

# KINETICS – Rates of reaction

## Introduction

In kinetic studies the rate of chemical reactions is investigated. Some of the factors which can affect the rate of a reaction are:

- The surface area of the reactants
- The concentration of the reactants
- The temperature at which the reaction is carried out
- The presence of a catalyst
- Light is important for photochemical reactions

## Experimental Methods for Following Reactions

The rate of a reaction can be determined by following some aspect of the materials which changes as the reaction proceeds. When the effect of concentration on the rate of reaction is being investigated, it is important to keep other factors, such as the temperature, constant during the process.

## Mass changes

Mass changes that take place during a reaction can be followed by placing the reaction vessel on a balance and reading the mass at specific intervals

## Volume changes

When a gas is given off in a reaction, that reaction can be followed by measuring the volume of gas collected at various times. To do this a reaction flask could be connected to a gas syringe.

## Pressure changes

One useful way of following the reactions of gases if a pressure change takes place is to connect the reaction flask to a pressure meter and measuring the pressure at given intervals.

## Titration

This could be used for following the reactions of an acid or alkali. It can also be used for following reactions involving iodine (using sodium thiosulphate). Pipette samples of the reaction mixture would be removed from the reaction vessel, placed in a flask and the reaction quenched. It can then be titrated to find the concentration of the reaction mixture at a particular time.

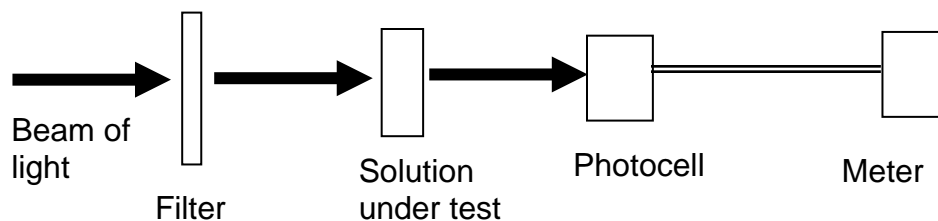
Polarimetry (suitable for reactions involving optically active substances)

Measuring conductivity (suitable for reactions producing or consuming ions)

## Colorimetric measurement

If a reactant or product is coloured the reaction can be followed by using a colorimeter. This measures changes in colour intensity.

A narrow beam of light is passed through the solution being investigated.



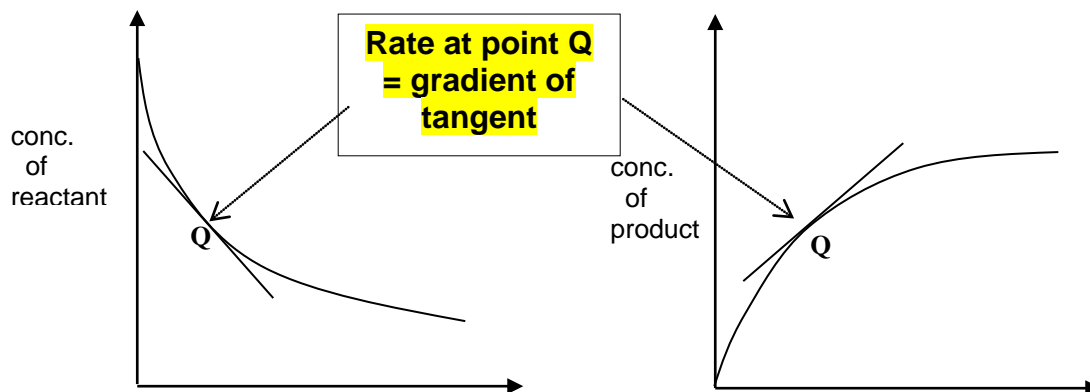
The filter allows an appropriate colour of light to be selected. The start and finish solutions might be tried with different filters to see which give the largest change in reading.

The meter is usually calibrated to measure the amount of light absorbed by the solution.

## Finding rate

The **rate** of a chemical reaction is measured by how rapidly the **concentration** of a substance is changing. The substance may be a reactant or a product, and the sign shows whether the substance is disappearing or being formed.

The rate is the instantaneous rate of fall in concentration of a reactant, or the instantaneous rate of increase in concentration of a product.



## Concentration and Rate

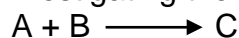
It might be thought that the rate of reaction is always directly proportional to the concentration of the reactants, but this is not the case. It is only the substances that are present in the slowest step (the rate determining step) of a reaction that actually affect the rate of the reaction.

To provide information about how the rate depends upon the concentration of reactants or catalysts the rate equation is used.

## The Rate Equation

The extent to which concentration determines the rate of a reaction is expressed as the rate equation. These values have to be determined by experiment; they cannot be deduced from a chemical equation (as equilibrium equations are).

Suppose that we were investigating the reaction;



then we would carry out experiments to see the effect of changing concentration of A and B.

Suppose we obtain the following results for A.

Concentration of A /mol dm <sup>-3</sup>	Initial rate /mol dm <sup>-3</sup> s <sup>-1</sup>
0.1	0.01
0.2	0.02
0.3	0.03
0.4	0.04

So we can write; Rate  $\propto$  [A] The rate is said to be first order with respect to A.

If we found the following results for B.

Concentration of B /mol dm <sup>-3</sup>	Initial rate /mol dm <sup>-3</sup> s <sup>-1</sup>
0.1	0.01
0.2	0.04
0.3	0.09
0.4	0.16

Rate  $\propto$  [B]<sup>2</sup> The rate is said to be second order with respect to B

These values can be expressed in the same equation;

$$\text{Rate} \propto [A][B]^2 \quad \text{or} \quad \text{Rate} = k[A][B]^2$$

This is called the **rate equation**

Here **k** is called the **rate constant** for the reaction. It is constant for all concentrations of A, and B, provided that the temperature and any other conditions not specified do not change. The rate constant and order of reaction are experimentally determined.

The power to which the concentration is raised is known as the **order of reaction**.

The general form of the rate equation is written:

$$\text{Rate} = k [A]^n [B]^m.$$

The value n + m is the overall order of the reaction.

### Units of rate and k.

Rate is measured in concentration/time: usually  $\text{mol dm}^{-3} \text{s}^{-1}$ .

Units of  $k$  depend on the order of reaction:

- For a **zero** order reaction, rate =  $k$ ; so  $k$  also has units of  $\text{mol dm}^{-3} \text{s}^{-1}$ .
- For a **first** order reaction, rate =  $k[\text{concentration}]$ , so  $k$  has units of  $\text{s}^{-1}$ .
- For a second order reaction, rate =  $k[\text{concentration}]^2$ ,  
so  $k$  has units of  $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ .

Although the preferred unit of time is the second, if data is provided in minutes or hours it may be best to keep to the unit specified.

### Finding order of reaction from initial rates.

You need to know three methods of measuring orders;

1. the initial rate method
2. use of rate–concentration graphs
3. the use of concentration-time graphs plus half-life.

The **initial rate** is the rate at the start of an experiment, when the concentrations are easy to measure since they have not had time to change. It is often not easy to *measure* the initial rate, but if it is known, the order of reaction is fairly easy to find. If possible, try to compare experiments in which only one concentration changes.

Then, for example:

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

- If concentration of A doubles but rate does not change,  $m = 0$  (zero order).
- If concentration of A doubles and rate doubles,  $m = 1$  (first order).
- If concentration of A doubles and rate quadruples,  $m = 2$  (second order).  
*[If conc. is  $\times 1.5$ , for 1<sup>st</sup> order rate will be  $\times 1.5$ ; for 2<sup>nd</sup> order  $\times 1.5^2$  i.e.  $\times 2.25$ ]*

If the information is presented as a number of moles, or a volume of solution, make sure that you first divide by the total volume to obtain concentrations (or at least check that the total volume is the same in all experiments).

Here is an example, which has been chosen to illustrate the use of units and the calculation of the rate constant:

The table shows the results of three experiments to establish the orders of reaction with respect to components A and B. Find these orders, and calculate the rate constant for the reaction. Concentrations are all  $1.0 \text{ mol dm}^{-3}$ .

Experiment	Volume of A/cm <sup>3</sup>	Volume of B/ cm <sup>3</sup>	Volume of water/ cm <sup>3</sup>	Rate/10 <sup>-5</sup> mol dm <sup>-3</sup> s <sup>-1</sup>
P	100	200	700	2.2
Q	200	200	600	4.4
R	300	400	300	26.6

The water is added to make up the volume to a suitable total, in this case  $1000 \text{ cm}^3$  in each case.

Calculation: assume **rate = k [A]<sup>m</sup>[B]<sup>n</sup>**

- Comparing P and Q: concentration of A doubles, and rate also doubles. Therefore reaction is **first order** in A (**m = 1**).

Note that we cannot find a direct comparison in which only B changes. We must allow for the effect of changing A first.

- Comparing P and R: concentration of A increases by a factor of three, so this alone would change the rate to  $3 \times 2.2 = 6.6$ . *In addition* the concentration of B doubles, and rate goes up by a further factor of 4 (i.e. from 6.6 to 26.6). Therefore, reaction is **second order in B**, (since rate  $\propto [B]^2$ ).

To find the rate constant we can substitute in the rate expression for any of the experiments.

Note the heading for Rate in the table: all the figures have been divided by  $10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ , so the rate for P is  $2.2 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ :

$$\text{rate} = k [\text{A}]^m [\text{B}]^n = k [\text{A}][\text{B}]^2$$

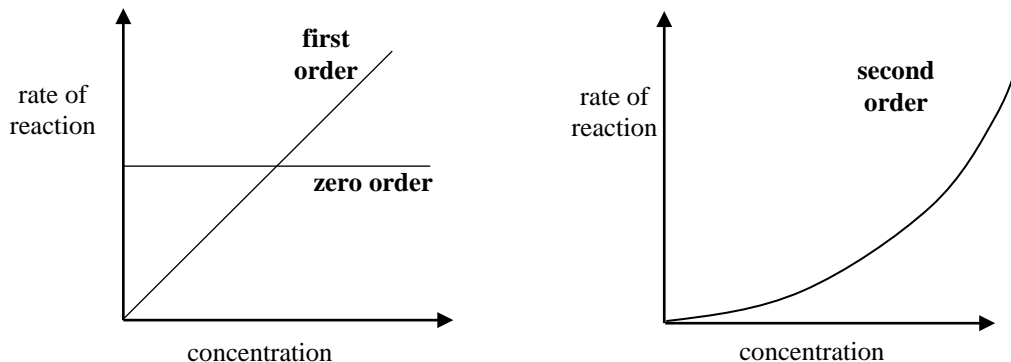
$$\text{Expt. P: } 2.2 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1} = k \left[100 \times \frac{1.0}{1000}\right] \times \left[200 \times \frac{1.0}{1000}\right]^2 \text{ mol}^3 \text{ dm}^{-9}$$

$$k = \frac{2.2 \times 10^{-5}}{0.1 \times 0.04} = 5.5 \times 10^{-3} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

### Rate-Concentration graphs:

If the rate can be measured at different concentrations (e.g. by the initial rate method), a zero order reaction will show no change (horizontal line), while a first order reaction will increase linearly.

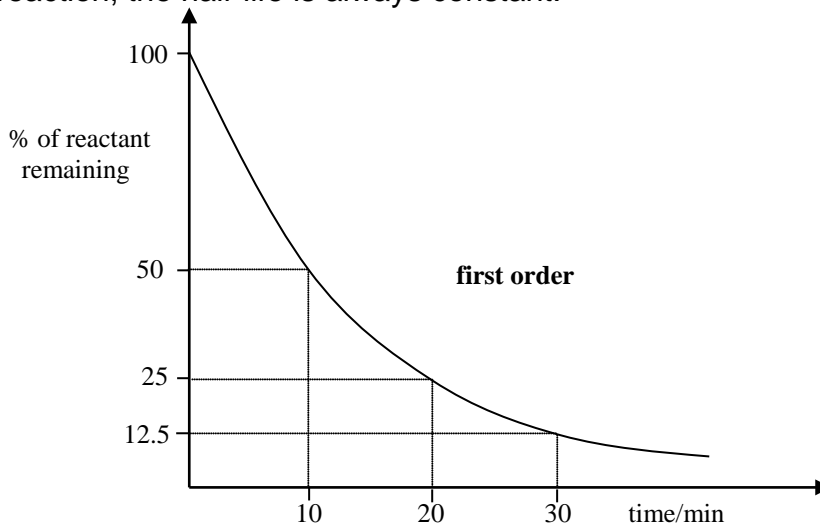
For a second order reaction,  $\text{rate} \propto [\text{conc}]^2$ , so a graph of rate against  $[\text{conc}]^2$  would be a straight line.



### Concentration–time graphs and half life.

The **half life** of a reactant which is not in excess is the time taken for its concentration to decrease to half its initial value.

For a **first order** reaction, the half-life is always constant:



Here it takes 10 min for the *% of reactant remaining* to fall from 100 to 50, and another 10 min to fall from 50 to 25 (or from 82 to 41, etc).

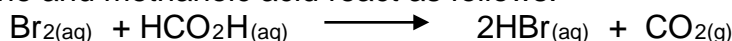
For a second order reaction successive half-lives double.

Note that if the graph of concentration against time is **straight**, order is **zero**. If it is curved (as above, or falling more steeply at first) you need to check successive half lives to find if they are constant (order 1) or if they double (order 2).

## Examples of concentration-rate studies

One method of determining rate is to follow the reaction over a period of time.

Bromine and methanoic acid react as follows:



The reaction can be followed by calorimeter, measuring the colour intensity of the bromine. A calibration plot of calorimeter readings for known concentrations would be made so that it is possible to convert calorimeter readings to bromine concentration.

In this experiment the effect of changing the bromine concentration, a high concentration of methanoic acid is used, so that its concentration changes very little as the concentration of the bromine changes significantly.

Readings for such an experiment are shown below;

Time /s	[Bromine] /mol dm <sup>-3</sup>
0	0.0100
30	0.0090
60	0.0081
90	0.0073
120	0.0073
180	0.0053
240	0.0044
360	0.0028
480	0.0020
600	0.0013

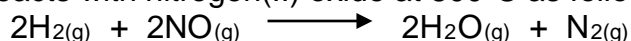
- \* Plot a graph of bromine concentration against time.
- \* Draw tangents at intervals to fill in the table below and find the rate of change of the bromine concentration at these times.

Time /s	[Br <sub>2</sub> ] /mol dm <sup>-3</sup>	Rate of reaction /mol dm <sup>-3</sup> s <sup>-1</sup>
50	0.0086	2.92 x 10 <sup>-5</sup>
100	0.0071	2.40 x 10 <sup>-5</sup>
150	0.0060	2.04 x 10 <sup>-5</sup>
200	0.0050	1.70 x 10 <sup>-5</sup>
250	0.0042	1.45 x 10 <sup>-5</sup>
300	0.0035	1.19 x 10 <sup>-5</sup>
400	0.0025	0.81 x 10 <sup>-5</sup>
500	0.0018	0.65 x 10 <sup>-5</sup>

- \* Plot a new graph of the rate values obtained against the bromine concentration. This graph produces a straight line showing the reaction to be first order with respect to bromine concentration.

Another method of determining rate is to measure the initial rate (before any significant concentrations changes have occurred) using different starting concentrations.

Hydrogen reacts with nitrogen(II) oxide at 800°C as follows:



Results of an initial rate investigation of this reaction are shown below.

Experiment	Initial [NO] / mol dm <sup>-3</sup>	Initial [H <sub>2</sub> ] / mol dm <sup>-3</sup>	Initial rate of reaction / mol dm <sup>-3</sup> s <sup>-3</sup>
1	6 x 10 <sup>-3</sup>	1 x 10 <sup>-3</sup>	3.0 x 10 <sup>-3</sup>
2	6 x 10 <sup>-3</sup>	2 x 10 <sup>-3</sup>	6.0 x 10 <sup>-3</sup>
3	6 x 10 <sup>-3</sup>	3 x 10 <sup>-3</sup>	9.0 x 10 <sup>-3</sup>
4	1 x 10 <sup>-3</sup>	6 x 10 <sup>-3</sup>	0.5 x 10 <sup>-3</sup>
5	2 x 10 <sup>-3</sup>	6 x 10 <sup>-3</sup>	2.0 x 10 <sup>-3</sup>
6	3 x 10 <sup>-3</sup>	6 x 10 <sup>-3</sup>	4.5 x 10 <sup>-3</sup>

Comparing experiments 1, 2 and 3, it can be seen that as the concentration of hydrogen increases, the rate of reaction increases proportionately. This shows that the reaction is first order with respect to the hydrogen.

Comparing experiments 4, 5 and 6, it can be seen that as the concentration of nitrogen(II) oxide increases, the rate of reaction increases by the square of the concentration increase.

Experiment	Initial [NO] / mol dm <sup>-3</sup>	Change in [NO]	Initial rate of reaction / mol dm <sup>-3</sup> s <sup>-3</sup>	Change in rate
4	1 x 10 <sup>-3</sup>		0.5 x 10 <sup>-3</sup>	
5	2 x 10 <sup>-3</sup>	Expt 4 x 2	2.0 x 10 <sup>-3</sup>	Expt 4 x 4
6	3 x 10 <sup>-3</sup>	Expt 4 x 3	4.5 x 10 <sup>-3</sup>	Expt 4 x 9

This shows that the reaction is second order with respect to the nitrogen(II) oxide.

So the rate equation is  $\text{Rate} = k[\text{H}_2][\text{NO}]^2$

By substituting in values the value of k can be determined.

Using experiment 3

$$9.0 \times 10^{-3} = k \times 3 \times 10^{-3} \times (6 \times 10^{-3})^2$$

$$k = \frac{9.0 \times 10^{-3}}{3 \times 10^{-3} \times (6 \times 10^{-3})^2} = 8.33 \times 10^{-4}$$

$$\text{Units of } k = \frac{\text{mol dm}^{-3} \text{ s}^{-3}}{\text{mol dm}^{-3} \text{ s}^{-3} \times (\text{mol dm}^{-3} \text{ s}^{-3})^2} = \text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$



## Reaction Mechanisms

Many reactions actually take place in a number of steps. The way in which atoms, ions or molecules interact, stage by stage, is known as the reaction mechanism. Rate studies can provide useful information about the reaction mechanism.

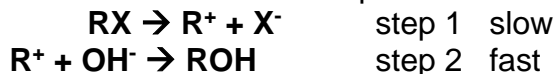
In a reaction which has several stages, the different stages will proceed at different rates. It is the slowest step which will determine how long the reaction takes. This step is called the rate determining step. Since the rate determining step controls how long the reaction takes, then the substances in this step will appear in the rate equation. The rate equation then provides evidence about the substances involved in the rate determining step.

The reaction between propanone and bromine is a first order reaction overall.

$$\text{Rate} = k [\text{propanone}]^1 [\text{bromine}]^0$$

The rate then is proportional to the concentration of propanone, but independent of the concentration of bromine. This suggests that the reaction takes place in a number of stages, and that only the propanone is involved in the rate determining step.

e.g. For an  $S_N1$  reaction two steps are involved



The rate depends on the slow step 1.      **rate =  $k[\text{RX}]$**       **first order**

For an  $S_N2$  reaction there is a rate determining slow step involving two species.



### Mechanisms and Kinetic data

Chemical reactions occur when molecules (or atoms, or free radicals, or ions) collide: at a given temperature a constant proportion of collisions is likely to be successful.

If molecules of A and B are in the same vessel, the number of collisions between A and B depends on their concentrations:

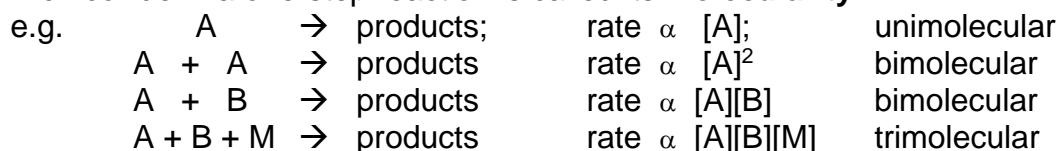
$$\text{number of A-B collisions} \propto [\text{A}] [\text{B}]$$

i.e. if we double the number of A molecules in the vessel we will get twice as many A-B collisions; if we double both A and B, there will be four times as many collisions.

If A and B take part in a simple, one-step reaction, the rate of reaction will depend on the number of A-B collisions:

$$\text{rate of reaction} \propto [\text{A}] [\text{B}]$$

In general, in a one-step reaction, the rate of reaction is proportional to the product of the concentrations of each species colliding. The number of species (atoms, molecules or ions) which collide in a one-step reaction is called its **molecularity**:

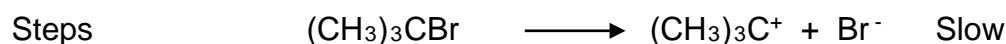
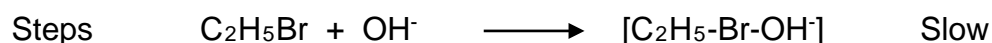
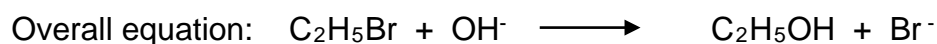
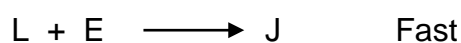
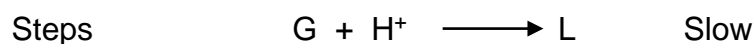
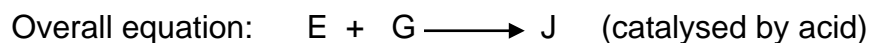
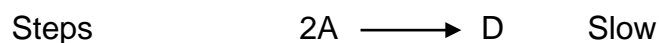


Trimolecular reactions are extremely unusual.

The mechanism for a reaction can be proposed with help from kinetic data but some speculation is needed.

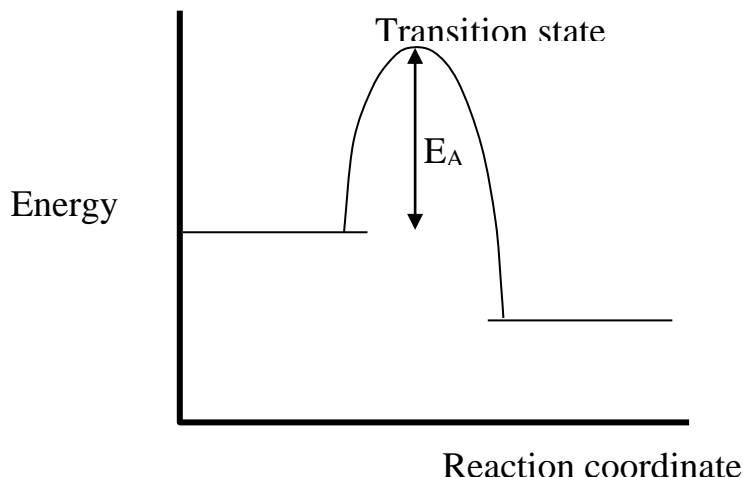
1. The rate equation gives us information about what reacts in the rate determining step.
2. Sensible products must be suggested for the rate determining step.
3. If more molecules of reactant remain and more product molecules are still to be formed more steps must be proposed.

Write rate equations for the following

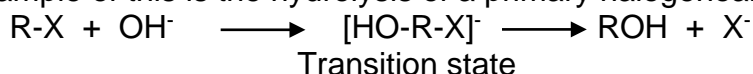


## The Transition State Theory

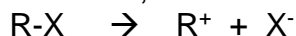
The transition state theory says that when molecules collide and react, they move through a state of instability or high potential energy. This state of high potential energy is called the transition state or the activated complex. The energy required to attain the transition state is the activation energy.



An example of this is the hydrolysis of a primary halogenoalkane.

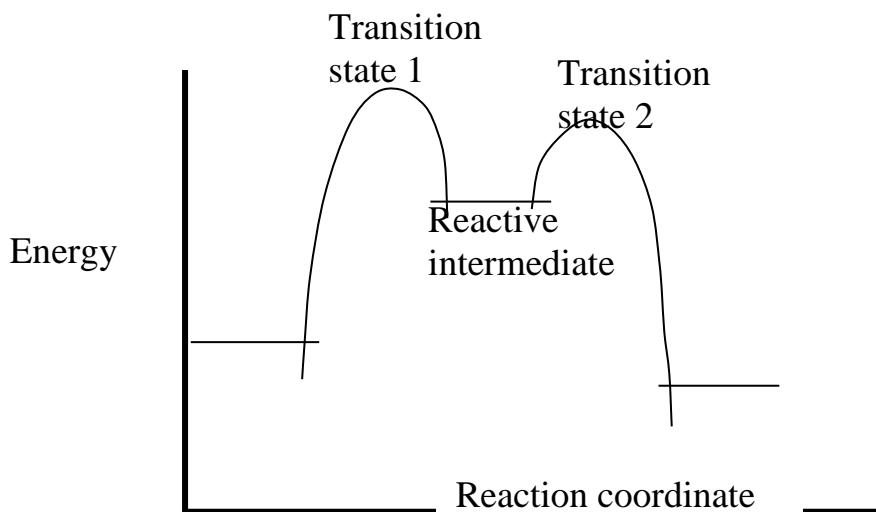


In some reactions an intermediate is formed. For example in the hydrolysis of a tertiary halogenoalkane, a carbocation is formed.



The  $\text{R}^+$  carbocation is a reactive intermediate. This then reacts with the  $\text{OH}^-$  to produce the alcohol.

When a reactive intermediate is formed the reaction goes through two transition states.



The higher the value of the activation energy, the lower the number of effective collisions and so the lower the rate constant.

## Rate and Reaction Mechanism in Real Systems

Results from kinetics studies provide information about reaction mechanism.

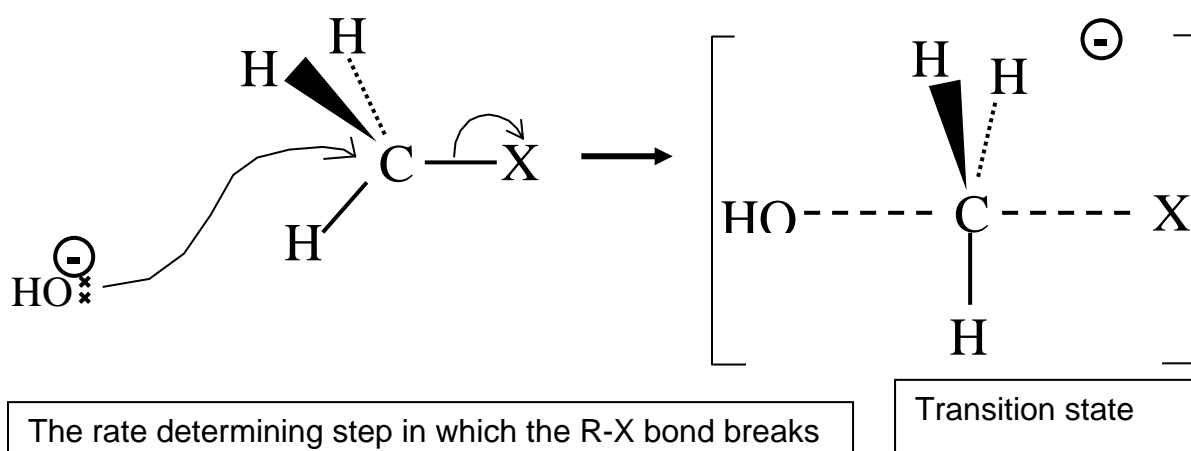
The rate equations for the hydrolysis of primary and tertiary halogenoalkanes are different.

For hydrolysis of primary halogenoalkanes the rate equation is:  $\text{Rate} = k[\text{RX}][\text{OH}^-]$

For hydrolysis of tertiary halogenoalkanes the rate equation is:  $\text{Rate} = k[\text{RX}]$

The different rate equations arise because the hydrolysis of primary halogenoalkanes takes place by a different mechanism than that for tertiary halogenoalkanes.

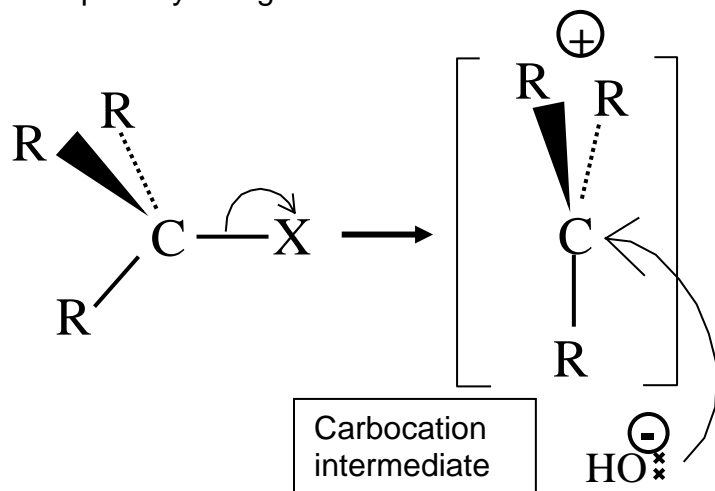
The reaction mechanism for the hydrolysis of primary halogenoalkanes is as follows:



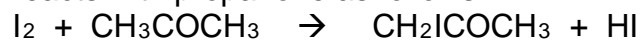
The rate determining step in which the R-X bond breaks involves the halogenoalkane and the hydroxide ion. Hence both these feature in the rate equation. It is designated  $\text{S}_{\text{N}}2$  because there are two species involved in the RDS.

The reaction mechanism for the hydrolysis of tertiary halogenoalkanes is as follows:

The stability of a tertiary carbocation means that the breaking of the R-X bond can occur without the necessity of the hydroxide ion. Hence only the RX features in the rate equation. It is designated  $\text{S}_{\text{N}}1$  because there is only species involved in the RDS.



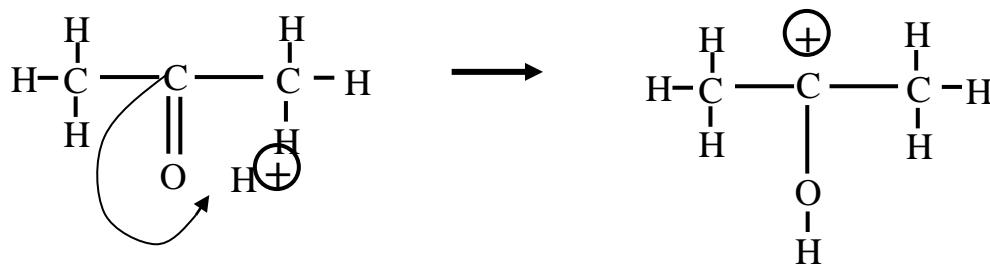
Iodine reacts with propanone as follows



This reaction is catalysed by the presence of an acid.

The rate equation for this reaction is  $\text{Rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$

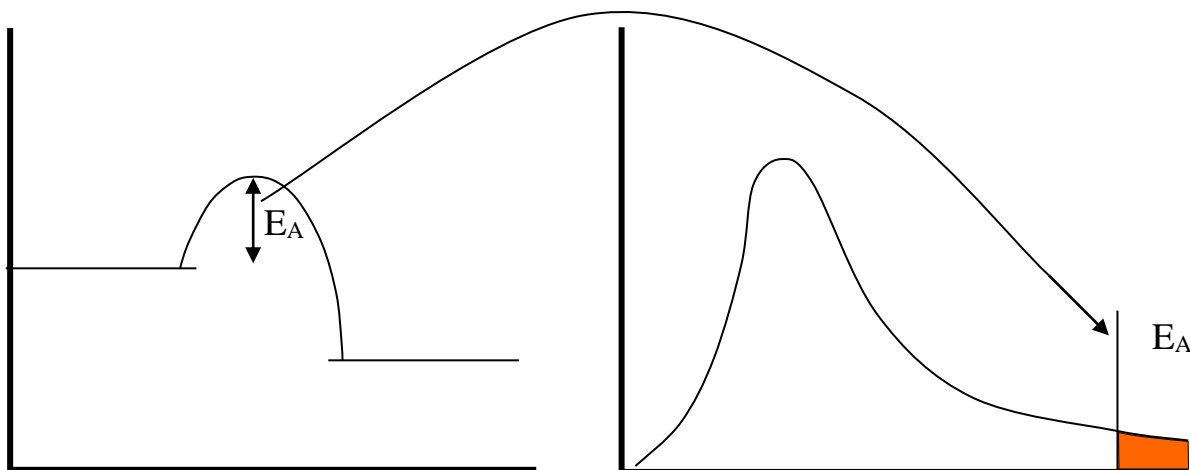
This tells us that the rate determining step for this reaction involves only the propanone and the hydrogen ions.



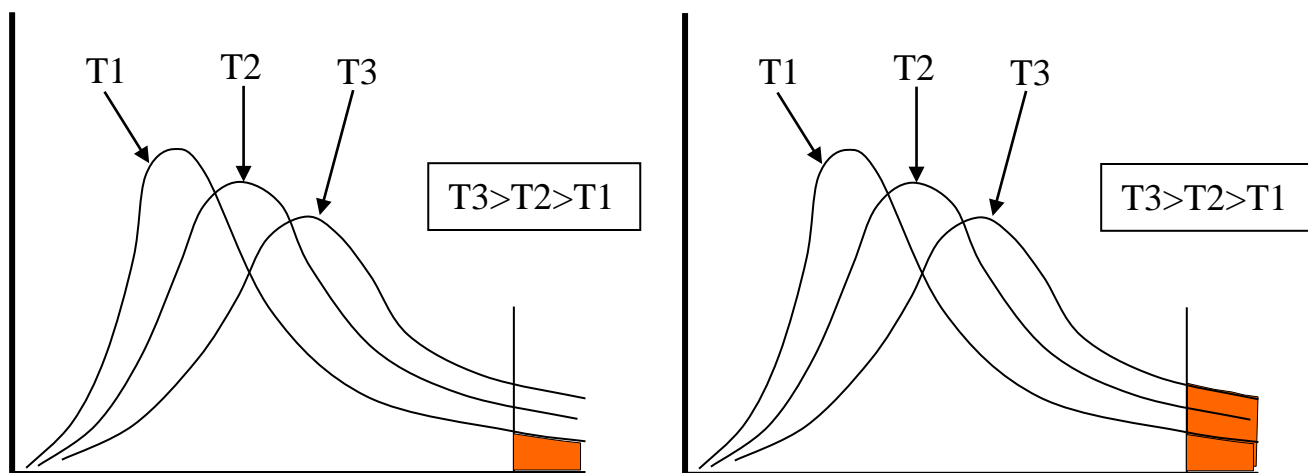
## Temperature and rate

Often an increase in temperature of 10°C can double the rate of reaction. In terms of absolute temperature this means a change of temperature from 395 K to 405 K; so the proportional change in rate vastly outweighs the proportional change in temperature. This cannot be explained in terms of speed of particles, as their speed is determined by the absolute temperature.

In topic 2.8, it was seen that activation energy is an important factor for rate of reaction when the temperature is altered. The activation energy was connected with the Boltzmann distribution of energy.



At a higher temperature the proportion of particles with an energy equal to, or greater than, the activation energy increases significantly.



## The Arrhenius Equation

An important equation linking activation energy, temperature and rate of reaction is the Arrhenius equation.

$$k = Ae^{-E_A/RT}$$

In this equation,  $k$  is the rate of reaction,  
 $E_A$  the activation energy,  
 $R$  the gas constant  
and  $T$  the temperature in Kelvin.  
 $A$  is the Arrhenius constant connected with the number of collisions and collision orientation.

It can be seen from this equation that as the activation energy increases, the rate constant will decrease and that as the temperature increases the rate constant also increases.

The table below shows how the rate constant might change with activation energy.

Activation energy / $\text{kJmol}^{-1}$	Rate constant
40	74800
50	1313
60	23.0
70	0.404

The table below shows how the rate constant might change with temperature. This is based on the kinetics for the reaction:



Temperature /K	Rate constant
273	$3.33 \times 10^{-26}$
473	$2.12 \times 10^{-10}$
673	$5.45 \times 10^{-4}$
773	$4.99 \times 10^{-2}$
873	1.62

Taking log to base  $e$  in  $k = Ae^{-E_A/RT}$

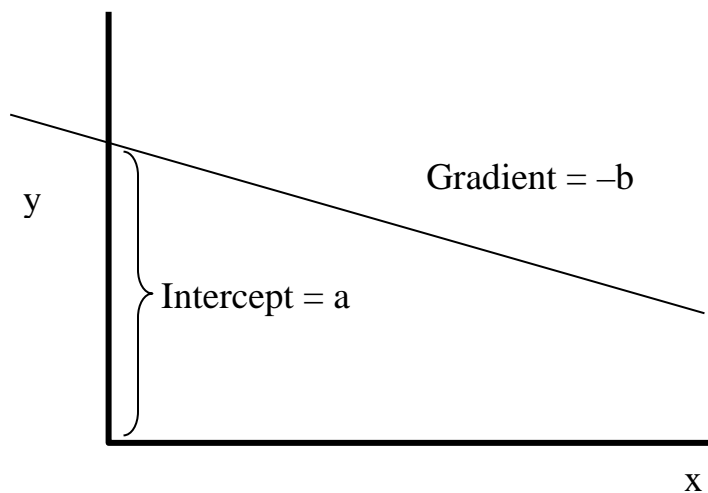
$$\ln k = \ln A + \ln e^{-E_A/RT}$$

$$\ln k = \ln A - E_A/RT$$

This can be used to find a value of the Activation Energy.

A graph of

$y = a - bx$ ,  
appears as follows

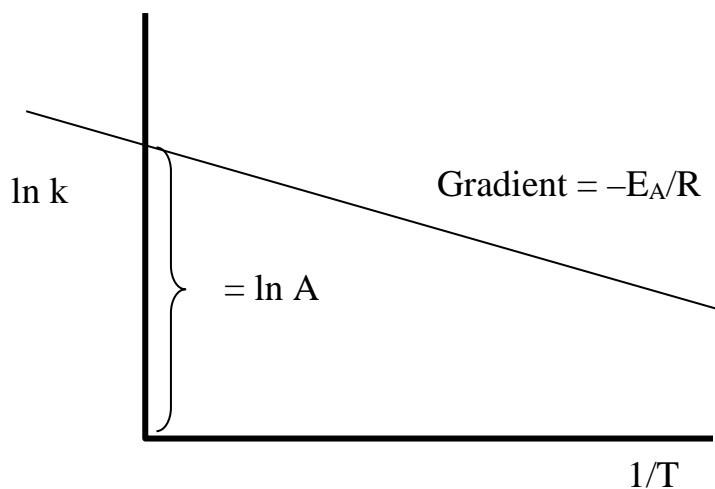


The log version of the Arrhenius equation can be plotted in a similar way

$$y = a - bx$$

$$\boxed{\ln k} = \boxed{\ln A} - \boxed{E_A/R} \boxed{(1/T)}$$

When a graph of  $\ln k$  is plotted against  $1/T$ , the slope of the line is  $-E_A/R$



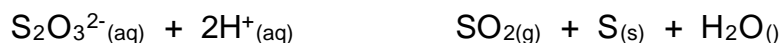
If  $k$  is calculated for different values of  $T$  then a plot of  $\ln k$  against  $1/T$  gives a line of gradient =  $-E_a/R$ .

If  $k$  is calculated for different values of  $T$  then a plot of **log k** against  $1/T$  gives a line of **gradient =  $-E_a/2.3R$** .

### Determination of the Activation Energy for a reaction

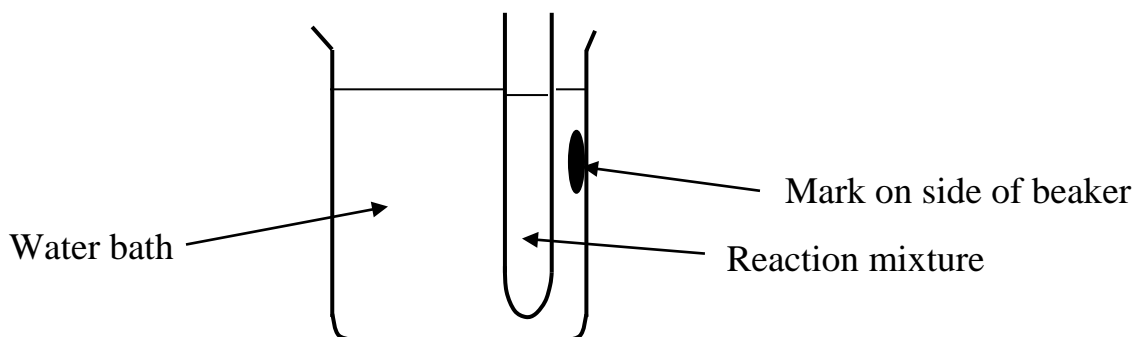


Sodium thiosulphate reacts with dilute hydrochloric acid according to the equation:



The sulphur forms a suspension and the mixture becomes progressively more cloudy.

The acid and the thiosulphate are mixed at a particular temperature and the time taken for the sulphur formed to obscure a mark behind the tube is noted.



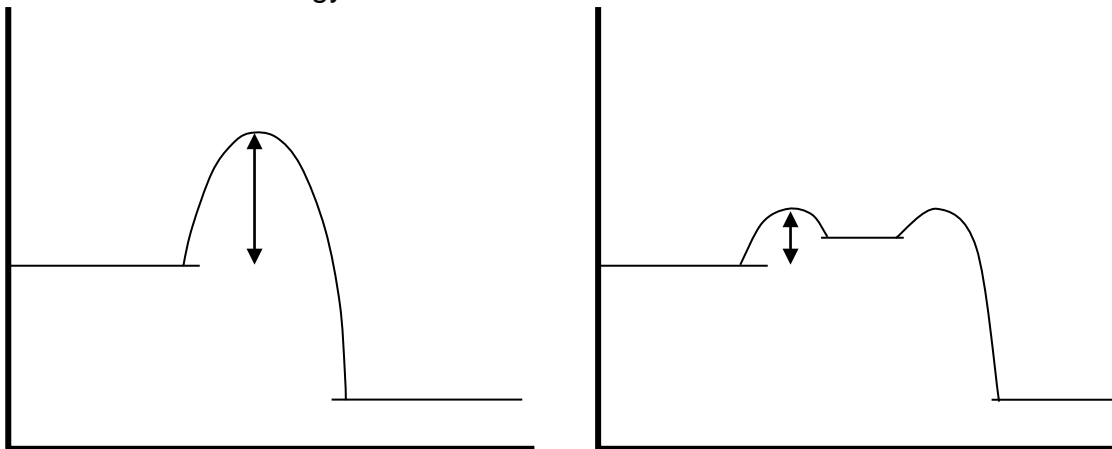
The reaction is then carried out at different temperatures. Results are shown below.

Temperature /°C	Temperature (T) /K	Time / s	1/T / K <sup>-1</sup>	1/time / s <sup>-1</sup> (rate)	ln 1/time
60	333	12	0.003003	0.083333	-2.48491
52	325	18.6	0.003077	0.053763	-2.92316
44.5	317.5	28	0.003150	0.035714	-3.3322
40	313	36	0.003195	0.027778	-3.58352
34.5	307.5	50	0.003252	0.020000	-3.91202
28	301	74	0.003322	0.013514	-4.30407
21	294	116	0.003401	0.008621	-4.75359

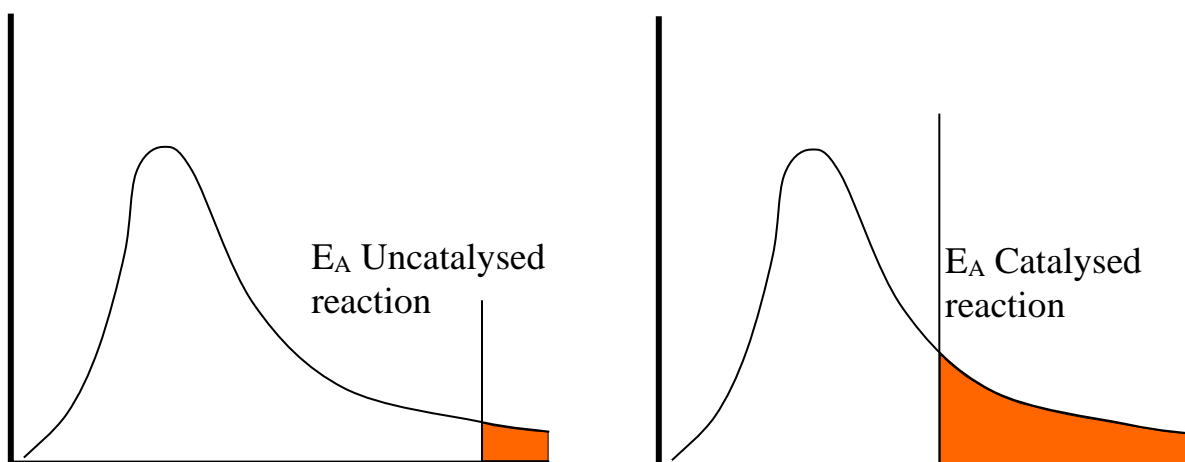
- \* Plot a graph of ln k against 1/T.
- \* Find the gradient
- \* Use the relationship, Gradient = -E<sub>a</sub>/R to calculate the activation energy for the reaction given that R = 8.3 JK<sup>-1</sup>mol<sup>-1</sup>.

## Catalysts and rate

In Unit 2, it was seen that catalysts work by providing an alternative path for the reaction at a lower activation energy.



The effect of this can be shown diagrammatically in a Maxwell-Boltzmann distribution curve.



The effect of lowering the activation energy even by proportionally small amounts is illustrated in the table in the “Arrhenius Equation” section. Many catalysts alter the activation energy considerably.