

CHEMICAL KINETICS

Reminder The following methods can be used to increase the rate of a reaction.

- increase surface area
- increase temperature
- add a catalyst
- use a light source (certain reactions only)
- increase pressure (gaseous reactions only)
- increase concentration

How they affect the rate has been studied in earlier work with special reference to Collision Theory.

CONCENTRATION

Introduction Increasing concentration = more frequent collisions = increased rate

However: Increasing the concentration of some reactants can have a greater effect than increasing others.

Rate Reactions start off at their fastest then slow as the reactant concentration drops.

eg In the reaction $A + 2B \rightarrow C$ the concentrations **might** change as shown

- the steeper the curve the faster the rate of the reaction
- reactions start off quickly because of the greater likelihood of collisions
- reactions slow down with time because there are fewer reactants to collide

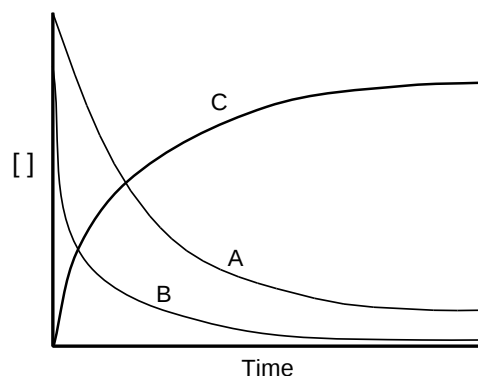
Reactants (A and B)

Concentration decreases with time

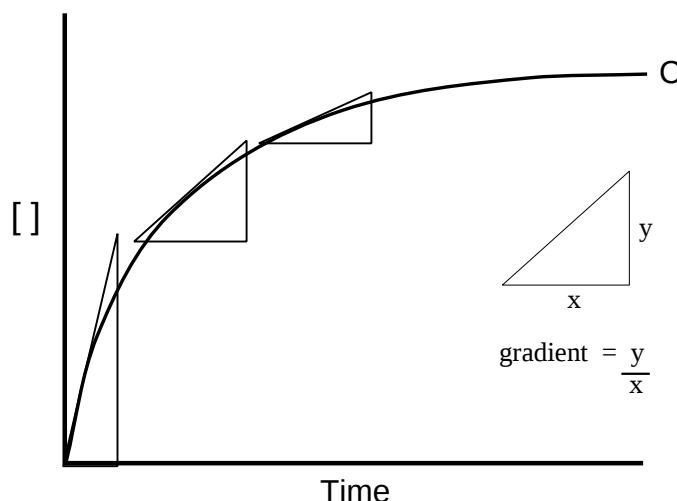
Products (C)

Concentration increases with time

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



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



- Investigation**
- the variation in concentration of a reactant or product is followed with time
 - method depends on the reaction type and the properties of reactants/products

- e.g.
- Extracting a sample from the reaction mixture and analysing it by titration
 - Using a colorimeter or UV / visible spectrophotometer
 - Measuring the volume of gas evolved or a change in conductivity

THE RATE EQUATION

- Format**
- links the rate of reaction to the concentration of reactants
 - can only be found by doing actual experiments, not by looking at the equation

the equation...



might have a rate equation like this $r = k [\text{A}] [\text{B}]^2$

where	r	rate of reaction	units	conc. / time	usually $\text{mol dm}^{-3} \text{ s}^{-1}$
	k	rate constant	units	depend on the rate equation	
	$[\]$	concentration	units	mol dm^{-3}	

Interpretation The above rate equation tells you that the rate of reaction is...

- proportional to the conc of reactant A doubling [A] - will double rate
- proportional to the square of the conc of B doubling [B] - will quadruple rate
- not proportional to the conc of X altering [X] - no effect on rate

Order of reaction

Individual order The power to which a concentration is raised in the rate equation

Overall order The sum of all the individual orders in the rate equation.

e.g. in the rate equation $r = k [\text{A}] [\text{B}]^2$

- | | | |
|-----|----------------------------------|-----------|
| | the order with respect to A is 1 | 1st Order |
| | the order with respect to B is 2 | 2nd Order |
| and | the overall order is 3 | 3rd Order |

- Value(s)**
- orders need not be whole numbers
 - orders can be zero if the rate is unaffected by how much substance is present

Remember The rate equation is derived from experimental evidence not by from an equation.

- species in the stoichiometric equation sometimes aren't in the rate equation
- substances not in the stoichiometric equation can appear in the rate equation

Q.1 State the overall order, and the individual orders, for the following ?

a) $\text{rate} = k[C]^3[D]$

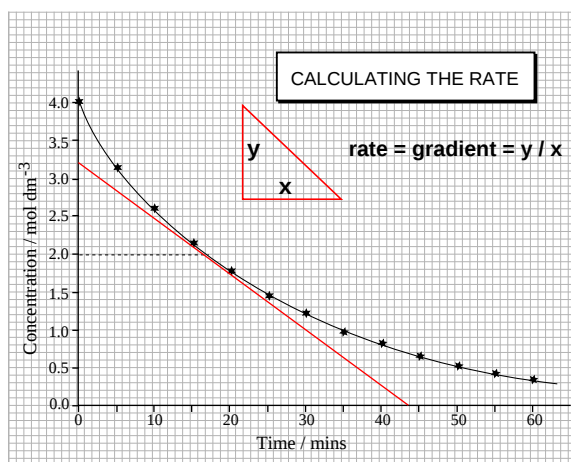
b) $\text{rate} = k[Z]$

Q.2 What substances appear in the rate, but not in the stoichiometric, equation ?

Experimental determination of order

Method 1 1. Plot a concentration/time graph

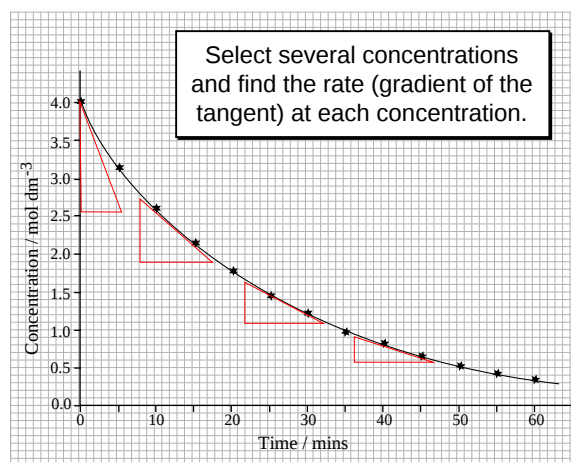
Calculate the rate (gradient) at points on the curve.



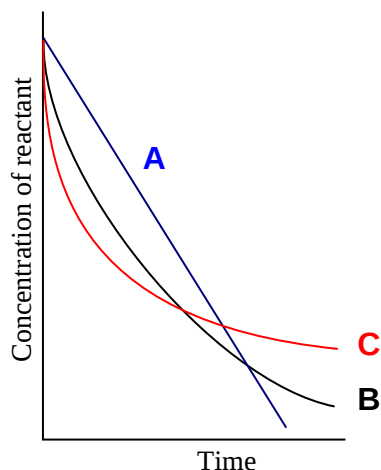
When the concentration is 2.0 mol dm^{-3}
the gradient = $\frac{-3.2 \text{ mol dm}^{-3}}{44 \text{ minutes}}$

The gradient is negative because
the concentration is decreasing

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



Notice how the gradient gets less as
the reaction proceeds. This shows
that the rate of reaction is getting less.



CONCENTRATION v. TIME GRAPHS

WHAT TO LOOK FOR

A ZERO ORDER

a straight line with constant slope

B FIRST ORDER

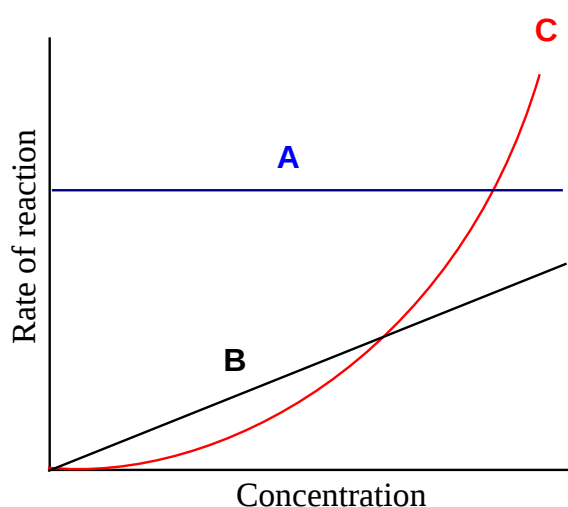
downwardly sloping curve with a constant half life

C SECOND ORDER

steeper downwardly sloping curve; levels out quicker

Method 1
(cont)

2. Plot another graph of rate (y axis) versus the concentration (x axis)



A ZERO ORDER

a straight line horizontal to the x axis
rate is independent of concentration

B FIRST ORDER

a straight line with a constant slope
rate is proportional to concentration

GRADIENT = RATE CONSTANT (k)

C SECOND ORDER

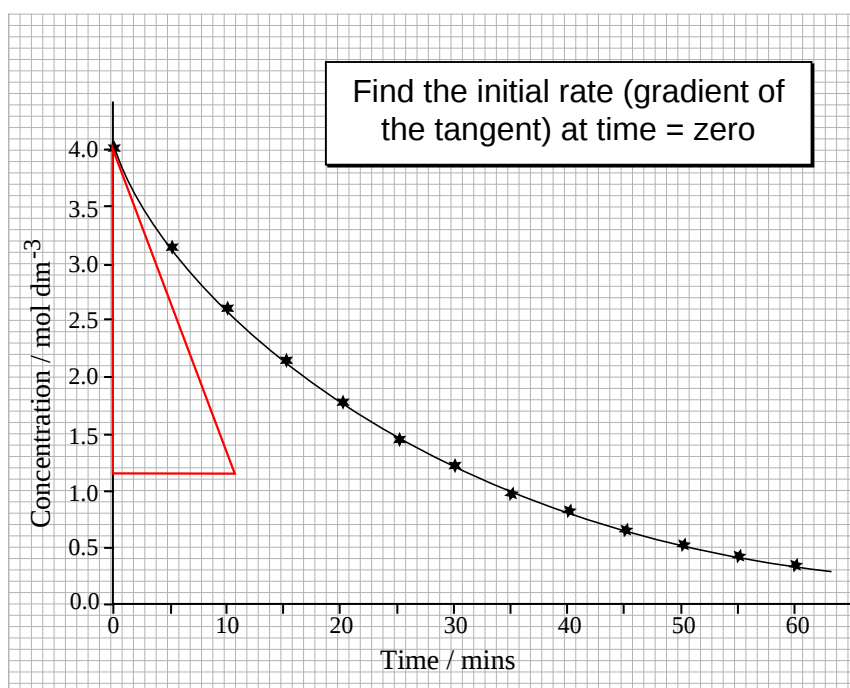
an upwardly sloping curve; plotting
rate v. conc^2 gives a straight line

Method 2

The initial rates method.

Do a series of experiments (at the same temperature) at different concentrations of a reactant but keeping all others constant.

- Plot a series of concentration / time graphs
- Calculate the initial rate (slope of curve at start) for each reaction.
- Plot each initial rate (y axis) against the concentration used (x axis)
- From the graph, calculate the relationship between concentration and rate
- Hence deduce the rate equation - see *the graph at the top of the page*
- To find order directly, logarithmic plots are required.



Half-life
($t_{1/2}$)

A characteristic of a FIRST ORDER REACTION is that it has a **constant half life** which is independent of the concentration. It is very similar to radioactive decay.

Definition

The time taken for the concentration of a reactant to drop to half of its original value.

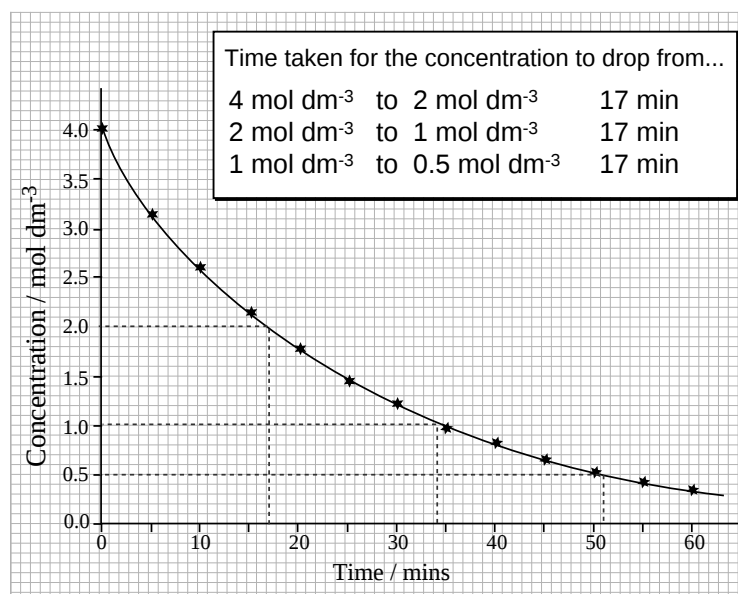
the time taken to drop...
from **1 to 1/2 = one half life**
1/2 to 1/4 = one half life
1/4 to 1/8 = one half life

A useful relationship

$$k t_{1/2} = \log_e 2$$

$$= 0.693$$

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



**TO CALCULATE THE RATE CONSTANT (k)
FOR A FIRST ORDER REACTION**

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

Q.3

In the reaction, $A + B \rightarrow X + Y$, the concentration of A was found to vary as shown in the table. It was later found that the order with respect to (wrt) B was 0.

- plot a graph of $[A]$ v. time
- calculate the time it takes for $[A]$ to go from...
1.30 to 0.65
1.00 to 0.50
0.50 to 0.25 (all in units mol dm⁻³)
- deduce from the graph that the order wrt A is 1
- calculate the value of the rate constant, k

Time / s	$[A]$ / mol dm ⁻³
0	1.30
20	1.05
40	0.85
60	0.68
80	0.55
100	0.45
120	0.36
140	0.29
160	0.24
180	0.19
200	0.15

Rate constant (k)

- Value**
- the value of the rate constant is **affected by temperature**
 - increasing the temperature increases the value of the rate constant**
 - if k increases, so does the rate
 - an increase of 10°C **approximately** doubles the rate of a reaction

Units The units of k depend on the overall order of reaction.

e.g. if the rate equation is **rate = k [A]²** the units of k will be **dm³ mol⁻¹ sec⁻¹**

Calculation Divide rate (conc per time) by as many concentrations that are in the rate equation

Overall Order	0	1	2	3
units of k	mol dm ⁻³ sec ⁻¹	sec ⁻¹	dm ³ mol ⁻¹ sec ⁻¹	dm ⁶ mol ⁻² sec ⁻¹

example in the rate equation $r = k [A]$ k has units of sec⁻¹
 in the rate equation $r = k [A] [B]^2$ k has units of dm⁶ mol⁻² sec⁻¹

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

$$r = k[C]^3[D]$$

$$r = k [Z]^2$$

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

Q.5 Using the data, construct the rate equation for the reaction between nitric oxide and oxygen. What is the value and the units of the rate constant (k) ?

Expt	Initial [NO] / mol dm ⁻³	Initial [O ₂] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	1	2	7
2	2	1	28
3	2	2	56
4	3	3	?

Hint Compare Expts. 2 and 3 to find the order with respect to O₂
 Compare Expts. 1 and 3 to find the order with respect to NO

The Arrhenius equation

Rate

Equation

- a typical rate equation may like this $r = k [A] [B]^2$
- it shows how rate is affected by the concentrations of reactants [A] and [B]
- the rate constant (**k**) shows how other variables affect the rate
- a **change of temperature** or the addition of **catalyst** affects the value of **k**
- it is expressed mathematically using the **Arrhenius equation**

Arrhenius equation

$$k = A e^{-\left(\frac{E_a}{RT}\right)}$$

rate constant

represents the fraction of the molecules in a gas which have energies equal to or greater than the activation energy at a stated temperature

includes factors like the frequency of collisions and their orientation. It varies slightly with temperature, although not much and is taken as constant across small temperature ranges.

k	rate constant	units depend on overall order
T	temperature	K (K = °C + 273)
R	gas constant	8.13 J K ⁻¹ mol ⁻¹
E_a	activation energy	J mol ⁻¹
e	constant	2.71828
A	pre-exponential factor (frequency factor)	no units

Calculations • values of A and E_a are obtained from the Arrhenius equation by the relationship

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

ln is a logarithmic term (log_e NOT log₁₀)
(it can be obtained from a calculator)

Graphical method

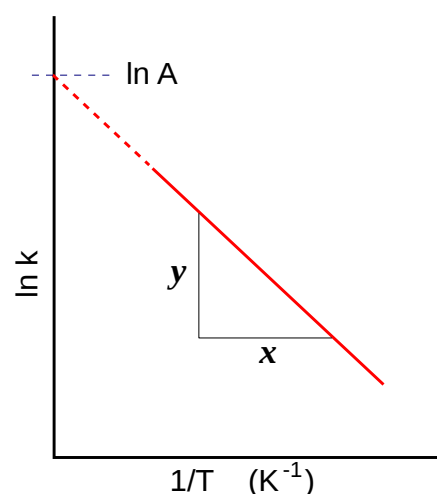
- convert and re-arrange the equation into the straight line formula **y = mx + c**

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

$$y = m x + c$$

- y axis plot **ln k**
- x axis plot **1/T**
- gradient (**m**) gives **- (E_a/R)**
- y intercept (**c**) gives **ln A**

gradient (**m**) = change in y / change in x



Rate determining step

- Explanation**
- many reactions consist of a series of separate stages
 - each of these stages has its own rate and hence its own rate constant
 - the overall rate of a multi-step process is governed by the slowest step
- *rather like a production line where the output can be held up by a slow worker*
 - the **slowest step is known as the rate determining step**
 - investigation of the rate equation gives an idea of whether, or not, a reaction takes place in a series of steps

Example Iodine reacts with propanone... $\text{CH}_3\text{COCH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$

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

- Why is $[\text{H}^+]$ in the rate equation? *the reaction is catalysed by acid*
- Why is $[\text{I}_2]$ not in the rate equation? *the reaction has more than one step and the slowest step doesn't involve iodine*

The rate determining step must therefore involve propanone and acid.

Example 2 The reaction $\text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2\text{I}^- \rightarrow \text{I}_2 + 4\text{H}_2\text{O}$ takes place in 3 steps

Step 1 $\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{IO}^- + \text{H}_2\text{O}$ slow

Step 2 $\text{IO}^- + \text{H}_3\text{O}^+ \rightarrow \text{HIO} + \text{H}_2\text{O}$ fast

Step 3 $\text{HIO} + \text{H}_3\text{O}^+ + \text{I}^- \rightarrow \text{I}_2 + 2\text{H}_2\text{O}$ fast

The rate determining step is STEP 1 as it is the slowest

Example 3 The reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ takes place in 3 steps

Step 1 $\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$ (occurs twice) slow

Step 2 $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$ fast

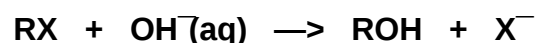
Step 3 $\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$ fast
from another Step 1

The rate determining step is STEP 1 as it is the slowest

The rate equation for the reaction is $\text{rate} = k [\text{N}_2\text{O}_5]$

The hydrolysis of halogenoalkanes

Introduction Haloalkanes (RX) are hydrolysed by aqueous hydroxide ions



There are **two possible mechanisms**

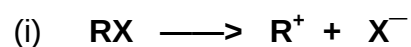
Mech. 1

- one step reaction
- requires both species to collide
- rate is affected by both reactants
- second order overall

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

Mech 2

- two step reaction



- step (i) is slower as it involves bonds breaking and will thus be the rate determining step
- rate depends only on [RX]
- first order overall

$$\text{rate} = k[\text{RX}]$$

Mechanism 2 is very common with tertiary (3°) haloalkanes whereas primary (1°) and secondary (2°) haloalkanes usually undergo hydrolysis via a second order process.

Molecularity

The number of individual particles of the reacting species taking part in the rate determining step of a reaction.

e.g. $\text{A} + 2\text{B} \longrightarrow \text{C} + \text{D}$ molecularity is 3 - one A and two B's need to collide

$\text{A} \longrightarrow 2\text{B}$ however has a molecularity of 1 - only one A is involved