1.9 Rate Equations

Rate Equations

The rate equation relates mathematically the rate of reaction to the concentration of the reactants.

For the following reaction, aA + bB → products, the generalised rate equation is: $r = k[A]^m[B]^n$

r is used as symbol for rate

The unit of r is usually **mol dm^{-3} s^{-1}**

m, n are called **reaction orders**

Orders are usually integers 0,1,2

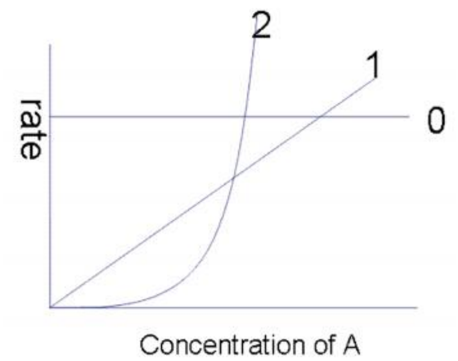
0 means the reaction is zero order with respect to that reactant
1 means first order
2 means second order

NOTE: the orders are **not the same** as the stoichiometric coefficients in the balanced equation. They are worked out experimentally.

The square brackets **[A]** means the concentration of A (unit **mol dm^{-3}**)

k is called the **rate constant**

The **total order** for a reaction is worked out by adding all the individual orders together (m+n)



For zero order: the concentration of A has no effect on the rate of reaction $\mathbf{r = k[A]^0 = k}$

For first order: the rate of reaction is directly proportional to the concentration of A $r = k[A]^1$

For second order: the rate of reaction is proportional to the concentration of A squared $\mathbf{r = k[A]^2}$

The rate constant (k)

1. The units of k depend on the overall order of reaction. It must be worked out from the rate equation
2. The value of k is independent of concentration and time. It is constant at a fixed temperature.
3. The value of k refers to a specific temperature and it **increases** if we **increase temperature**

For a 1st order overall reaction the unit of k is **s^{-1}**

For a 2nd order overall reaction the unit of k is **mol^{-1}dm^{3}s^{-1}**

For a 3rd order overall reaction the unit of k is **mol^{-2}dm^{6}s^{-1}**

Example 1 (first order overall)

Rate = $k[A][B]^0$ m = 1 and n = 0
- reaction is first order in A and zero order in B
- overall order = 1 + 0 = 1
- usually written: Rate = k[A]

Remember: the values of the reaction orders must be determined from experiment; they cannot be found by looking at the balanced reaction equation

Calculating units of k

1. Rearrange rate equation to give k as subject

$$k = \frac{Rate}{[A]}$$

2. Insert units and cancel

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

Unit of k = s^{-1}

Example 2: Write rate equation for reaction between A and B where A is 1st order and B is 2nd order.

$r = k[A][B]^2$ overall order is 3

Calculate the unit of k

1. Rearrange rate equation to give k as subject

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

2. Insert units and cancel

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

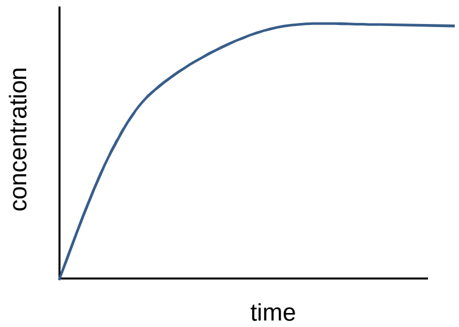
3. Simplify fraction

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

Unit of k = $mol^{-2}dm^6s^{-1}$

Continuous Monitoring

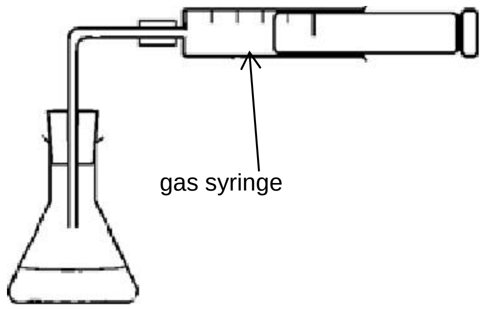
When we follow one experiment over time recording the change in concentration we call it a continuous rate method.



The gradient represents the rate of reaction. The reaction is fastest at the start where the gradient is steepest. The rate drops as the reactants start to get used up and their concentration drops. The graph will eventual become horizontal and the gradient becomes zero which represents the reaction having stopped.

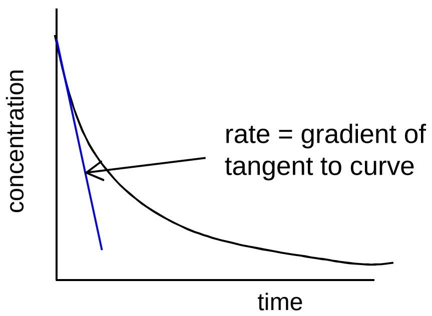
Measurement of the change in volume of a gas

This works if there is a change in the number of moles of gas in the reaction. Using a gas syringe is a common way of following this. It works quite well for measuring continuous rate but a typical gas syringe only measures 100ml of gas so you don't want a reaction to produce more than this volume. Quantities of reactants need to be calculated carefully.



$Mg + 2HCl \rightarrow MgCl_2 + H_2$

The initial rate is the rate at the start of the reaction, where it is fastest. It can be calculated from the gradient of a continuous monitoring conc vs time graph at time = zero. A measure of initial rate is preferable as we know the concentrations at the start of the reaction.



Typical Method

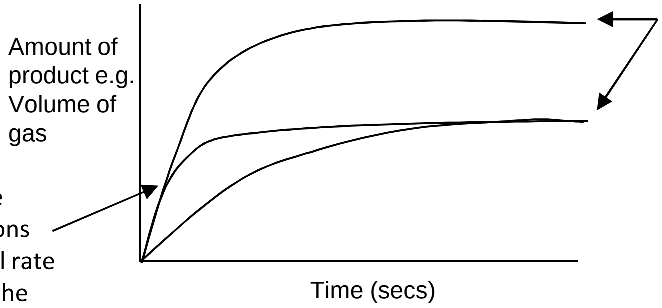
- Measure 50 cm^3 of the 1.0 mol dm^{-3} hydrochloric acid and add to conical flask.
- Set up the gas syringe in the stand
- Weigh 0.20 g of magnesium.
- Add the magnesium ribbon to the conical flask, place the bung firmly into the top of the flask and start the timer.
- Record the volume of hydrogen gas collected every 15 seconds for 3 minutes.

Large excess of reactants
In reactions where there are several reactants, if the concentration of one of the reactant is kept in a large excess then that reactant will appear not to affect rate and will be pseudo-zero order . This is because its concentration stays virtually constant and does not affect rate.

Comparing continuous rate curves

The higher the concentration/ temperature/ surface area the faster the rate (steeper the gradient)

If the magnesium or marble chips is in excess of the acid, then the final volume of gas produced will be proportional to the amount of moles of acid.



Need to calculate/ compare initial moles of reactants to distinguish between different finishing volumes.

e.g. the amount of product is proportional to the moles of reactant

Different volumes of the same initial concentrations will have the same initial rate (if other conditions are the same) but will end at different amounts

Initial rate method

The initial rate can be calculated from taking the gradient of a continuous monitoring conc vs time graph at time = zero

Initial rate can also be calculated from clock reactions where the time taken to reach a fixed concentration is measured.

A Common Clock Reaction

Hydrogen peroxide reacts with iodide ions to form iodine. The thiosulfate ion then immediately reacts with iodine formed in the second reaction as shown below.

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

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

When the I_2 produced has reacted with all of the limited amount of thiosulfate ions present, excess I_2 remains in solution. Reaction with the starch then suddenly forms a dark blue-black colour.
A series of experiments is carried out, in which the concentration of iodide ions is varied, while keeping the concentrations of all of the other reagents the same. In each experiment the time taken (t) for the reaction mixture to turn blue is measured.

In clock reactions there are often two successive reactions. The end point is achieved when one limited reactant runs out, resulting in a sudden colour change.

By repeating the experiment several times, varying the concentration of a reactant e.g. I^-, (keeping the other reactants at constant concentration)you can determine the order of reaction with respect to that reactant

The initial rate of the reaction can be represented as (1/t)

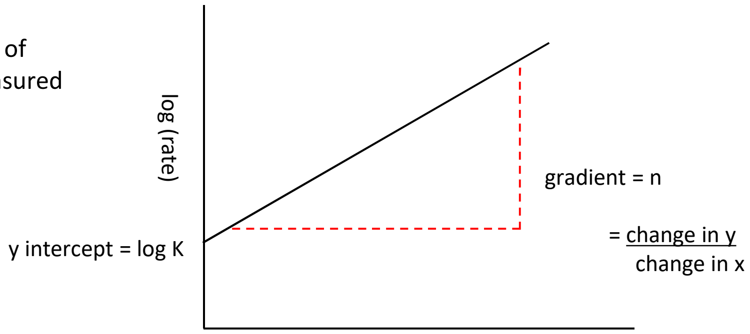
Experiment	Volume in cm^3 Sulfuric acid (H^+)	Volume in cm^3 Starch	Volume in cm^3 Water	Volume in cm^3 Potassium iodide(I^-)	Volume in cm^3 Sodium Thiosulfate $S_2O_3^{2-}$
1	25	1	20	5	5
2	25	1	15	10	5
3	25	1	10	15	5
4	25	1	5	20	5
5	25	1	0	25	5

Working out orders from experimental initial rate data

Normally to work out the rate equation we do a series of experiments where the initial concentrations of reactants are changed (one at a time) and measure the initial rate each time.

Working out order graphically

In an experiment where the concentration of one of the reagents is changed and the reaction rate measured it is possible to calculate the order graphically



Taking rate equation

Rate = k $[Y]^n$

Log both sides of equation

Log rate = log k + n log [Y]

Y = c + m x

A graph of log rate vs log [Y] will yield a straight line where the gradient is equal to the order n

In this experiment high concentrations with quick times will have the biggest percentage errors.

Initial rate data can also be presented in a table.

Example 3: Deduce the rate equation for the following reaction, **A+ B+ 2C → D + 2E,** using the initial rate data in the table

Experiment	[A] mol dm^{-3}	[B] mol dm^{-3}	[C] mol dm^{-3}	Rate mol dm^{-3} s^{-1}
1	0.1	0.5	0.25	0.1
2	0.2	0.5	0.25	0.2
3	0.1	1.0	0.25	0.4
4	0.1	0.5	0.5	0.1

In order to calculate the order for a particular reactant it is easiest to compare two experiments where **only that reactant** is being changed.

If conc is doubled and rate stays the same: order= 0

If conc is doubled and rate doubles: order= 1

If conc is doubled and rate quadruples : order= 2

For reactant **A** compare between experiments **1 and 2**

For reactant **A** as the concentration **doubles** (B and C staying constant) so does the rate. Therefore the order with respect to reactant **A is first order**

For reactant **B** compare between experiments **1 and 3** :

As the concentration of **B doubles** (A and C staying constant) the rate **quadruples**.

Therefore the order with respect to **B is 2nd order**

For reactant **C** compare between experiments **1 and 4** :

As the concentration of **C doubles** (A and B staying constant) the rate **stays the same**.

Therefore the order with respect to **C** is zero order

The overall rate equation is r = k [A] $[B]^2$

The reaction is 3rd order overall and the unit of the rate constant =$mol^{-2}dm^6s^{-1}$

Working out orders when two reactant concentrations are changed simultaneously

In some questions it is possible to compare between two experiments where only one reactant has its initial concentration changed. If, however, both reactants are changed then the effect of both individual changes on concentration are multiplied together to give on overall change on rate.

In a reaction where the rate equation is r = k [A] $[B]^2$

If the [A] is x2 that rate would **x2**

If the [B] is x3 that rate would $x3^2$= **x9**

If these changes happened at the same time then the rate would x2x9= **x 18**

Example 4 Deduce the rate equation for the reaction, between X and Y, using the initial rate data in the table

Experiment	Initial concentration of X/ mol dm^{-3}	Initial concentration of Y/ mol dm^{-3}	Initial rate/ mol dm^{-3} s^{-1}
1	0.05	0.1	0.15×10^{-6}
2	0.10	0.1	0.30×10^{-6}
3	0.20	0.2	2.40×10^{-6}

For reactant X compare between experiments **1 and 2**

For reactant X as the concentration **doubles** (Y staying constant) so does the rate. Therefore the order with respect to reactant **X is first order**

Comparing between experiments 2 and 3 :

Both **X and Y double** and the **rate goes up by 8**

We know X is first order so that will have doubled rate

The effect of Y, therefore, on rate is to have quadrupled it.

Y must be second order

The overall rate equation is r = k [X] $[Y]^2$

The reaction is 3^{rd} order overall and the unit of the rate constant =$mol^{-2}dm^6s^{-1}$

Calculating a value for k using initial rate data

Using the above example, choose any one of the experiments and put the values into the rate equation that has been rearranged to give k. Using experiment 3:

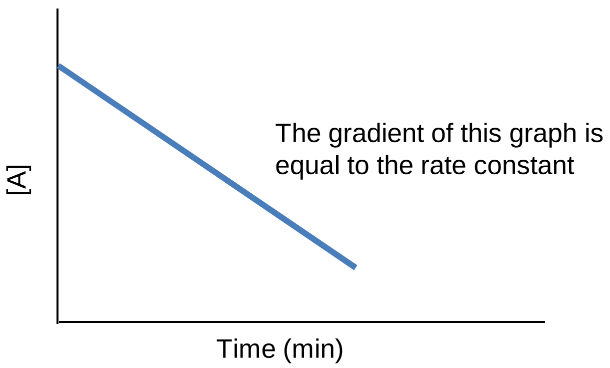
$$r = k [X] [Y]^2 \longrightarrow k = \frac{r}{[X][Y]^2} \qquad k = \frac{2.40 \times 10^{-6}}{0.2 \times 0.2^2} \qquad \mathbf{k = 3.0 \times 10^{-4}\ mol^{-2}dm^6s^{-1}}$$

Remember k is the same for all experiments done at the same temperature.

Increasing the temperature increases the value of the rate constant k

zero order: Calculating k from concentration-time graphs

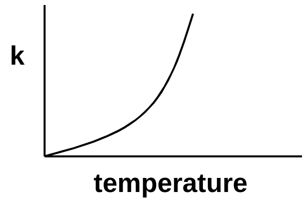
For zero order reactants, the rate stays constant as the reactant is used up. This means the concentration of that reactant has no effect on rate.
Rate = k $[A]^0$ so rate = k
As the rate is the gradient of the graph on the right, the gradient is also the value of the rate constant.



Effect of temperature on rate constant: the Arrhenius equation

Increasing the temperature increases the value of the rate constant k

Increasing temperature increases the rate constant k.
The relationship is given by the Arrhenius equation $\mathbf{k} = Ae^{-E_A/RT}$ where A is the Arrhenius constant, R is the gas constant, and E_A is activation energy.



Using the Arrhenius equation (equations will be given in the exam)

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

The Arrhenius equation is usually rearranged to

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

You should be able to do rearrangements and substitute values into both these equations.

Units
Temperature uses the unit **K**
R = 8.31 J $mol^{-1}K^{-1}$
Activation energy will need to be in **J mol^{-1}** to match the units of R
The unit of the Arrhenius constant A will be the same as the unit of the rate constant k

Example 5
A reaction carried out at 35°C has a value of $k = 4.26 \times 10^{-8}\ s^{-1}$
The activation energy $Ea = 95.8$ kJ mol^{-1}
The gas constant $R = 8.31$ J $K^{-1}\ mol^{-1}$
Calculate a value for the Arrhenius constant, A, for the reaction.

Using Equation $\mathbf{k} = Ae^{-E_A/RT}$

Rearrange to $A = \dfrac{k}{e^{-E_A/RT}} = \dfrac{4.26 \times 10^{-8}}{e^{-95800/(8.31 \times 308)}} = \dfrac{4.26 \times 10^{-8}}{e^{-37.4}} = \dfrac{4.26 \times 10^{-8}}{5.55 \times 10^{-17}}$

$= 7.67 \times 10^{8}\ s^{-1}$

Example 6
A reaction carried out at 25°C has a value of $k = 3.3 \times 10^{-3}\ mol^{-1}\ dm^{3}\ s^{-1}$
$\ln A = 17.1$
The gas constant $R = 8.31$ J $K^{-1}\ mol^{-1}$
Calculate a value for the activation energy in kJ mol^{-1}

Using Equation $\ln k = \ln A - E_A/(RT)$

Rearrange to $E_A = (\ln A - \ln k) \times RT$

$= (17.1 - -5.71) \times 8.31 \times 298$

$= 56486$ J mol^{-1}

$= 56.5$ kJ mol^{-1}

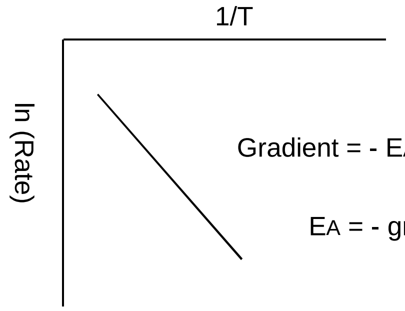
Calculating the activation energy graphically from experimental data

Using the rearranged version

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

k is proportional to the rate of reaction so ln k can be replaced by ln(rate)

From plotting a graph of ln(rate) or ln k against 1/T the activation energy can be calculated from measuring the gradient of the line.



Gradient = $- E_A / R$

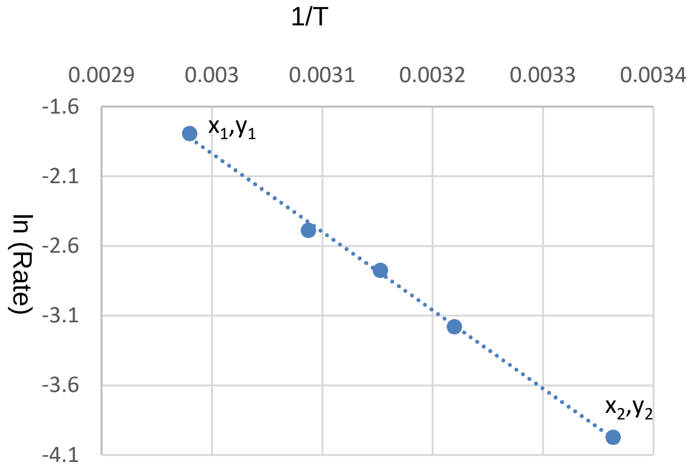
E_A = - gradient x R

Example 7

Temperature T (K)	1/T	time t (s)	1/t	Ln (1/t)
297.3	0.003364	53	0.018868	-3.9703
310.6	0.00322	24	0.041667	-3.1781
317.2	0.003153	16	0.0625	-2.7726
323.9	0.003087	12	0.083333	-2.4849
335.6	0.00298	6	0.166667	-1.7918

gradient = $\dfrac{y_2 - y_1}{x_2 - x_1}$

The gradient should always be -ve



- use a line of best fit
- the plotted points should fill all graph paper (generally don't start at the origin)
- choose points far apart on the graph to calculate the gradient

In above example gradient =-5680

E_A = - gradient x R (8.31)
= - -5680 x8.31
= 47200 J mol^{-1}

The unit of E_A using this equation will be J mol^{-1} .
Convert into kJ mol^{-1} by dividing 1000
E_A = +47.2 kJ mol^{-1}

Rate Equations and Mechanisms

A mechanism is a series of steps through which the reaction progresses, often forming intermediate compounds. If all the steps are added together they will add up to the overall equation for the reaction

Each step can have a different rate of reaction. The slowest step will control the overall rate of reaction. **The slowest step is called the rate-determining step**.

The molecularity (number of moles of each substance) of the molecules in the slowest step will be the same as the order of reaction for each substance.
e.g. 0 moles of A in slow step would mean A is zero order.
1 mole of A in the slow step would mean A is first order

Example 8

overall reaction

A + 2B + C → D + E

Mechanism

Step 1 **A + B → X + D** **slow**
Step 2 X + C → Y fast
Step 3 Y + B → E fast

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

C is zero order as it appears in the mechanism in a fast step after the slow step

Example 9

overall reaction

A + 2B + C → D + E

Mechanism

Step 1 A + B → X + D fast
Step 2 **X + C → Y** **slow**
Step 3 Y + B → E fast

$r = k [X]^1[C]^1$

The intermediate X is not one of the reactants so must be replaced with the substances that make up the intermediate in a previous step

A + B → X + D

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

Example 10

Overall Reaction

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Mechanism:

Step 1 $NO_2 + NO_2 \rightarrow NO + NO_3$ slow
Step 2 $NO_3 + CO \rightarrow NO_2 + CO_2$ fast

• NO_3 is a reaction intermediate

NO_2 appears twice in the slow steps so it is second order. CO does not appear in the slow step so is zero order.

$r = k [NO_2]^2$

Example 11

Using the rate equation rate = $k[NO]^2[H_2]$ and the overall equation $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$, the following three-step mechanism for the reaction was suggested. X and Y are intermediate species.

Step **1 NO + NO → X**
Step **2 X + H_2 → Y**
Step **3 Y + H_2 → N_2 + $2H_2O$**

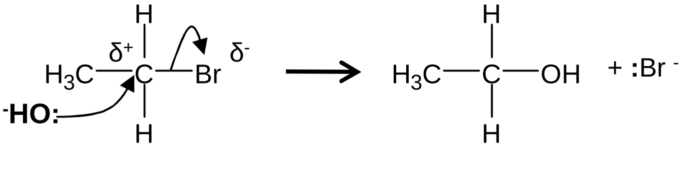
Which one of the three steps is the rate-determining step**?**

Step 2 – as H_2 appears in rate equation and combination of step 1 and 2 is the ratio that appears in the rate equation.

Example12: S_N1 or S_N2? You don't need to remember the details here.

Remember the nucleophilic substitution reaction of halogenoalkanes and hydroxide ions.

This is a one step mechanism



$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$ slow step

The rate equation is

$r = k [CH_3CH_2Br] [OH^-]$

This is called S_N2.
Substitution, **N**ucleophilic, **2** molecules in rate determining step

The same reaction can also occur via a different mechanism

Overall reaction

$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$

Mechanism:

$(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$ slow
$(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ fast

The rate equation is

$r = k [(CH_3)_3CBr]$

This is called S_N1.
Substitution, **N**ucleophilic, **1** molecule in rate determining step