
| 4 | rate = *k* x (concentration) *4* | mol-3 dm9 s-1 |

To calculate the value of *k* the concentration of each substance shown in the rate equation and the rate must be known.

***Sheet: Rate constant units***

***Application: CGP53 PQ1-3***

***Fact recall: CGP53 Q1-4***

**Determining the rate equation**

The **rate** of a reaction at a fixed temperature **decreases** as it proceeds because the **concentrations of reactants fall** as they are **used up**.

There are **2 methods** of determining the rate equation:

* Initial rate method
* Using rate-concentration graphs

Initial rate method

The initial rates method can be used to work out the order of reaction for each reactant.

At the start of a reaction the **concentrations are known exactly** and the rate is called the **initial rate**. By **changing the initial concentration** the **initial rate will change** and the rate equation can be derived.

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| A **number of experiments are carried out** at constant temperature.  Each starts with a **different initial concentration** of reactants (or catalyst), then the concentration of one reactant is followed and a **concentration-time graph** is plotted.  Then at **time = 0** the **tangent** to the graph is drawn and the **gradient calculated** to find the **initial rate** of each experiment. |  |

**Example – CGP55**

The table below shows the results of a series of initial rate experiments for the reaction

2NO + Cl2 → 2NOCl

Write the rate equation for the reaction. The temperature remained constant.

|  |  |  |  |
| --- | --- | --- | --- |
| **Experiment** | **Initial [NO] / mol dm-3** | **Initial [Cl2] / mol dm-3** | **Initial rate / mol dm-3** |
| 1 | 0.125  ] x 2 | 0.125 | 1.79 x 10-7  ] x 4 |
| 2 | 0.250 | 0.125  ] x 2 | 7.16 x 10-7  ] x 2 |
| 3 | 0.250 | 0.250 | 1.43 x 10-6 |

Consider pairs of experiments in which one of the reactants remains constant.

Experiments 1 & 2:

[NO] doubles and [Cl2] constant

Rate increases by factor of (7.16 x 10-7 / 1.79 x 10-7) = 4 or 22 i.e. quadrupled

So: rate [NO]2 second-order with respect to NO



Experiments 2 & 3:

[Cl2] doubled and [NO] constant

Rate increases by factor of (1.43 x 10-6 / 7.16 x 10-7) = 2 or 21 i.e. doubled

So: rate [Cl2]1 first-order with respect to Cl2



Overall: rate [NO]2 [Cl2]1



So: **rate = *k* [NO]2 [Cl2] third-order overall** Units: mol-1 dm3 s-1

***Task: Determine the order of reaction with respect to components P and Q and deduce the units of the rate constant.***

2P + Q → R + S

|  |  |  |  |
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| **Experiment** | **Initial**  **[P] / mol dm-3** | **Initial**  **[Q] / mol dm-3** | **Initial**  **rate / mol dm-3** |
| 1 | 0.5  ] x 2 | 0.5 | 0.002  ] x 4 |
| 2 | 1.0 | 0.5  ] x 2 | 0.008  ] x 0 |
| 3 | 1.0 | 1.0 | 0.008 |
| 4 | 1.5 | 1.5 | 0.018 |

Consider pairs of experiments in which one of the reactants remains constant.

Experiments 1 & 2:

[Q] constant and [P] doubled

Rate increases by factor of (0.008/0.002) = 4 or 22 i.e quadrupled

So: rate [P]2 second-order with respect to P



Experiments 2 & 3:

[Q] doubled and [P] constant

Rate is unchanged i.e. independent of [Q]

So: rate [Q]0 zero-order with respect to Q



Overall: rate [P]2 [Q]0



So: **rate = *k* [P]2 second-order overall** Units: mol-1 dm3 s-1

**A more mathematical approach**

This is sometimes useful for more challenging exam questions.

Rate = k [P]*x* [Q]*y*

where *x* is the order with respect to P and *y* is the order with respect to Q

So rate of experiment 2 = *k* [P]2 *x* [Q]2 *y*

rate of experiment 1 *k* [P]1 *x* [Q]1 *y*

Putting in the numbers from the table:

0.008 = *k* (1.0)2 *x* (0.5)2 *y*

0.002 *k* (0.5)1 *x* (0.5)1 *y*

0.008 = *k* (1.0)2 *x* ~~(0.5)~~2 *y*

0.002 *k* (0.5)1 *x* ~~(0.5)~~1 *y*

4 = 2*x* *x* = 2 Therefore rate is **second-order with respect to P**

***Sheet: Kinetics calculations 1 & 2***

***Starter: 1.4 – Determine the rate equation (extra questions if needed)***

***PP: Rate of Reactions questions & answers (extra)***

***Application: CGP57 PQ1-3***

***Fact recall: CGP57 Q1-2***

***Required practical 7a***: Measuring the rate of reaction by an initial rate method

(The iodine clock reaction – CGP58-59)

***Fact recall: CGP59 Q1-3***

Rate-concentration graphs

The **shape** of a **concentration-time graph** and **rate-concentration graph** can be used to work out the order of the reactions. A rate-concentration graph can be plotted using the data from a concentration-time graph.

Initially a graph of **concentration against time** is plotted and **tangents** drawn at different concentrations to **determine the gradient** which gives the **change in concentration over time**.

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|  | gradient = [A] = mol dm-3  time s  **mol dm-3 s-1** i.e. the rate |

These **values of rate** can then be used to **construct a second graph** of **rate against concentration**; the shape of the graph indicates the order.

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| --- | --- | --- |
| **Order** | **Concentration-time graph** | **Rate-concentration graph** |
| **Zero**  rate = *k* [A]*m*  If *m* is zero then: rate = *k*  So the **rate** is **constant** and is **independent** of the concentration of A because [A]0 = 1  Changing concentration has **no effect on the rate**.  Plotting **rate against time** gives a **flat line** showing the **rate doesn’t change** with time. |  |  |
|  |  |  |
| First  rate = *k* [A]*m*  If *m* is **1** then: rate = k  So the **rate** **varies** and is **dependent** on the concentration of A, if [A] changes then the **rate changes is proportional to the amount**.  Plotting **concentration of reactant against time** shows how the concentration of the reactant decreases with time. The **rate decreases** as the reaction proceeds **so A is used up more slowly** therefore **[A] decreases gradually**. |  |  |
| Second  rate = *k* [A]*m*  If *m* is **2** then: rate = *k* [A]2  So the **rate** **varies** and is **dependent** of the concentration of A, if [A] doubles then the **rate quadruples**.  Plotting **concentration of reactant against time** shows how the concentration of the reactant decreases with time. The **rate decreases faster at the beginning** so **[A] is used up more quickly** therefore it gives a **steeper graph**. |  |  |

**Comparing graphs**

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***Sheet: Stretch & challenge – Decomposition of nitrogen (V) oxide – using a graph***

***Application: CGP61 PQ1-2***

***Fact recall: CGP61 Q1-3***

The effect of temperature on *k*

**Small changes** in **temperature** produce **large changes** in reaction **rates**. Looking at a rate equation the following can be deduced.

Rate = k[A] [B]

**Temperature** has **no effect** on **concentration**, so it must be the **rate constant** **that changes** with temperature. The rate constant allows the rate of reactions to be compared.

*Values of the rate constant, k, at different temperatures for the reaction 2HI(g) → I2(g) + H2(g)*

|  |  |
| --- | --- |
| **Temperature / K** | ***k* / mol-1 dm3 s-1** |
| 633 | 0.0178 x 10-3 |
| 666 | 0.107 x 10-3 |
| 697 | 0.501 x 10-3 |
| 715 | 1.05 x 10-3 |
| 781 | 15.1 x 10-3 |

The **larger** the value of the **rate constant** the **faster** the **rate**.

**Temperature** is a measure of the **mean kinetic energy of particles**, so increasing the **temperature increases the rate** of a reaction. At **higher temperatures** molecules have **more energy** so **move** **more quickly** giving **a higher frequency** of **successful collisions**.

Particles will **only react** together if their **collisions have enough energy** to **start breaking** **bonds**, the activation energy. So the **increase in the energy** **of the collisions** is more **important** than the **increase** in **collision rate**.

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|  | The graph shows how the **energies of the particles are distributed** at two **different** **temperatures**.  As the **temperature increases**, a **greater proportion** of molecules have **enough energy to react** so there are **many more molecules with**  **E > Ea**. |

A **small increase in temperature** give rise to **large increases in rate**. A rough rule is that every **10K rise doubles the rate** – this results in an **exponential increase**.

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| rate = *k* [A]m [B]n | The graph shows the **increase** in **rate with temperature**, it is **exponential**.  This means that when the **temperature** **increases** by a **certain number of degrees** the **rate** **constant** **increases** by a **fixed factor** i.e. 2x or 10x **depending** on the **size** of the **temperature increase**. |
|  |
|  |

***Sheet: Rate equations questions***

**Rate determining step**

Most reactions take place in **more than one step**. For example, this reaction involves 7 molecules:

**2C2H2 + 5O2 → 4CO2 + 2H2O**

This shows that two molecules of ethene (C2H2) react with 5 molecules of oxygen. According to the collision theory, molecules must collide in order to react. But it is **highly unlikely that 7 molecules would collide together all at once**.

***Activity: Rate determining step in a reaction***

*In pairs*, each has a crumpled up a piece of paper. Sitting facing one another, with knees almost touching, toss your pieces of paper together, trying to get them to hit while still in the air.   
Do this 10 times - how many successful collisions?

*In threes*, this time, a successful collision will only occur when all three pieces of paper hit together simultaneously - just two out of three won't do.   
Out of 10 tosses, how many are successful?

*All together* and repeat the exercise, a successful collision is when all pieces of paper must collide at the same instant.

**Chemical reactions** follow the same principles, so they must take place in **several steps** with the steps producing very **short-lived intermediates**. The steps are called the **reaction mechanism** with the **combined steps** giving the **overall reaction equation**. These **intermediate species** are **difficult** or **impossible** **to isolate** and therefore identify, so **other methods must be used to work out the mechanism.**

***Definition***: The **reaction mechanism** for a reaction consists of a proposed sequence of discrete chemical reaction steps that can be deduced from the experimentally observed rate equation.

In a **multi-step reaction** the steps nearly always follow after each other, so **products of one reaction** are the **reactants of another**, each **step** may have a **different reaction rate**. The **overall rate** is **determined** by the **step with the slowest rate**. The **slowest step forms a ‘bottle-neck’** called the **rate-determining** step or **rate-limiting** step. The rate-determining step doesn’t have to be the first step.

***Definition***: The **rate-determining** step is the **slowest step** in a multi-step reaction sequence; it **dictates the overall rate of reaction**.

***Demo: Beaker & conical flask***

Water flows out of a beaker faster because there is no bottle-neck

**Example: Making a cup of coffee**

The rate of getting your drink will be governed by the slowest step; this will be the time it takes for the water to boil, no matter how quickly you get the cup out of the cupboard or coffee in the cup.

***Task: Another analogy?***

Driving from Leeds to Dover – A1, M25, Dartford toll bridge, M20 – which step in the journey will determine the time you arrive at Dover?

Could be M25, most likely to be the toll bridge – it will be the ‘bottle-neck’. Your journey time will be dictated by how long it takes you to get over the bridge, vehicles need to stop to pay the toll and it is only 2 lanes of traffic.

In a reaction, **any step** that occurs **after the rate-determining** step **will not affect the rate**, providing that it is **fast compared to the rate-determining step**.

So any **species** that are involved **after** the **rate-determining step** **do not appear** in the **rate equation**.

**A + B + C → Y + Z**

Might occur in the following steps:

fast

1. **A + B** D (1st intermediate)

**slow**

2. D E (2nd intermediate)

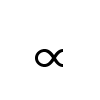
fast

3. E + **C** **Y +** **Z**

**Step 2 is the slowest** so **determines the rate**; as soon as **E** is produced it **rapidly reacts with C** to produce **Y** and **Z**.

But the rate of **step 1 might affect the overall rate** as the concentration of D used in step 2 affects the rate of this step. Therefore, any **species in or before the rate-determining step** could **affect the overall rate** and so **appear in the rate equation**. Any **species after** the **rate-determining step** will **not appear** in the **rate equation**.

Rate [A] [B] [D]



The **rate equation** can therefore be **used to work out the reaction mechanism** by **identifying** the **reactants** that are **involved** in the **rate-determining step**. Remember if a reactant or a species derived from it appears in the rate equation it must affect the rate.

Orders of reaction and rate-determining step

The **order of a reaction** with **respect** to a **reactant** **shows** how many **molecules of that reactant** are **involved** in the **rate-determining step**. So, if a reactant is second order with respect to X, there will be two molecules of X in the rate-determining step.

**Example – CGP62**

The mechanism for the reaction between chlorine free radicals (Cl•) and ozone (O3) consists of 2 steps:

Cl• + O3 → ClO• + O2 This step is slow – rate-determining step

ClO• + O3 → Cl• + 2O2 This step is fast

Cl• + O3 are both in the rate-determining step so must appear in the rate equation. There is only one molecule of each species so the order with respect to each is first. The reaction of ClO• is not in the rate-determining so does not appear in the rate equation.

**Rate = *k* [Cl•] [O3]**

Finding reaction mechanisms

If you know which reactants are in the rate-determining step, you can work out the mechanism.

**Example – CGP62 extended**

Structural isomers of bromobutane C4H9Br all undergo hydrolysis with an alkali by nucleophilic substitution.

C4H9Br + OH- → C4H9OH + Br-

Two mechanisms are possible:

a) Two-step:

slow

Step 1: C4H9Br C4H9 + + Br- Slow - breaking C-Br bond (rate-determining)

fast

Step 2: C4H9 + + OH- C4H9OH Fast - reaction between oppositely charged ions

b) One-step:

Step 1: C4H9Br + OH- → C4H9OH + Br- C-Br breaking and C-OH forming at same time

Two possible isomer reactants that can be used:

|  |  |
| --- | --- |
| **1-bromobutane** | **2-bromo-2-methylpropane** |
| CH3CH2CH2CH2Br | (CH3)3CBr |

**Experiments show hydrolysis of 1-bromobutane** reacts by a **second-order** mechanism:

CH3CH2CH2CH2Br + OH- → CH3CH2CH2CH2OH + Br-

rate = *k* [CH3CH2CH2CH2Br] [OH-]

So the **rate depends** on the **concentration** of **both** bromobutane and the hydroxide ions, this suggests **mechanism b) with a single-step**.

**Experiments show hydrolysis of 2-bromo-2-methylpropane** reacts by a **first-order** mechanism:

(CH3)3CBr + OH- → (CH3)3COH + Br-

rate = *k* [(CH3)3CBr]

This suggests **mechanism a) with two-steps**, the breaking of the C-Br bond is the rate-determining step. The **hydroxide ion** is **not** **in** the **rate equation** so it’s **not involved** in the **rate-determining step** and **must be after** the rate-determining step.

**Example – CGP63**

The oxidation of nitrogen (II) oxide produces nitrogen dioxide

2NO + O2 → 2NO2

The reaction mechanism is in two-steps involving the formation of a dimer:

Step 1: 2NO → N2O2

Step 2: N2O2 + O2 → 2NO2

The rate equation is: rate = *k* [NO]2[O2]

Comment

From the rate equation, the rate-determining step must involve **2 molecules of NO** and **1 molecule of O2**. Neither step 1 nor step 2 contains all the molecules expected form the rate equation, but **step 2 contains an intermediate** molecule N2O2, **derived** **from** 2 molecules of **NO** and then reacts with O2. So **step 2** must be the **rate-determining step**.

fast

2NO N2O2

slow

N2O2 + O2 2NO2

***Starter: 1.1 – Rate determining step***

***Sheet: Stretch & challenge – Reaction rates and mechanisms***

***Application: CGP63 PQ1-2***

***Fact recall: CGP63 Q1-2***

**Arrhenius equation**

The **rate** of a chemical reaction will **increase greatly** for relatively **small** **rises** in **temperature**. An increase in temperature will **increase** the number of **collisions** between reactant molecules but this is not enough to account for the large increase in the rate.

The increase in temperature also **increases** the number of **molecules** with **energy equal or greater** than the **activation** **energy**.

|  |  |
| --- | --- |
| This is shown on the Maxwell-Boltzman distribution curve. |  |

The fraction of molecules with energy greater than the activation energy is given by exponential function:

**e-Ea / RT**

**e is a fixed irrational number** (like π) with an **infinite number of decimal places**.

e = 2.71828182845904523536028747135266249775724709369995...

It’s usually raised to a power, i.e. **e*x*** and is then known as the ‘**exponential function’**.

**Help**: Function button on calculator: e▪ (shift ln)

**Example CGP283**

e9 = 8103.1

e-4 = 0.01832

e0 = 1

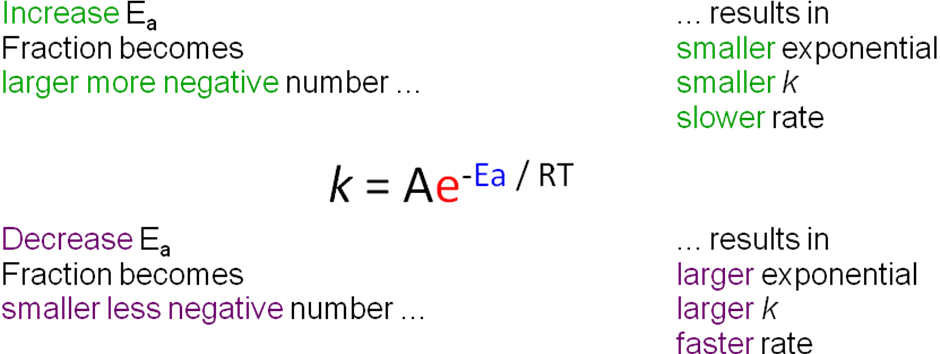
The **activation energy** can be **linked** to the **rate constant** by the **Arrhenius equation**.

|  |  |  |
| --- | --- | --- |
| ***k* = Ae-Ea / RT** |  | *k* = rate constant  A = Arrhenius constant (related to the number of collisions, units s-1)  e = mathematical constant (approx. 2.718)  Ea = activation energy (J mol-1)  T = temperature (K)  R = ideal gas constant (8.31 J K-1 mol-1) |
| This will be given in the exam question |  |

The rate constant and activation energy

The Arrhenius equation is a helpful tool for **working out what happens to the rate constant** if the **temperature or activation energy** **changes** in a reaction.

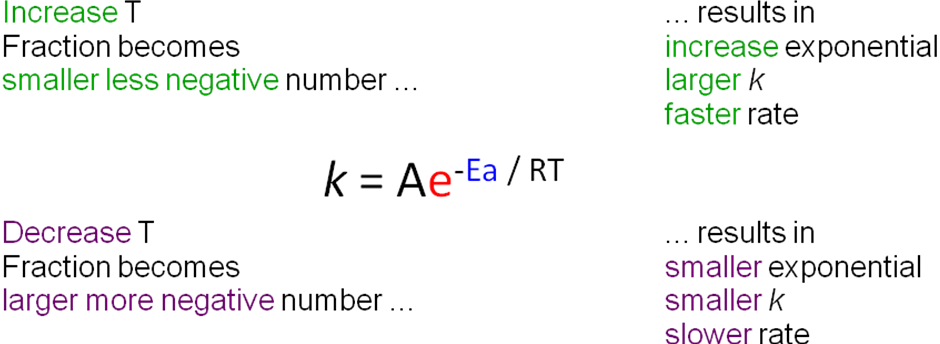
This is how the **rate constant** is **changed** when the **activation energy changes**.



So, a **large activation energy** means a **slower rate** of reaction as very **few molecules** will have **energy** that is **greater than or equal to the activation energy**.

The rate constant and temperature

The equation also shows that as the **temperature increases**, ***k* increases**, giving a **faster** **reaction**.



**Higher temperatures** mean **more reactant particles** with **energy greater than** or **equal** to the **activation** **energy** and so there will be a **higher frequency** of **successful collisions**.

Using the Arrhenius equation

**Example**

Calculate the value of the rate constant at room temperature. State its units.

A reaction has an activation energy of 120 kJ mol-1 at room temperature. The gas constant is 8.31 J K-1 mol-1. The Arrhenius constant is 2.2 x 1012 s-1.

|  |  |
| --- | --- |
| Calculate Ea / RT = 120 x 103 / (8.31 x 298) = 48.46  *k* = Ae-Ea / RT  *k* = 2.2 x 1012 x e-48.46 = **1.98 x 10-9 s-1** | *Units*  *J/J K-1 x K*  *So, no units* |
| Comment on the units: Shows the overall order is first order | *Units for k is s-1*  *So, shows it’s 1st order* |

***Task: Re-calculate the value of the rate constant at 308K. The Arrhenius constant is unchanged.***

Calculate Ea / RT = 120 x 103 / (8.31 x 308) = 46.88

*k* = Ae-Ea / RT

*k* = 2.2 x 1012 x e-46.88 = **9.57 x 10-9 (9.61 x 10-9) s-1**

Comment on the value of the rate constant.

*k* increased from 1.98 x 10-9 s-1

Large increase in the rate of reaction (almost 5x) for a small increase in temperature

***Task: A catalyst for this reaction lowers the activation energy to 100 kJ mol-1 at 298K. The Arrhenius constant is unchanged. Calculate the new rate constant.***

Calculate Ea / RT = 100 x 103 / (8.31 x 298) = 40.38

*k* = Ae-Ea / RT

*k* = 2.2 x 1012 x e-40.38 = **6.39 x 10-6 s-1**

Comment on the value of the rate constant.

Ea increased from 120 kJ mol-1

Catalyst gives a much larger increase in the rate of reaction

Log equation

The Arrhenius equation is **easier** to use by taking **logs of both sides** to the **base e**, these are called **natural logs**.

A **log** shows how **many times a number** (the **base**) has been **multiplied** **by itself** to get another number. They are the **opposite of powers**.

If an = *x* then loga *x* = n

E.g. 102 = 100 then log10  100 = 2

It’s often useful to know how many times the **base 10** is multiplied by itself so **log10** is usually just written as **log**. The **natural logarithm** is the log with a **base of e** and **loge** is written as **ln**. **e** and **ln** are **inverses** and can be used to ‘get rid’ of each other.

**Help**: Function button on calculator: ln

**Examples**

ln 14 = 2.64

ln 7 = 1.95

Depending on what the **Arrhenius equation** is used to find it can be helpful to write out the **log version** as it gives a form that can be **re-arranged** and used more simply.

***k* = Ae-Ea / RT**

ln*k* = lnAe-Ea / RT

ln*k* = lnA + lne-Ea / RT

**ln*k* = lnA - Ea/RT**

**Example CGP65**

The decomposition of N2O5 at 308K has a rate constant of 1.35 x 10-4 s-1.

The Arrhenius constant for this reaction is 4.79 x 1013 s-1.

Calculate the activation energy of this reaction. (R = 8.31 J K-1 mol-1).

*k* = Ae-Ea / RT

Log: ln*k* = lnA - Ea

RT

Re-arrange: Ea = lnA – ln*k*

RT

Ea = (lnA – ln*k*) x RT

Ea = ((ln 4.79 x 1013) – (ln 1.35 x 10-4)) x (8.31 x 308)

Ea = ((31.5) – (-8.91)) x (2559.48)

Ea = 40.41 x 2559.48 = 103429.54 J mol-1

**Ea = 103 kJ mol-1**

***Task: The same reaction is set up at a different temperature, and the rate constant is found to be 2.4 x 10-3 s-1. The Arrhenius constant for this reaction is 6.22 x 1013 s-1, all other conditions remain the same, calculate the temperature at which this reaction occurs.***

*k* = Ae-Ea / RT

Log: ln*k* = lnA - Ea

RT

Re-arrange: Ea = lnA – ln*k*

RT

Ea = T (lnA – ln*k*)

R

T = Ea u( N.B. Ea needs to be in J because units for R J K-1 mol-1

R (lnA – ln*k*)

T = 103429.54 = 103429.54

8.31 x (ln 6.22 x 1013 – ln 2.4 x 10-3) 314.065

**T = 329 K**

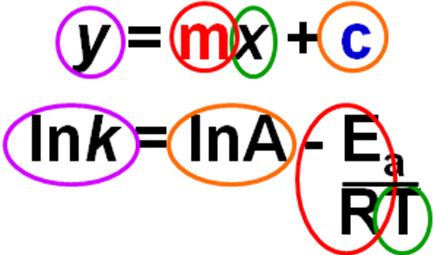
***Sheet: Arrhenius equation Q1-5***

**Arrhenius plots**

By taking logs to the base e (natural logs) of both sides of the Arrhenius equation, the following is derived.

ln*k* = lnA - Ea

RT



If this is re-arranged it can look like this: **ln*k* = - Ea x 1 + lnA**

**R T**

Which is in the format: *y =* m*x* + c

*y* and *x* are the axes ln*k* = *y*-axis 1/T = *x*-axis

m is the gradient -Ea/R = gradient

c is the y-intercept lnA = *y*-intercept

So **plotting ln*k* against 1/T** will be a **straight line** with **the gradient -Ea/R**. The Arrhenius plot can then be used to find the **activation energy** and the **intercept** will give the value of the **Arrhenius** **constant**.

|  |  |
| --- | --- |
|  | The plot an Arrhenius plot san experiment must be completed a number of times and the **rate of reaction measured at different temperatures**. |

**Example CGP67**

The rate constants for a reaction at a variety of temperatures are shown in the table below. Use the data to create an Arrhenius plot, and therefore work out the activation energy and Arrhenius constant.

|  |  |  |  |
| --- | --- | --- | --- |
| **T / K** | ***k* / s-1** | **1/T / K-1** | **ln*k*** |
| 150 | 4.59 x 10-48 | 0.0067 | -109 |
| 200 | 2.44 x 10-36 | 0.0050 | -82.0 |
| 250 | 5.90 x 10-29 | 0.0040 | -65.0 |
| 300 | 9.60 x 10-24 | 0.0033 | -53.0 |
| 350 | 1.05 x 10-20 | 0.0029 | -46.0 |
| 400 | 4.25 x 10-18 | 0.0025 | -40.0 |

Steps

* If just given the values of T and *k* then convert to 1/T and ln*k* before plotting
* Plot 1/T and ln*k*, draw a line of best fit
* Find Ea start by calculating the gradient (∆*y/*∆*x*)

gradient = -78 / 0.0047 = -16595.7

gradient = -Ea/R, where R = 8.31 J K-1 mol-1 (ideal gas constant)

-Ea/R = -16595.7 (*times both side by R*)

-Ea = -16595.7 x 8.31

Ea = 137910.6 J mol-1 = **140 kJ mol-1 (2 s.f.)**

* To find A, substitute the value of Ea just calculated, T and k from the table into the equation: *k* = Ae-Ea / RT

Using the data point at 150K: A = *k*

e-Ea / RT

A = 4.59 x 10-48 / e-137910.6 /(8.31 x 150)

A = **5.1 s-1 (2 s.f.)**

***Sheet: Arrhenius equation Q6***

***Starter: 1.5 – Arrhenius and rate***

***Application: CGP68 PQ1-3***

***Fact recall: CGP68 Q1-4***

***Exam questions: Oxford p38-39 Q1-3***