1.9 Rate equations

Recap:

- Reacting molecules have to collide with enough energy to break the initial bonds, **the activation energy**.

Activation energy

Activation energy
The minimum amount of energy that particles require to react when they collide by the breaking of bonds

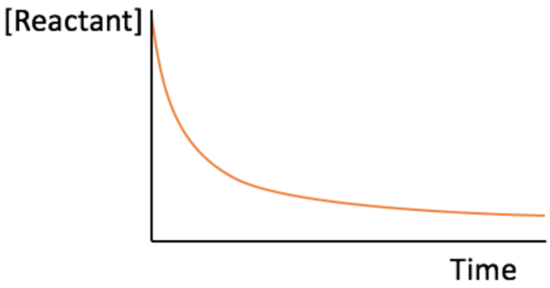
Rate of reaction

Rate
The rate of a reaction is the change in concentration of a reactant or product in a given time

Units of rate:

$$\textbf{Rate} = \frac{\textbf{Change in concentration}}{\textbf{Time}} \qquad \textbf{Units:}\ \frac{\textbf{mole dm}^{-3}}{\textbf{s}} = \textbf{mol dm}^{-3}\ \textbf{s}^{-1}$$

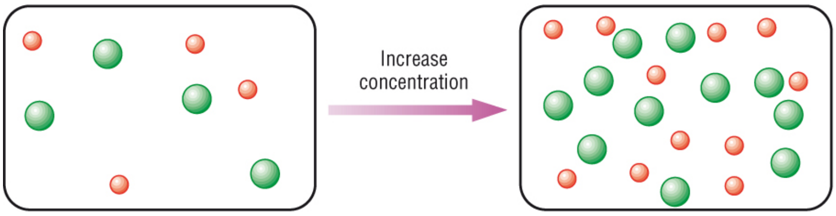
A reaction:



- As a reaction proceeds, the rate slows down.
- This is because the concentration of the reactants decreases.
- Gradient is a measure of rate:
  $\Delta y / \Delta x$ → change in concentration / time

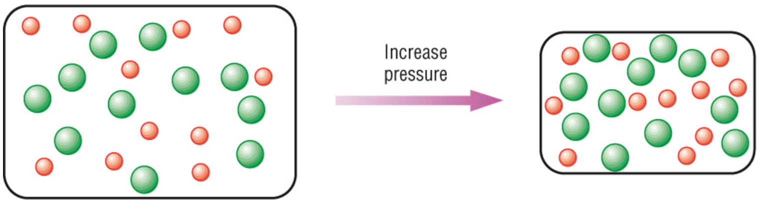
Factors affecting the rate of a chemical reaction:

1) **Increasing concentration increases reaction rate:**



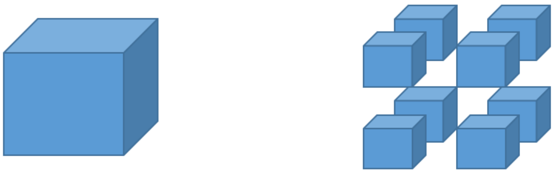
- Increasing concentration increases the **number of particles per unit volume.**
- This **increases the number of successful collisions per unit time.**
- **Increasing the rate** of reaction.

2) Increasing pressure increase reaction rate:



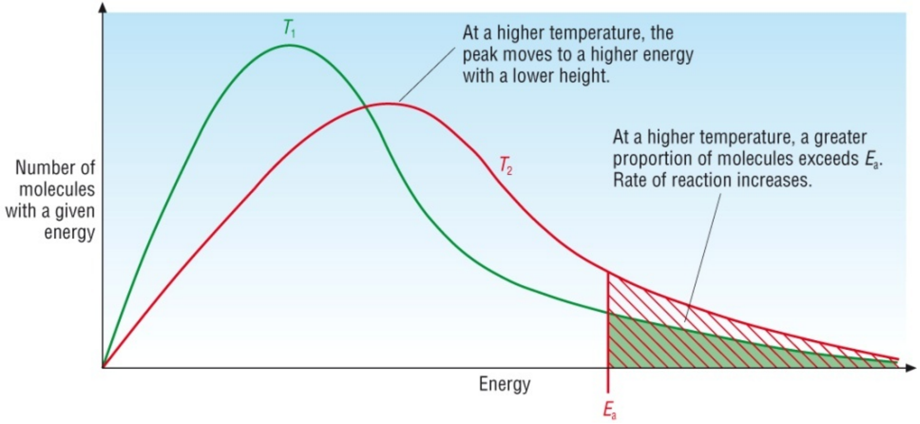
- Increasing the pressure decreases the volume.
- Increases the **number of particles per unit volume.** (same as concentration)
- This **increases the number of successful collisions per unit time.**
- **Increasing the rate** of reaction.

3) Increasing surface area increase reaction rate:



- Decreasing the particle size reveals more surface for the other reagent to react with.
- Increases the **number of successful collisions per unit time.**
- **Increasing the rate** of reaction

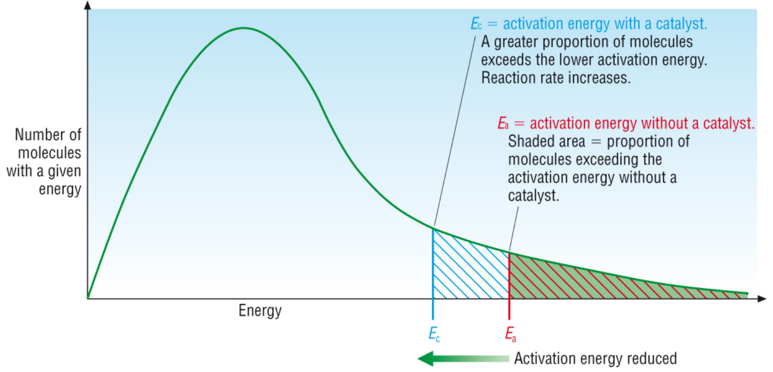
4) Increasing temperature increase reaction rate:



Explanation:

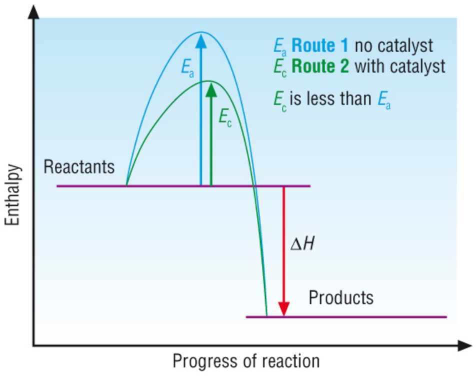
- Temperature $T_2 > T_1$
- Peak lowers and moves to the right
- Same area as same number of particles
- Increase in temperature increases the kinetic energy of the particles
- More particles have $E > E_a$ so more successful collisions per unit time
- There is also an increase in collision frequency as the particles are moving faster
- These 2 effects give a large increasing the rate of reaction

5) Catalyst increase reaction rate:



E_c = activation energy with a catalyst. A greater proportion of molecules exceeds the lower activation energy. Reaction rate increases.

E_a = activation energy without a catalyst. Shaded area = proportion of molecules exceeding the activation energy without a catalyst.



Explanation:

- Catalysts provide an alternative route with a lower activation energy
- More particles now have energy greater than the lowered catalytic activation energy
- Increases the number of successful collisions per unit time.
- Increasing the rate of reaction
- Catalysts come out unchanged

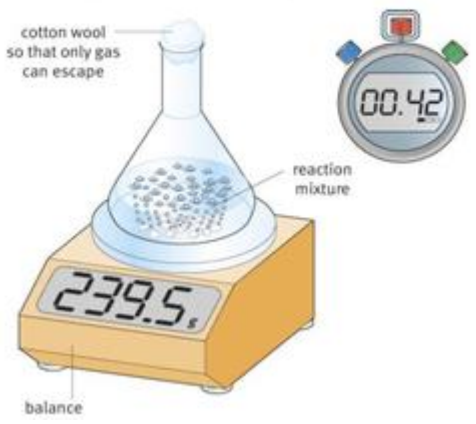
Measuring rates of reaction – continuous monitoring:

- In order to find the rate, you need to monitor the reaction all the way through.
- This is called **continuous monitoring:**

1) Change in mass

- Record the time as a reaction that loses mass proceeds:

$$Na_2CO_{3(aq)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$



Measuring the loss of mass as a gas forms

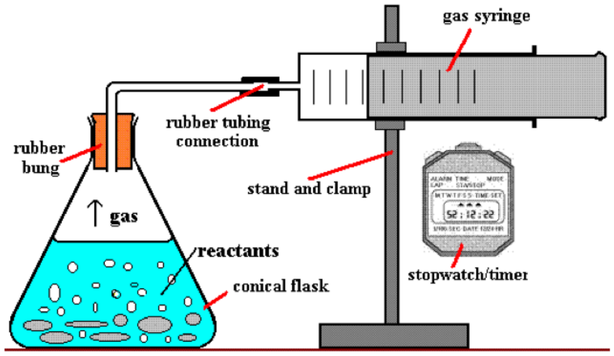
- Carbon dioxide is made which escapes the reaction mixture.
- This will change the mass on the balance.
- As the reaction proceeds, the concentration of the acid decreases.
- The rate at which the mass is lost will be proportional to the concentration of the acid.
- As the reaction proceeds, the rate therefore will slow down.

- This can be used to investigate the effect of temperature or concentration.

2) Gas volumes

- Record the time as a reaction that loses mass proceeds:

$$Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$$



- Carbon dioxide is made which escapes the reaction mixture.
- This can be collected in a gas syringe.
- As the reaction proceeds, the concentration of the acid decreases.
- The rate at which the gas is collected will be proportional to the concentration of the acid.
- As the reaction proceeds, the rate therefore will slow down.

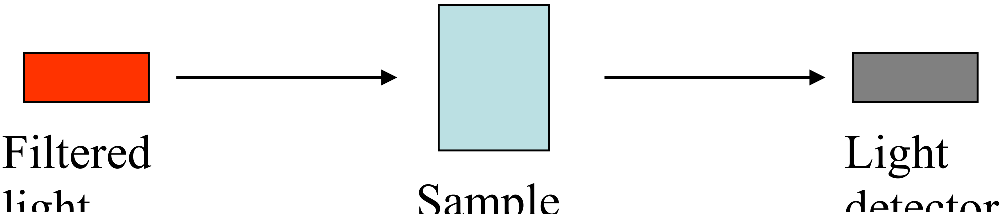
- This can be used to investigate the effect of temperature or concentration:

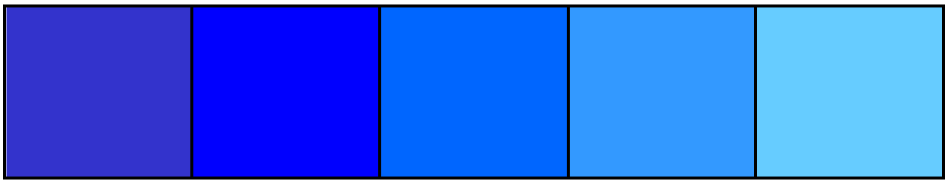
3) Colorimeter

- Adding iron fillings to a solution of copper sulphate makes iron sulphate and copper:

$$Fe_{(s)} + \underset{\textbf{Blue solution}}{CuSO_{4(aq)}} \rightarrow \underset{\textbf{Colourless solution}}{Fe_2SO_{4(aq)}} + Cu_{(s)}$$

- The solution gradually gets paler as the concentration of copper sulphate decreases and the concentration of iron sulphate increases.





Concentration of copper sulphate solution

1M	0.8M	0.6M	0.4M	0.2M

- A colorimeter will monitor the intensity of the colour which is proportional to the concentration of copper sulphate.
- This will produce a graph that we can use to measure the rate.

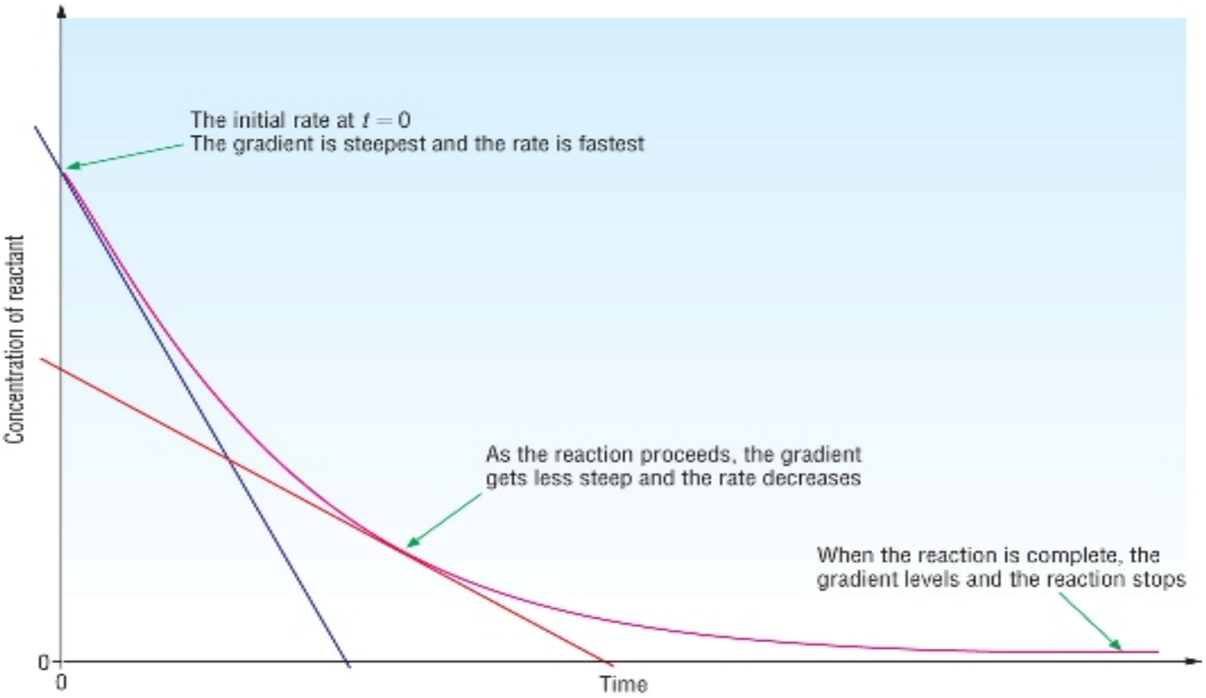
Other methods include:

Acid - Base reactions	Gas production	Visible changes
Titrations	Change in volume (gas collection)	Precipitation (colorimeter)
pH meter	Loss in mass	Colour changes (colorimeter)

- Basically we can use any method to follow a reaction that produces a measurable change.

Measuring the rate from a concentration - time graph

A) Measuring the decrease in concentration of a reactant:

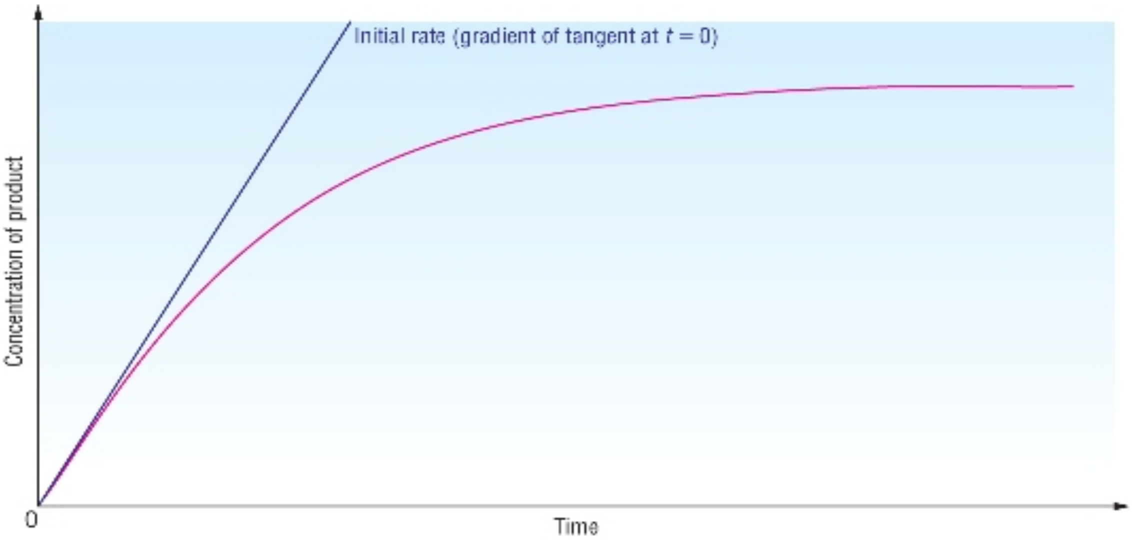


- The rate can be determined by measuring the concentration of a reactant or product at regular time intervals.
- The results can then be plotted giving a **concentration - time** graph.
- At any point, the rate is equal to the gradient of the curve
- The gradient of a curve is measured by drawing tangents:

$$\textbf{Gradient} = \frac{\Delta Y}{\Delta X} \qquad \textbf{Rate} = \frac{\textbf{Change in concentration}}{\textbf{Change in time}}$$

- The gradient at **t = 0** is at the start of the reaction. We call this the **initial rate**.

B) Measuring the increase in concentration of a product:



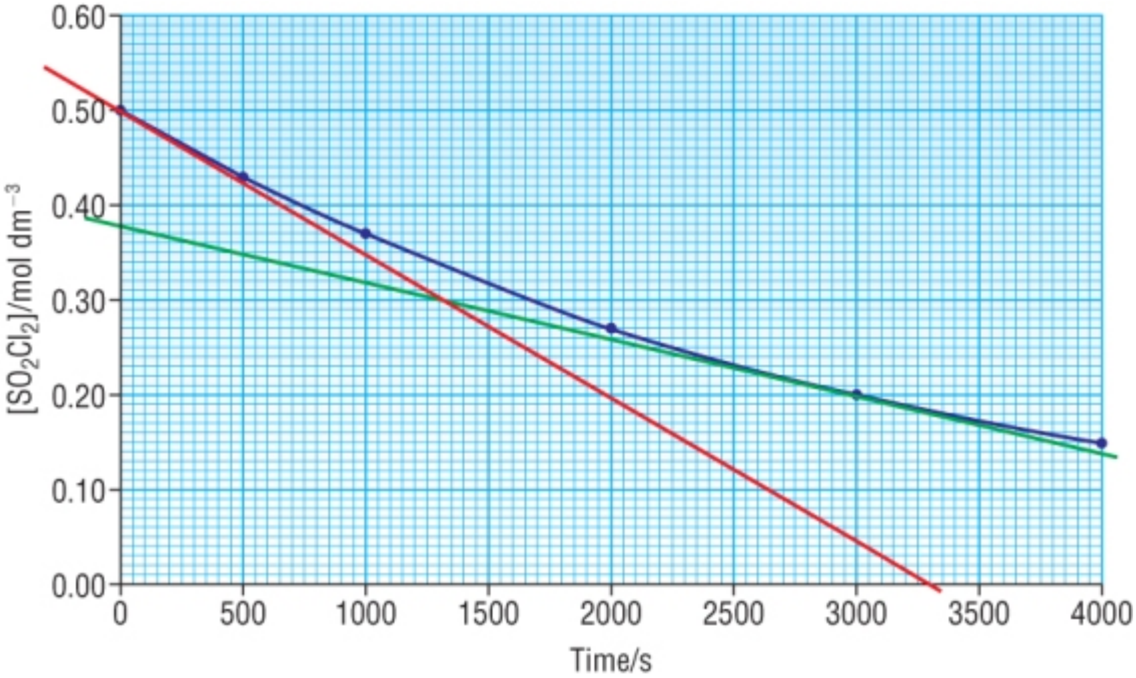
- As products are being produced, we measure the rate of increase in concentration.
- The gradient at **t = 0** is at the start of the reaction. We call this the **initial rate**.

Measuring reaction rates

- Sulphur dioxide decomposes producing sulphur dioxide and chlorine:

$SO_2Cl_{2(g)}$ → $SO_{2(g)}$ + $Cl_{2(g)}$

- The concentration of SO_2Cl_2 was measured and plotted



Red tangent is at t = 0 (initial rate):

rate = $\frac{0.50 - 0.00}{3300 - 0}$

rate = 1.5×10^{-4} mol dm^3 s^{-1}

Green tangent is at t = 3000:

rate = $\frac{0.38 - 0.14}{4000 – 0}$

rate = 6.0×10^{-5} mol dm^3 s^{-1}

Question:

The decomposition of hydrogen peroxide was monitored and the following data was collected:

H_2O_2 → H_2O + ½O_2

t (s)	0	1	3	5	10	20	40	100
[H_2O_2]	43	37	30	24.6	17.4	10.9	6.4	2.7

- Plot a graph of [H_2O_2] against time
- Determine the initial rate (at t=0)
- Determine the rate at 20s

Orders and the rate equation

Orders:

- A reaction occurs when reactants collide with energy greater than the activation energy.
- **Doubling the concentration** of a reactant can have one of 3 effects on the rate of a reaction:

  1) No effect
  2) Double the rate
  3) Quadruple the rate

- This means there is a mathematical relationship between concentration and the rate of a reaction
- The order determines the effect a change in concentration of a reactant will have on the rate:

Rate is proportional to the concentration

$$\text{Rate} \quad \alpha \quad [A]^{x}$$

x is the order

The rate equation and the rate constant:

- To remove the α we have to add a constant of proportionality.
- This is called the **rate constant**.
- The rate then is:

Rate is proportional to the concentration

$$\text{Rate} = k\ [A]^{x}$$

- To look at how the order effects the rate we'll keep the numbers simple.
- Let's make:

$k = 3$
$[A] = 1$ **Doubling the concentration of A from 1M to 2M**
$[A] = 2$

➢ **Zero order - where $x = 0$:**

$$\text{Rate} = k\ [A]^{x}$$

$$\text{Rate} = 3\ [1]^{0} \qquad \text{Rate} = 3$$

Now double the concentration of A

$$\text{Rate} = 3\ [2]^{0} \qquad \text{Rate} = 3$$

Doubling the concentration has no effect on the rate – proportional to $[\ ]^{0}$

- **First order - where x = 1:**

  Rate = k $[A]^x$
  Rate = 3 $[1]^1$ Rate = 3

  Now double the concentration of A

  Rate = 3 $[2]^1$ Rate = 6

  Doubling the concentration doubles the rate wrt [A] – proportional to $[\ ]^1$

- **Second order - where x = 2:**

  Rate = k $[A]^x$
  Rate = 3 $[1]^2$ Rate = 3

  Now double the concentration of A

  Rate = 3 $[2]^2$ Rate = 12

  Doubling the concentration quadruples the rate wrt [A] – proportional to $[\ ]^2$

The rate equation:

- Remember - a reaction usually has more than one reactant:

A + B + C → Products

- This means that the rate could depend on all 3 reactants:

Rate α $[A]^0$ Rate α $[B]^1$ Rate α $[C]^2$

- Combining these 3 give:

Rate α $[A]^0$ $[B]^1$ $[C]^2$

- The **rate constant, k** links the rate with the concentrations:

Rate = k $[A]^0$ $[B]^1$ $[C]^2$

- Remember anything to the power 0 is always equal to 1, the rate equation then is:

Rate = k $[B]^1$ $[C]^2$

Overall order:

- This is the sum of all the orders of all the reactants in the rate equation, for:

Rate = k $[B]^1$ $[C]^2$

- Overall order is **1 + 2 = 3**

Orders of reaction and the rate equation can only be determined experimentally.

Units of rate constants:

- The units for rate constants will vary as each reaction will have different numbers of reactants and orders.
- To work the units out rewrite the rate equation substituting the rate and concentrations with their corresponding units (just llike in K_c)
- Use algebra to cross cancel and obtain k on its own:

$$\text{Rate} = k\,[A]^{1}$$

$$k = \frac{\text{Rate}}{[A]^{1}}$$

$$k = \frac{\text{mol dm}^{-3}\ \text{s}^{-1}}{\text{mol dm}^{-3}}$$

$$k = \frac{\cancel{\text{mol dm}^{-3}}\ \text{s}^{-1}}{\cancel{\text{mol dm}^{-3}}}$$

$$k = \text{s}^{-1}$$

$$\text{Rate} = k\,[A]^{2}$$

$$k = \frac{\text{Rate}}{[A]^{2}}$$

$$k = \frac{\text{mol dm}^{-3}\ \text{s}^{-1}}{\text{mol dm}^{-3} \quad \text{mol dm}^{-3}}$$

$$k = \frac{\cancel{\text{mol dm}^{-3}}\ \text{s}^{-1}}{\cancel{\text{mol dm}^{-3}} \quad \text{mol dm}^{-3}}$$

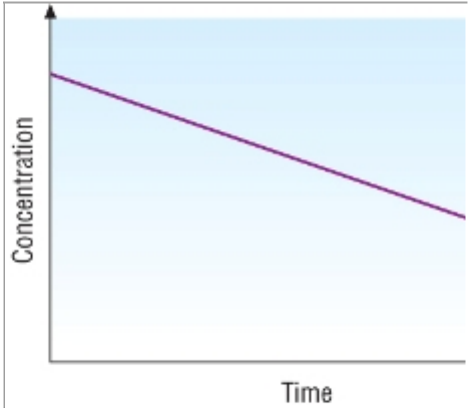
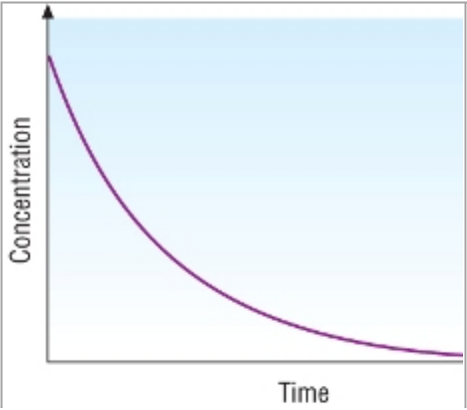
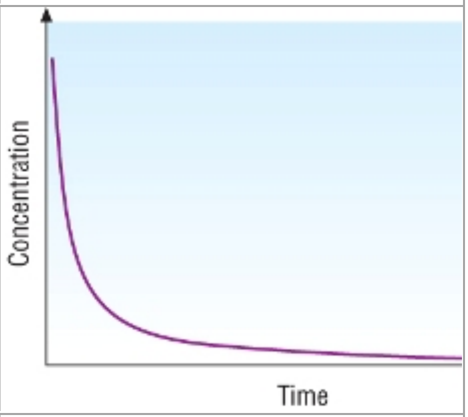
$$k = \frac{\text{s}^{-1}}{\text{mol dm}^{-3}}$$

$$k = \text{s}^{-1}\ \text{mol}^{-1}\ \text{dm}^{3}$$

Continuous monitoring of rates:

1) Concentration - time graphs:

- The **concentration** of a reaction is monitored then plotted against **time**.
- The order of the reaction wrt that reactant can be determined from the shape of the graph:

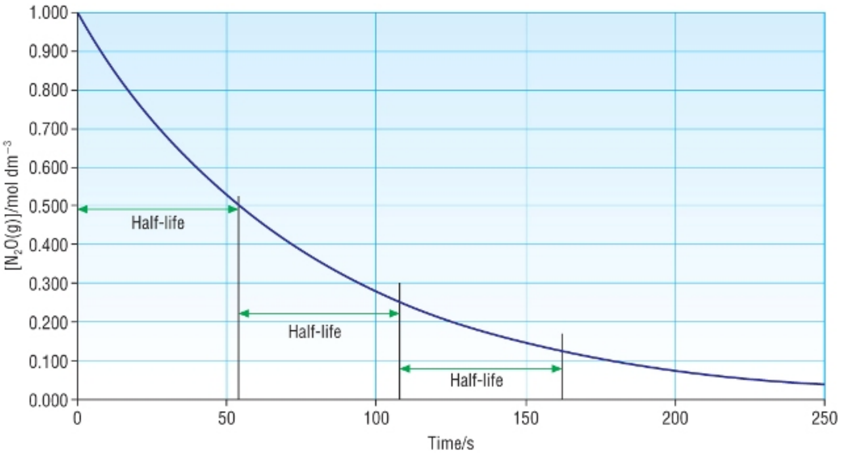
Zero order	First order	Second order
		
• Concentration decreases at a constant rate - **Straight line** • Remember, this reactant has no effect on the rate but will get used up in the reaction.	• Concentration halves at equal time intervals - **Constant half - lives**. • As the concentration halves the rate also halves.	• Concentration decreases rapidly - **Half life increases**. • As the concentration halves, the rate reduces by 1/4 so half lives increase.

Half - life:

- This is the time taken for the concentration of a reactant to half.
- It is an important feature of **concentration time** graphs:

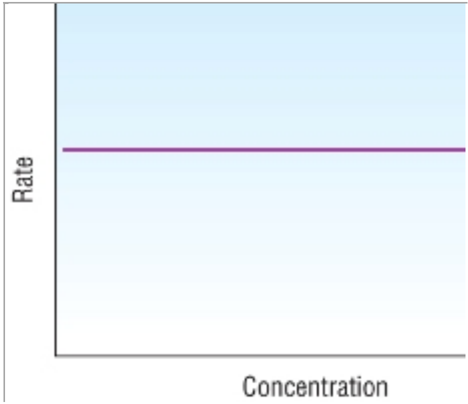
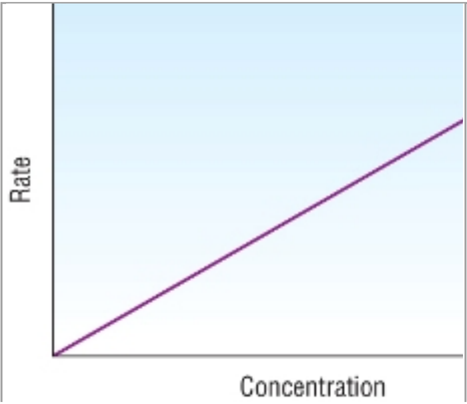
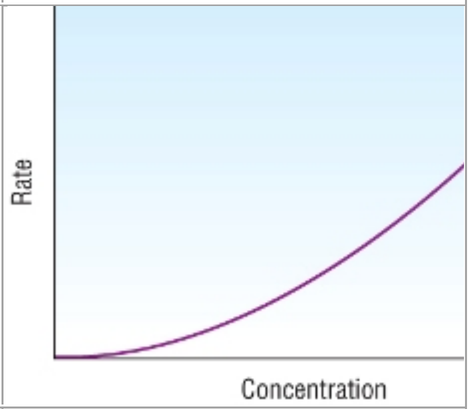
Concentration - time graph for a first order reaction:

- First order reactions half constant half lives.
- No matter what the initial concentration is, the time taken for the concentration to halve will be the same.



2) Rate - concentration graphs

- Orders can also be determined by plotting rate against concentration.
- Different orders give different shaped graphs:

Zero order	First order	Second order
		
• Remember, this reactant has no effect on the rate. • The rate continues at a steady pace. **Horizontal straight line**	• As the concentration doubles the rate also doubles, as the concentration triples, the rate triples. • The rate and concentration are in direct proportion to each other. **Proportional straight line**	• As the concentration doubles the rate also quadruples, as the concentration triples, the rate increases by 9. • The rate increases by the square of the concentration. • What if rate - concentration^2 was plotted? **Proportional curve**

Question:

1) The reaction between HCl of propene was monitored and the following data was collected:

$$HCl \quad + \quad CH_3CH{=}CH_2 \quad \rightarrow \quad CH_3CH_2CH_2Cl$$

t (s)	0	30	60	90	120	150	180	210	240
[HCl]	1.20	0.85	0.60	0.43	0.30	0.21	0.15	0.11	0.07

a) Plot a graph of [HCl] against time, t

b) Draw half lives on the graph. Determine the order of the reaction wrt HCl.
Explain your answer.

c) Determine the initial rate (t=0)

d) Determine the rate at 0.60 mol dm^{-3}

e) Determine the rate at 0.30 mol dm^{-3}

f) Determine the rate at 0.15 mol dm^{-3}

g) Put your results from (c) – (f) in the table below. Use 1/t as the rate:

[HCl] / mol dm^{-3}				
Rate (1/t) / s^{-1}				

h) Plot a graph of Rate against [HCl]. What does the shape of the graph tell you about the order?

i) Write the rate equation.

j) Determine the value and **units** of the rate constant.

The initial rates method – clock reactions:

- Initial rates can be determined in one of 2 ways:

A) From concentration - time graphs:

- Draw a tangent at t=0, the gradient of this tangent is the initial rate.

B) From clock reactions:

- Clock reactions are when after a certain time a sharp change is observed:

appearance of a precipitate
disappearance of a solid
a change in colour

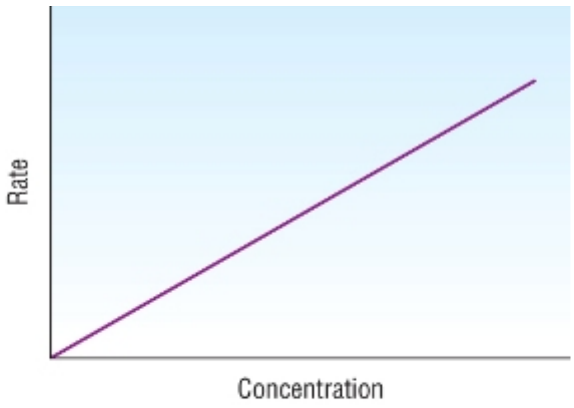
- During these types of reactions, you are measuring the rate for the initial period of the reaction – a specific amount of reactant lost or product made.
- Repeating each experiment with different concentrations for one reactant then again with another reactant.
- Plot graphs for each one a determine the order.

Example - Sodium thiosulphate and hydrochloric acid:

$$Na_2S_2O_{3(aq)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + S_{(s)} + SO_{2(aq)} + H_2O_{(l)}$$

- The experiment is repeated with different [HCl]
- And again with different [$Na_2S_2O_3$]
- Graphs are plotted for each:

$Na_2S_2O_3$

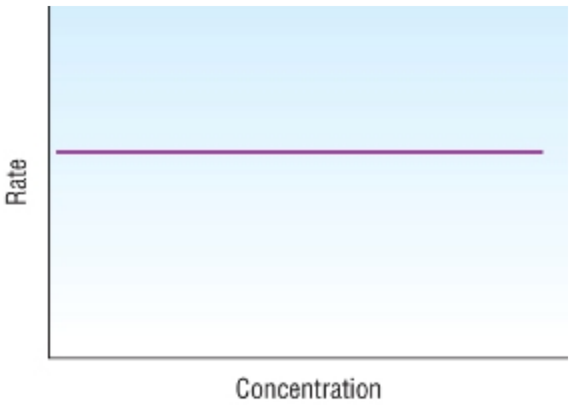


- As the concentration doubles the rate also doubles, as the concentration triples, the rate triples.
- The rate and concentration are in direct proportion to each other.

Proportional straight line

1st order wrt [$Na_2S_2O_3$]

HCl



- Remember, this reactant has no effect on the rate.
- The rate continues at a steady pace.

Horizontal straight line

zero order wrt [HCl]

$$\text{Rate} = k\,[Na_2S_2O_3]^{1}\,[HCl]^{0}$$
$$\text{Rate} = k\,[Na_2S_2O_3]$$

Initial rates and the rate constant

Determination of orders by inspection:

- Sometimes it is easier to look at the raw data for different initial concentrations of reactants.
- Comparing the rates and concentrations of the different reactants allows you to find the orders and therefore the rate equation:

Example:

- Consider the reaction:

$$2NO_{(g)} \quad + \quad O_{2(g)} \quad \rightarrow \quad 4NO_2$$

- Some results are:

Experiment	Initial concentration [NO] (mol dm^{-3})	Initial concentration [O_2] (mol dm^{-3})	Initial rate (mol dm^{-3} s^{-1})
1	0.00100	0.00100	1.82×10^{-6}
2	0.00100	0.00300	5.46×10^{-6}
3	0.00200	0.00100	7.28×10^{-6}

Order for NO:

- Experiments **1** and **3**: The concentration has **doubled** - The rate has **quadrupled**, $[NO]^2$
- The order wrt [NO] = **2**

Order for O_2:

- Experiments **1** and **2** The concentration has doubled - The rate has also doubled, $[O_2]^1$
- The order wrt [O_2] = **1**

Rate equation:

$$\text{Rate} = k\,[NO]^2\,[O_2]^1$$

$$\text{Rate} = k\,[NO]^2\,[O_2]^1$$

$$k = \frac{\text{Rate}}{[NO]^2\,[O_2]^1}$$

$$k = \frac{5.46 \times 10^{-6}}{(0.00100)^2 \times (0.00300)}$$

$$k = 1820$$

$$\text{Rate} = k\,[NO]^2\,[O_2]^1$$

$$k = \frac{\text{Rate}}{[NO]^2\,[O_2]^1}$$

$$k = \frac{\text{mol dm}^{-3}\ \text{s}^{-1}}{(\text{mol dm}^{-3})^2 \quad \text{mol dm}^{-3}}$$

$$k = \frac{\cancel{\text{mol dm}^{-3}}\ \text{s}^{-1}}{(\text{mol dm}^{-3})^2 \quad \cancel{\text{mol dm}^{-3}}}$$

$$k = \frac{\text{s}^{-1}}{(\text{mol dm}^{-3})^2}$$

$$k = \text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1}$$

Questions:

In each of the following questions, use the initial rate data to find:

- the order with respect to each reactant and the total order
- the rate equation
- the rate constant k (including its units) at the experiment's temperature

1) A reacts with B to form C. $A + B \rightarrow C$

Experiment	Initial [A] (mol dm^{-3})	Initial [B] (mol dm^{-3})	Initial rate (mol dm^{-3} s^{-1})
1	1	1	1
2	1	2	4
3	2	2	8

2) D reacts with E to form various products. $D + E \rightarrow$ products

Experiment	Initial [D] (mol dm^{-3})	Initial [E] (mol dm^{-3})	Initial rate (mol dm^{-3} s^{-1})
1	1	1	0.20
2	2	1	0.20
3	4	4	0.80

3) HI dissociates to form hydrogen and iodine: $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$

Experiment	1	2	3	4
Initial [HI] (mol dm^{-3})	1.64	3.28	4.92	6.56
Initial rate (mol dm^{-3} s^{-1})	0.41	1.64	3.69	6.56

Rate - determining step

- We have already seen in the organic chemistry that there is a series of steps to an overall reaction. This is called a mechanism.
- Each step could occur at different rates and it usually does so.
- The overall rate of a reaction can only occur as fast as its slowest step.
- This slowest step is called the **rate determining step**:

Analogy - Making ham sandwiches

Step 1	Step 2	Step 3
Get out 2 slices of bread	**Butter the bread add the ham between the slices and assemble the sandwich**	**Put the sandwich in a sandwich bag**

- **Step 2 is the slowest** step in this process so this would be the **rate determining step**.
- If I offered to help the students in step 1 or 3, the rate of sandwich making would not increase.
- If I offered to help the students in step 2, the rate of sandwich making would increase.
- This makes **step 2 the rate determining step**.

Predicting reaction mechanisms from rate equations:

$$\mathbf{NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}}$$

- The overall equation does not tell you anything about the rate equation or the mechanism.
- The rate equation can only be determined experimentally and this gives you clues to the mechanism (or at least the **RDS**).
- Experimental data tells us:

Second order wrt NO_2 **Zero order wrt CO**

Determining the rate equation from the mechanism:

- Consider the reaction:

$Cl^{\cdot} + O_3 \rightarrow ClO^{\cdot} + O_2$ Slow **RDS**

$ClO^{\cdot} + O_3 \rightarrow Cl^{\cdot} + 2O_2$ Fast

- The rate determining step is the first step.
- In the first step there is:
  - 1 $Cl^{\cdot}$ Therefore, the rate is first order wrt $Cl^{\cdot}$
  - 1 O_3 Therefore, the rate is first order wrt O_3
- The rate equation therefore is:

$$r = k\,[Cl^{\cdot}]^{1}\,[O_3]^{1}$$

Determining the mechanism from the rate equation and the overall equation:

The reasoning:

- Rate equation – Tells you what and how many in the RDS

Indicates what species
are present in the RDS

$$r = k\ [\overset{\downarrow}{NO_2}]^{2} \leftarrow$$

Indicates how many
present in the RDS

- Overall equation – Used as a tally to work out what and how many you have used / made.

$$NO_2 + CO \rightarrow NO + CO_2$$

1) The reactants in the RDS: From the rate equation

Indicates what species
are present in the RDS

$$r = k\ [\overset{\downarrow}{NO_2}]^{2} \leftarrow$$

Indicates how many
present in the RDS

- So 2 NO_2 molecules used in the RDS:

RDS: $2NO_2 \rightarrow$

- Tally these off on your overall equation:

$$\underset{||}{NO_2} + CO \rightarrow NO + CO_2$$

2) 1st product and intermediate in the RDS:

- Pick one of the products from the overall equation that you can make using the reactants in you RDS:
    - ➢ Product: Only **NO** can be made.

RDS: $2NO_2 \rightarrow NO$

- The remaining elements from the reactants in your RDS must form your intermediate
    - ➢ Intermediate: N_2O_3 can be made.

RDS: $2NO_2 \rightarrow NO + NO_3$

- Tally these off on your overall equation:

$$\begin{array}{ccccccc} NO_2 & + & CO & \rightarrow & NO & + & CO_2 \\ || & & & & | & & \end{array}$$

3) The second reaction – The reactants:

- As the intermediate does not feature in the overall equation it must be used up as a reactant in the second reaction:

RDS: $2NO_2 \rightarrow NO + NO_3$

$NO_3 \rightarrow$

- The remaining reactant in the overall equation must also be used:

RDS: $2NO_2 \rightarrow NO + NO_3$

$CO + NO_3 \rightarrow$

- Tally this off on your overall equation:

$$\begin{array}{ccccccc} NO_2 & + & CO & \rightarrow & NO & + & CO_2 \\ || & & | & & | & & \end{array}$$

4) The second reaction – adding the products:

- Any products not used so far must be added to the second reaction here:

RDS: $2NO_2 \rightarrow NO + NO_3$

$CO + NO_3 \rightarrow CO_2$

- Tally this off on your overall equation:

$$\begin{array}{ccccccc} NO_2 & + & CO & \rightarrow & NO & + & CO_2 \\ || & & | & & | & & | \end{array}$$

- Looking at the tally, you've used 1 extra NO_2 than you have in the overall equation.
- This can be removed by adding it as a product, it'll cancel out in the overall equation:

RDS: $2NO_2 \rightarrow NO + NO_3$

$CO + NO_3 \rightarrow CO_2 + NO_2$

- Adjust your tally on your overall equation:

$$\begin{array}{ccccccc} NO_2 & + & CO & \rightarrow & NO & + & CO_2 \\ | & & | & & | & & | \end{array}$$

5) Check the mechanism works:

- Add the two mechanism steps together to check it adds up to the overall equation:

$$2NO_2 \rightarrow NO + NO_3$$

$$CO + NO_3 \rightarrow CO_2 + NO_2$$

$$2NO_2 + CO + NO_3 \rightarrow CO_2 + NO_2 + NO + NO_3$$

$$\mathbf{NO_2 + CO \rightarrow CO_2 + NO}$$

Summary:

- Remember the rate equation cannot be determined from the stoichiometry of a reaction.
- A first order reaction with respect to 1 species suggests a unimolecular (1 of them) rate determining step.
- A second order reaction with respect to 1 species suggests a bimolecular (2 of them) rate determining step.
- If a reactant appears in the rate equation, then that reactant takes part in the slow step of the reaction (RDS).
- If it does not appear in the rate equation, then the reactant does not participate in the slow step (RDS).

Questions:

1) Hydrogen peroxide solution reacts with iodide ions in aqueous acid, iodine is liberated.

$$H_2O_2(aq) + 2\,H^+(aq) + 2\,I^-(aq) \rightarrow 2\,H_2O(l) + I_2(aq)$$

The following table gives some experimental results for the reaction.

Experiment	Initial concentration (mol dm^{-3}) $[H_2O_2]$	$[I^-]$	$[H^+]$	Initial reaction rate (mol dm^{-3} s^{-1})
1	0.010	0.010	0.10	1.75×10^{-6}
2	0.020	0.010	0.10	3.50×10^{-6}
3	0.030	0.010	0.10	5.25×10^{-6}
4	0.030	0.020	0.10	1.05×10^{-5}
5	0.030	0.020	0.20	1.05×10^{-5}

a) Find the order of the reaction with respect to the concentration of $H_2O_2(aq)$.

b) Find the order of the reaction with respect to the concentration of $I^-(aq)$.

c) Find the order of the reaction with respect to the concentration of $H^+(aq)$.

d) What is the overall order of the reaction?

e) Write the rate equation for the reaction.

f) Calculate the value of the rate constant for this reaction, including its units.

g) A proposed mechanism for this reaction is shown below. Is this mechanism consistent with the rate equation? Explain your reasoning.

$H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slow)

\`$H^+ + IO^- \rightarrow HIO$ (fast)

$HIO + H^+ + I^- \rightarrow I_2 + H_2O$ (fast)

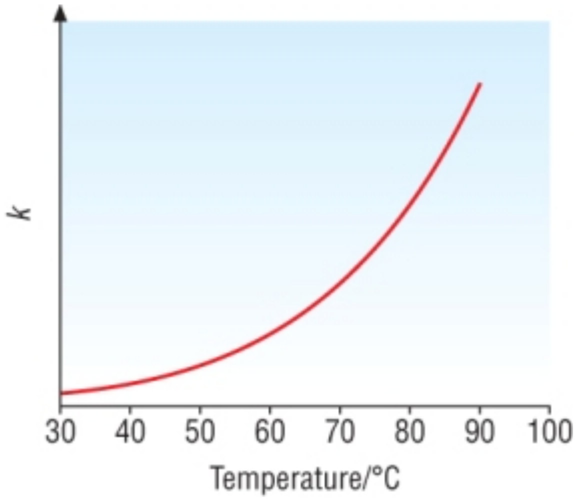
The rate constant, k:

- The rate depends on 2 things:
    - **Concentrations, [ ]**
    - **Rate constant, k**
- A fast reaction must therefore have a large rate constant.

The effect of temperature on the rate constant

- We know that if we increase the temperature, the rate also increases.
- If the concentrations don't change, something else must – **Rate constant, k** must increase

$$\mathbf{r = k\,[A]^x\,[B]^y}$$



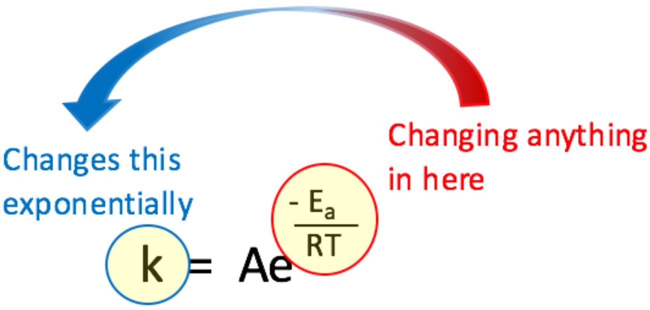
- You can see that as T increases, k increases exponentially

The Arrhenius equation:

- This equation shows the relationship between temperature, T and the rate constant, k

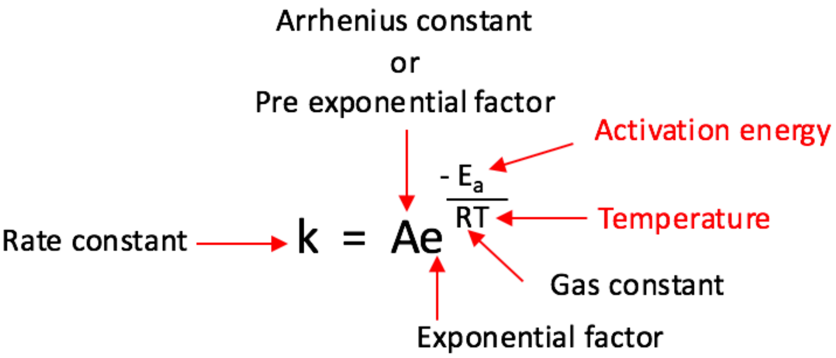
$$k = Ae^{\frac{-E_a}{RT}}$$

k	Rate constant
E_a	Activation energy (j mol^{-1})
T	Temperature (K)
R	Gas constant (8.31 j K^{-1} mol^{-1})
A	Arrhenius constant
e	Euler's number (2.72) – a function for exponential growth (or decay)



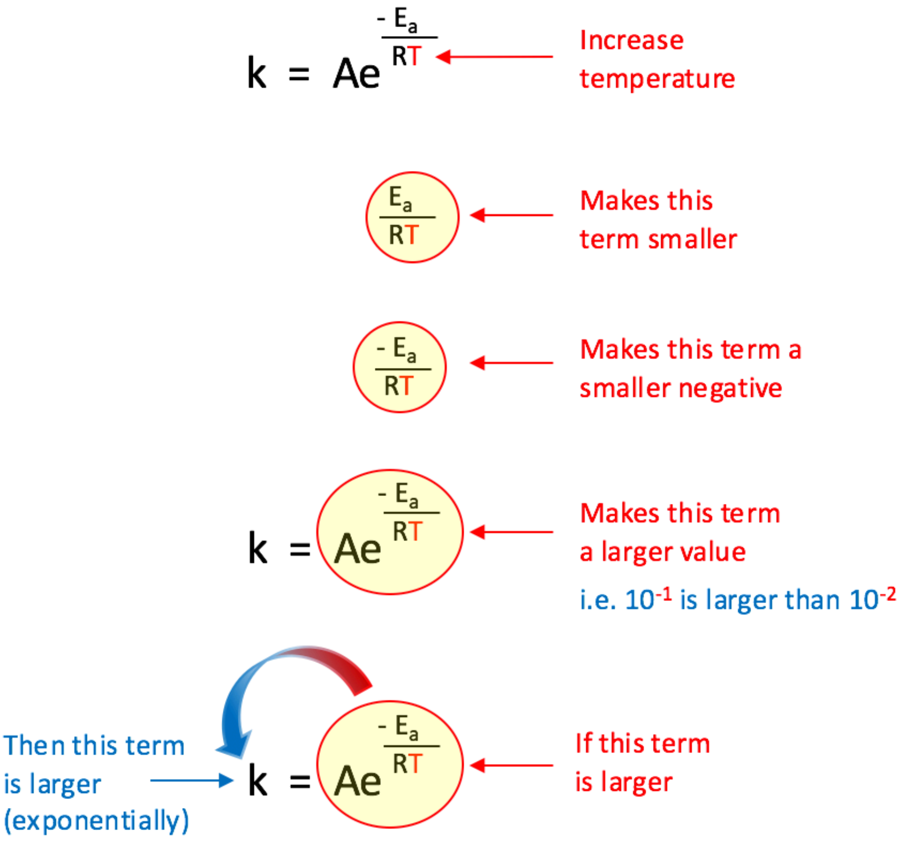
Using the Arrhenius equation to explain changes in:

- This equation shows the relationship between temperature, T or the activation energy, E_a and the rate constant, k

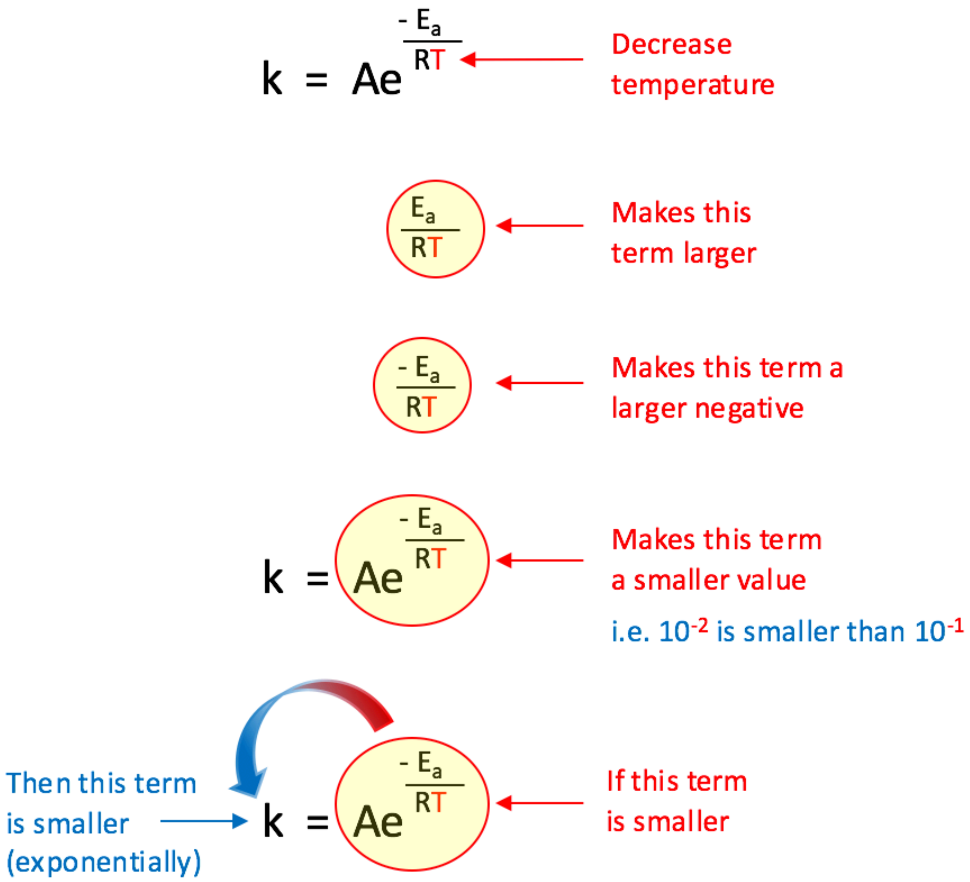


- They are all constants except for temperature, T and Activation energy, E_a
- You need to be able to follow through the effect on the rate constant, k with changes is either of these:

1) **Temperature:**
    a. Increase temperature:



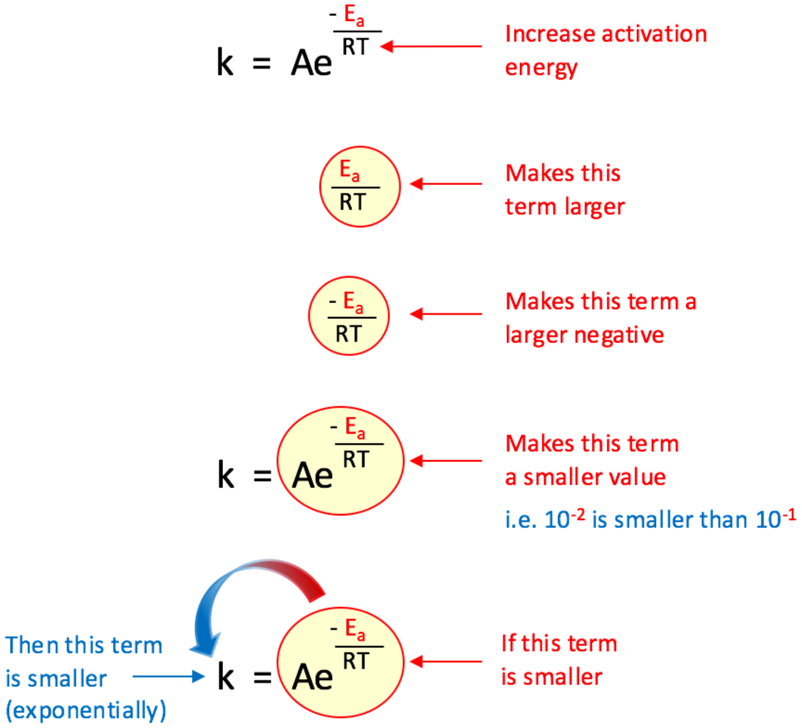
b. Decrease temperature:



- If you think about it, this makes sense, an increase in temperature will increase the energy the particles have.
- This means more particles will have equal or greater than the activation energy.
- They will also collide more frequently.
- This increase the rate.

2) Activation energy:

a. Increase activation energy:



$$k = Ae^{\frac{-E_a}{RT}}$$

Increase activation energy

$$\frac{E_a}{RT}$$

Makes this term larger

$$\frac{-E_a}{RT}$$

Makes this term a larger negative

$$k = Ae^{\frac{-E_a}{RT}}$$

Makes this term a smaller value

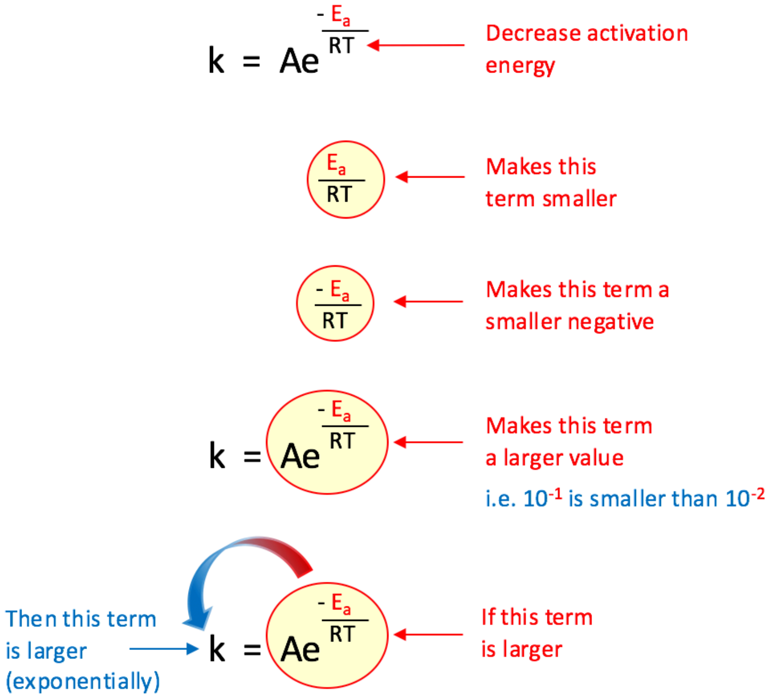
i.e. 10^{-2} is smaller than 10^{-1}

$$k = Ae^{\frac{-E_a}{RT}}$$

If this term is smaller

Then this term is smaller (exponentially)

b. Decrease activation energy:



$$k = Ae^{\frac{-E_a}{RT}}$$

Decrease activation energy

$$\frac{E_a}{RT}$$

Makes this term smaller

$$\frac{-E_a}{RT}$$

Makes this term a smaller negative

$$k = Ae^{\frac{-E_a}{RT}}$$

Makes this term a larger value

i.e. 10^{-1} is smaller than 10^{-2}

$$k = Ae^{\frac{-E_a}{RT}}$$

If this term is larger

Then this term is larger (exponentially)

Summary:

- Using a common sense approach:

- Increasing temperature increases k, which increases the rate
- Adding a catalyst decreases the activation energy, increases k, which increases the rate

Using the Arrhenius equation to calculate rate constant, k:

Calculate the rate constant for the reaction occurs if:

- The Arrhenius constant, A is 9×10^{10} $s^{-1,}$
- Temperature is 350 K
- Activation energy is 120 kJ mol^{-1} * This must be converted to Joules as R is in Joules

$$\boxed{k = Ae^{\frac{-E_a}{RT}}}$$

$$k = 9 \times 10^{10} \times e^{\frac{-120000}{(8.31 \times 350)}}$$

$$k = 9 \times 10^{10} \times e^{-41.26}$$

$$k = 9 \times 10^{10} \times 1.2 \times 10^{-18}$$

$$k = 1.08 \times 10^{-7}$$

Using the Arrhenius equation to calculate temperature or activation energy:

More maths:

- To calculate T or E_a the equation needs rearranging to get T or E_a on its own.
- This isn't easy maths as both T and E_a are in the power.
- If you take natural logs, ln of this equation, it removes the exponential factor, e (as ln is to the base e) and brings the power to format that can easily be re arranged.
- You don't need to know the maths for this, just learn the equation:

$$k = Ae^{\frac{-E_a}{RT}}$$

$$\ln k = \ln(A \times e^{\frac{-E_a}{RT}})$$

$$\ln k = \ln(A) + \ln(e^{\frac{-E_a}{RT}})$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\boxed{\ln k = \ln A - \frac{E_a}{RT}}$$

1) **To calculate E_a:**

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln k - \ln k = \ln A - \frac{E_a}{RT} - \ln k$$

$$0 = \ln A - \frac{E_a}{RT} - \ln k$$

$$\frac{E_a}{RT} = \ln A - \ln k$$

$$\boxed{E_a = (\ln A - \ln k) \times RT}$$

2) To calculate T:

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln k - \ln k = \ln A - \frac{E_a}{RT} - \ln k$$

$$0 = \ln A - \frac{E_a}{RT} - \ln k$$

$$\frac{E_a}{RT} = \ln A - \ln k$$

$$\frac{RT}{E_a} = \frac{1}{\ln A - \ln k}$$

$$RT = \frac{E_a}{\ln A - \ln k}$$

$$\boxed{T = \frac{E_a}{(\ln A - \ln k) \times R}}$$

Summary:

$$\boxed{k = Ae^{\frac{-E_a}{RT}}}$$

$$\boxed{\ln k = \ln A - \frac{E_a}{RT}}$$

$$\boxed{E_a = (\ln A - \ln k) \times RT}$$

$$\boxed{T = \frac{E_a}{(\ln A - \ln k) \times R}}$$

Example calculations:

1) **Calculating E_a**

Calculate the activation energy if:

- The Arrhenius constant, A is 15 x 10^{10} $s^{-1,}$
- Rate constant is 12 x 10-6 s^{-1}
- Carried out at 298K

$$\boxed{E_a = (\ln A - \ln k) \times RT}$$

$$E_a = \{\ln(15 \times 10^{10}) - \ln(12 \times 10^{-6})\} \times 8.31 \times 298$$

$$E_a = \{25.73 - -11.33\} \times 2476.38$$

$$E_a = 37.06 \times 2476.38$$

$$E_a = 91774.64 \text{ J mol}^{-1}$$

$$E_a = 91.77 \text{ kJ mol}^{-1}$$

2) **Calculating T**

Calculate the temperature at which the reaction occurs if:

- The Arrhenius constant, A is 13 x 10^{9} $s^{-1,}$
- Rate constant is 11 x 10^{-7} s^{-1}
- Activation energy is 82 kJ mol^{-1} * This must be converted to Joules as R is in Joules

$$\boxed{T = \frac{E_a}{(\ln A - \ln k) \times R}}$$

$$T = \frac{82000}{\{\ln(13 \times 10^{9}) - \ln(11 \times 10^{-7})\} \times 8.31}$$

$$T = \frac{82000}{\{23.29 - -13.72\} \times 8.31}$$

$$T = \frac{82000}{37.01 \times 8.31}$$

$$T = \frac{82000}{307.55}$$

$$T = 266.6 \text{ K}$$

Questions:

1) Calculate the rate constant given the following data:

- Arrhenius constant = 2.3×10^{9} s^{-1}
- Activation energy = 121 kJ mol^{-1}
- Temperature = 298 K

Ans = 1.38×10^{-12}

2) Calculate the rate constant given the following data:

- Arrhenius constant = 3.2×10^{22} s^{-1}
- Activation energy = 315 kJ mol^{-1}
- Temperature = 150 °C

Ans = 3.86×10^{-17}

3) Calculate the activation energy given the following data:

- Arrhenius constant = 2.3×10^{9} s^{-1}
- Rate constant = 1×10^{-10} s^{-1}
- Temperature = 298 K

Ans = 11.0×10^{4} J

4) Calculate the activation energy given the following data:

- Arrhenius constant = 2.3×10^{21} s^{-1}
- Rate constant = 2.2×10^{-20} s^{-1}
- Temperature = 150 °C

Ans = 332×10^{3} J

5) Calculate the temperature given the following data:

- Arrhenius constant = $1.9 \times 10^{21}\ s^{-1}$
- Rate constant = $2.6 \times 10^{-20}\ s^{-1}$
- Activation energy = 120 kJ mol^{-1}

Ans = 153.5 K

6) Calculate the temperature given the following data:

- Arrhenius constant = $1.3 \times 10^{19}\ s^{-1}$
- Rate constant = $1.7 \times 10^{-18}\ s^{-1}$
- Activation energy = 230 kJ mol^{-1}

Ans = 325.9 K

The Arrhenius plot:

- The logarithmic format of the Arrhenius equation when plotted gives a straight line.
- This means we can use the ‘equation of a straight line:

$$\boxed{\ln k = \ln A - \frac{E_a}{RT}}$$

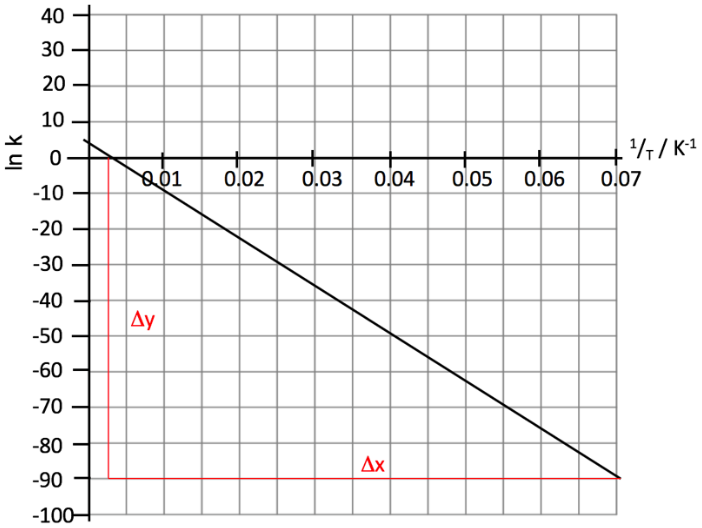
$$\ln k = \frac{-E_a}{RT} + \ln A$$

$$\ln k = \left\{\frac{-E_a}{R} \times \frac{1}{T}\right\} + \ln A$$

$$y = m \times x + c$$

$$\boxed{\begin{matrix}\ln k\\ \\ y\end{matrix}} \begin{matrix}=\\ \\ =\end{matrix} \left\{\boxed{\begin{matrix}\frac{-E_a}{R}\\ \\ m\end{matrix}} \begin{matrix}\times\\ \\ \times\end{matrix} \boxed{\begin{matrix}\frac{1}{T}\\ \\ x\end{matrix}}\right\} \begin{matrix}+\\ \\ +\end{matrix} \boxed{\begin{matrix}\ln A\\ \\ c\end{matrix}}$$

Example:



y axis: $y = \ln k$

Gradient: $m = -E_a / R$

x axis: $x = 1/T$

Intercept: $c = \ln A$

Intercept: $c = \ln A = 5$ Kj mol^{-1}

Gradient: $m = -E_a / R = \frac{\Delta Y}{\Delta x}$

$$-E_a / R = \frac{(-90.0 - 0.0)}{(0.070 - 0.0025)}$$

$$-E_a / R = \frac{-90}{0.0675}$$

$$-E_a / R = -1333.3$$

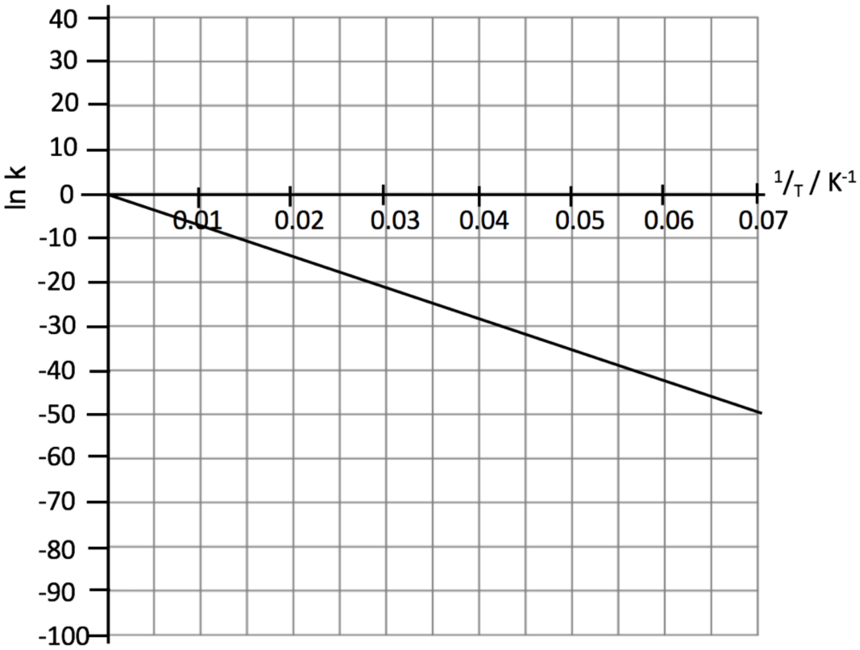
$$E_a = 1333.3 \times 8.31$$

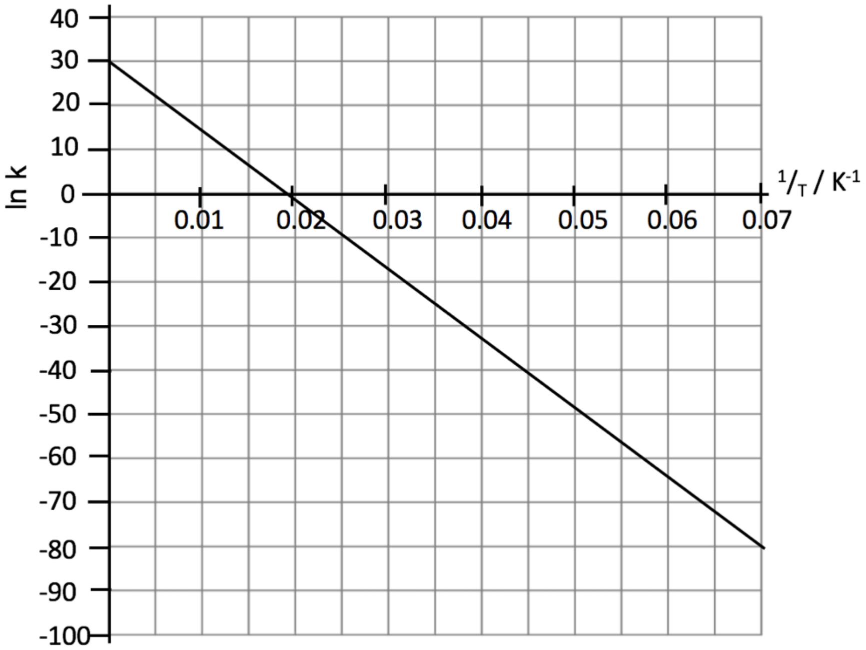
$$E_a = 11080 \text{ J mol}^{-1}$$

$$E_a = 11.08 \text{ kJ mol}^{-1}$$

Questions:

Calculate the Arrhenius constant and the Activation energy from the following plots:





Problems determining orders using the continuous method:

Hydrogen peroxide solution reacts with iodide ions in aqueous acid, iodine is liberated.

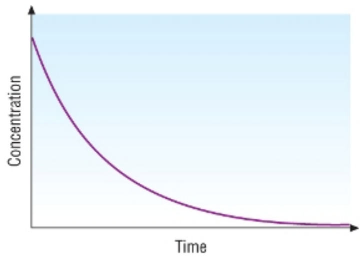
$$A \quad + \quad B \quad \rightarrow \quad \text{Products}$$

The orders for the reaction:

- 1st order with respect to A
- 1st order with respect to B

The rate equation:

$$r = k[A]^1[B]^1$$



- As both are 1st order, they both affect the rate as each of them get used up and each of their concentration decreases

- This means that the rate (gradient) changes as the A is used up.
- The rate (gradient) also changes as the B is used up ***at the same time***.

Problem 1: They are both are affecting the rate at the same time meaning it is impossible to determine the order with respect to one of them!

- The concentration of one reagent must be kept constant in order to determine the effect on the rate due to a change in concentration of the other reagent eg:

  - The concentration of the [B] must be kept constant if you want to see the effect on the rate due to a change in concentration of the [A]

  - The concentration of the [A] must be kept constant if you want to see the effect on the rate due to a change in concentration of the [B]

Solution 1: This is done by making one of the reagents concentration an excess, using numbers to get the idea:

	A	+	B	→	Products
Nº at the start:	10		1000		
Nº at half:	5		995		
% change:	50		1		

- You can see that the [A] has halved
- The [B] has hardly changed
- Any effect therefore must be down to the [A]
- Effectively the rate equation has become:

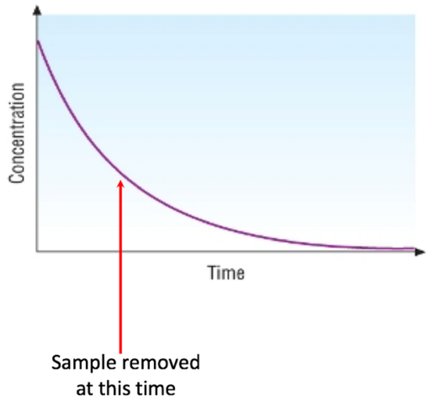
$$r = k[A]^1$$

As [B] has no effect (minimal) on rate.

Summary:

- To keep a reagent's concentration constant during a reaction you need to:
- Have it in a large excess – 1 mark.
- So that any change in its concentration is minimal – 1 mark.

Problem 2: When monitoring the rate of a continuous reaction you have to remove samples to perform chemical tests to determine its concentration at that time:



- By the time, you have carried out the test and determined its concentration, the reaction has probably continued for a further 5 minutes!

Solution 2: **‘**Quench’ the reaction:

- This can be done by rapidly cooling the removed sample or by diluting it.
- This almost completely stops the reaction allowing a more accurate determination of the concentration at the time the sample was removed.