6.2 Rate expression and reaction mechanism (HL)

6.2.1 The rate equation/rate expression

Learning objectives

- Explain the terms rate constant and order of reaction
- Work out the rate expression (rate equation) from numerical data and solve problems related to it
- Sketch and explain graphs of concentration against time and rate against time for zero-, first-and second-order reactions

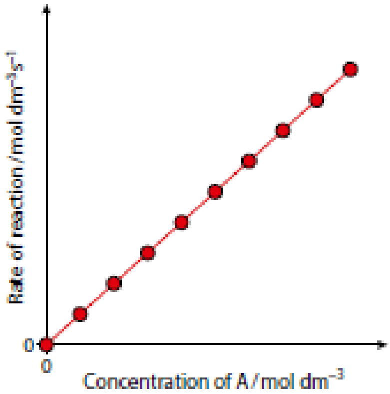
A rate of reaction is usually affected by a change in concentration of the reactants.
Consider the reaction A → B. If a series of experiments is carried out in which the concentration of A is varied and the rate of reaction measured plotted against concentration is a straight line through the origin, the rate of reaction is directly proportional to the concentration of A.

$$\text{rate} \propto [A]$$

where [A] is the concentration of A.

$$\text{so, rate} = k[A]$$

This equation is called a **rate equation** or **rate expression** – *k* is called the **rate constant**. A rate equation is also called a rate law.



The rate equation is an experimentally determined equation that relates rate of reaction to the concentrations of substances in the reaction mixture in a series of experiments.
For example, for the reaction:
W + X → Y + Z we can write: **rate = $k[W]^m[X]^n$**
The rate constant is only a constant for a particular reaction at a chosen temperature. The powers m and n are called order of the reaction.
In the rate equation above, the order with respect to W is *m* and the order with respect to X is *n*. The overall order is *m* + *n*.

If rate =k[A], this reaction is first order with respect to A and first order overall.

Fractional orders are only found in complex chain reactions. For example,the pyrolysis of ethane to ethene and hydrogen:

$C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$ involves a complex chain reaction and has a rate equation of the form:

rate = $k[C_2H_6]^{1/2}$.

6.2.2 Experimental determination of a rate equation

For the reaction A + B → C, the dependence of the reaction rate on the concentrations of A and B can be determined by conducting the following set of experiments. The initial rate is taken because this is the only point at which we know the concentration of A and concentration of B – none has been used up.

1. A series of experiments is carried out using a fixed amount of B and changing the concentration of A each time. Plot a graph of concentration of A against time and find the initial rates. Plot a graph of initial rate against concentration of A to find the reaction order with respect to A.

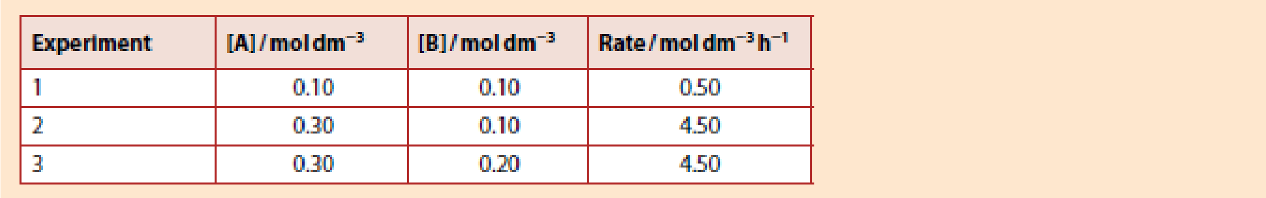
2. Next, the experiments are repeated using a fixed amount of A and varying the concentration of B. This allows the order of reaction with respect to B to be calculated.

3. Use the orders with respect to A and B to find the rate equation, and hence a value for the rate constant.

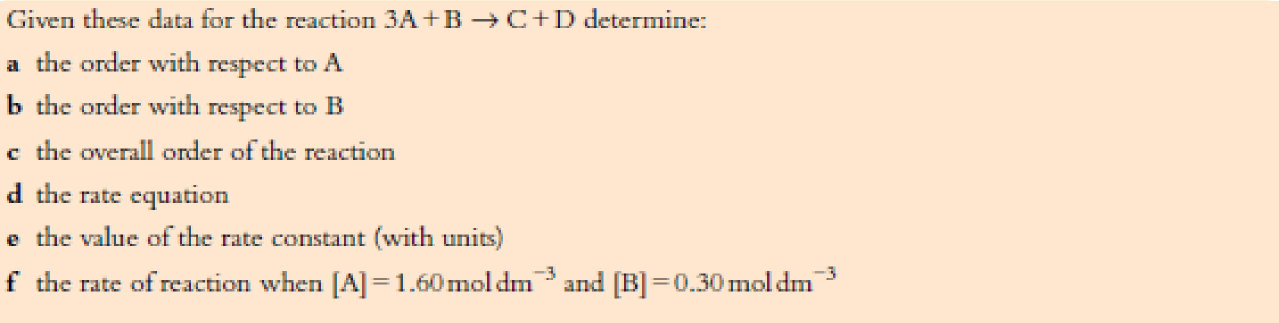
Example 1:
Consider the data for the reaction 2A → B, given in Table below to find;
a.the order with respect to A
b.the rate equation
c.the value of the rate constant (with units)
d.the rate of reaction when [A] = 1.3 mol dm^{-3}.

Experiment	**[A] / mol dm^{-3}**	**Rate / mol dm^{-3} s^{-1}**
1	1.0	0.60
2	2.0	1.20
3	5.0	3.00

Example 2



Experiment	[A] / mol dm^{-3}	[B] / mol dm^{-3}	Rate / mol dm^{-3} h^{-1}
1	0.10	0.10	0.50
2	0.30	0.10	4.50
3	0.30	0.20	4.50



Given these data for the reaction $3A + B \rightarrow C + D$ determine:

a the order with respect to A

b the order with respect to B

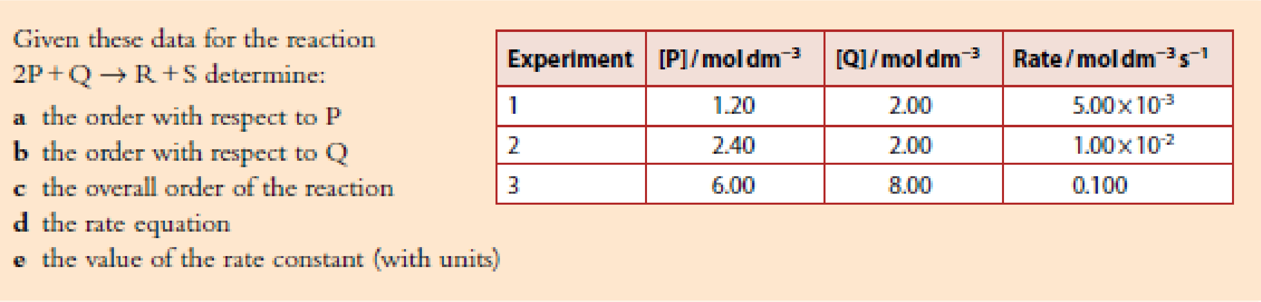
c the overall order of the reaction

d the rate equation

e the value of the rate constant (with units)

f the rate of reaction when $[A] = 1.60$ mol dm^{-3} and $[B] = 0.30$ mol dm^{-3}

Example 3



Given these data for the reaction $2P + Q \rightarrow R + S$ determine:

a the order with respect to P
b the order with respect to Q
c the overall order of the reaction
d the rate equation
e the value of the rate constant (with units)

Experiment	**[P] / mol dm^{-3}**	**[Q] / mol dm^{-3}**	**Rate / mol dm^{-3} s^{-1}**
1	1.20	2.00	5.00×10^{-3}
2	2.40	2.00	1.00×10^{-2}
3	6.00	8.00	0.100

Graphical representations of reaction kinetics

Zero-order reaction

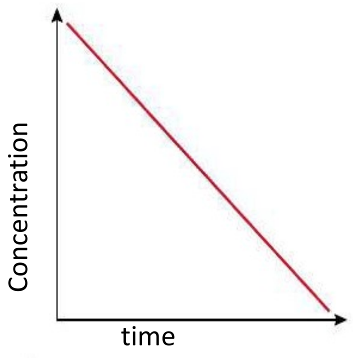
Here the concentration of reactant A does not affect the rate of the reaction.
rate = $k[A]^0$ or rate = k

For example,the decomposition of ammonia on a tungsten surface:

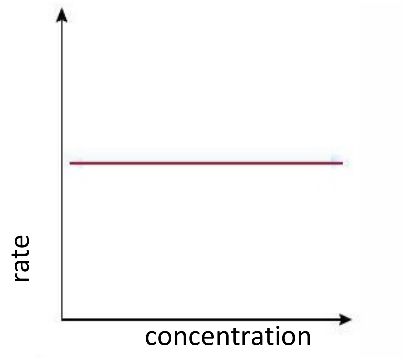
$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

The concentration of ammonia decreases at a constant rate in this reaction.

So the concentration–time graph is a straight line, showing a constant rate. The gradient of the line = k. The rate–concentration graph is a horizontal line.



a

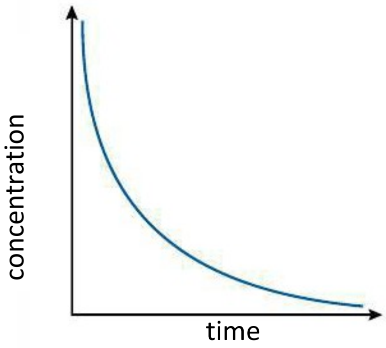


b

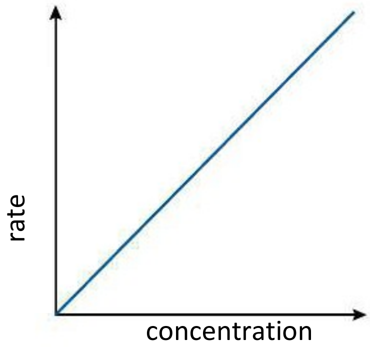
Changing the concentration of ammonia has no effect on the rate of the reaction (b).
The rate equation is rate = k, which shows that the rate is constant.
The units of the rate constant are the same as the rate: *concentration* × *time*$^{-1}$. A set of units for the rate constant could therefore be mol dm^{-3} s^{-1}.

First-order reaction

Here the rate is directly proportional to the concentration of A.
rate = k_[A]
So the concentration–time graph is a curve showing rate decreasing with concentration , the rate–concentration graph is a straight line passing through the origin with gradient k



a



b

For example the decomposition of hydrogen iodide on a platinum surface.

$2HI(g) \rightarrow H_2(g) + I_2(g)$

The rate of this reaction is directly proportional to the concentration of HI, as shown by the straight line through the origin (b).

The graph in Fig (a) shows how the concentration of HI decreases with time. This shows an exponential decay and a constant **half-life**. The time taken for the concentration to drop by half does not depend on concentration in a first-order reaction.

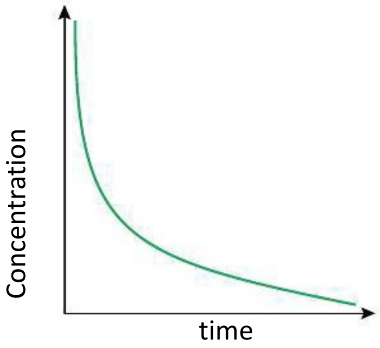
The rate equation for this reaction is: rate = k[HI].
The units of k are time^{-1}.

Second-order reaction

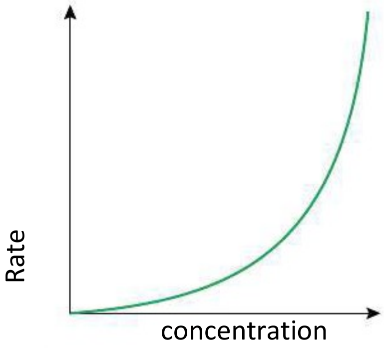
Here the rate is proportional to the square of the concentration of A.

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

So the concentration–time graph is also a curve, steeper at the start than the first-order graph and levelling off more. The rate–concentration graph is a parabola, characteristic of the square function. The gradient here is proportional to the concentration and is initially zero.



a



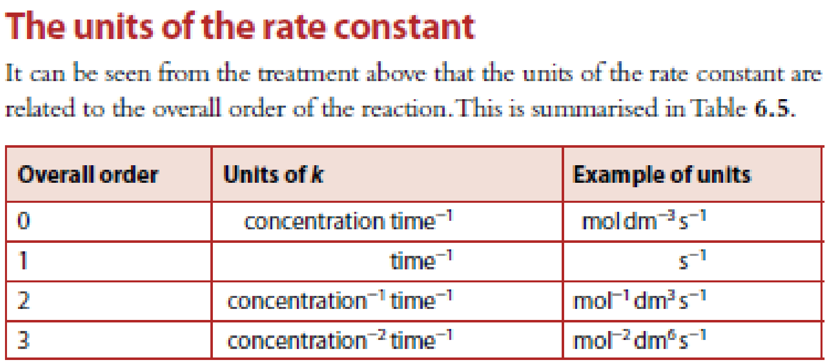
b

Example: the decomposition of hydrogen iodide without a catalyst:

$2HI(g) \rightarrow H_2(g) + I_2(g)$

It can be proved that a reaction is second order (rather than third order, etc.) by plotting a graph of rate against concentration of HI squared. As the rate is proportional to $[HI]^2$, this graph is a straight line through the origin.

The rate equation for this reaction is rate = $k[HI]^2$.
The units of the rate constant are concentration^{-1} time^{-1} (i.e. units could be mol^{-1} dm^3 s^{-1}).



The units of the rate constant

It can be seen from the treatment above that the units of the rate constant are related to the overall order of the reaction. This is summarised in Table **6.5**.

Overall order	Units of *k*	Example of units
0	concentration time^{-1}	mol dm^{-3} s^{-1}
1	time^{-1}	s^{-1}
2	concentration^{-1} time^{-1}	mol^{-1} dm^3 s^{-1}
3	concentration^{-2} time^{-1}	mol^{-2} dm^6 s^{-1}

For a zero-order reaction, the units of *k* are the same as that of the rate. Each time the overall order increases by 1 the units of *k* are divided by concentration.

6.2.3 Reaction mechanism

Learning objectives

- Understand what is meant by the mechanism of a reaction and the rate-determining step
- Work out reaction mechanisms from experimental data and relate a given mechanism to the experimental data

Introduction

Most reactions that occur at a measurable rate occur as a series of simple steps, each involving a small number of particles (collision theory).
This sequence of steps is known as the **reaction mechanism**. The individual steps, called **elementary steps**, usually cannot be observed directly, so the mechanism is in effect a *theory* about the sequence of events.
It is worth noting though, that while kinetic evidence can help to support a particular mechanism, **it cannot *prove* it to be correct – only that it is consistent with the observed data.**

The order of a chemical equation cannot be derived directly from a chemical equation.

If in the reaction; $2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$ were all to occur in one single step, all three molecules must collide together at exactly the same time.

The rate of reaction in this case would therefore depend on [NO2]2 and [F2], and the rate equation would be:

rate = $k[NO_2]2[F_2]$

The actual rate equation obtained from experiment is, however,

rate = $k[NO_2][F_2]$

So the reaction does not occur in just one step in which all three molecules collide and break apart to form the products. The chance of three gas molecules all colliding at exactly the same time is extremely small.
It is most likely that each step involves just two molecules colliding.

A reaction mechanism consists of a series of steps that make up a more complex reaction. Each simple step involves a maximum of two molecules colliding.

The proposed mechanism for this reaction is:

$NO_2 + F_2 \rightarrow NO_2F + F$ step 1
$NO_2 + F \rightarrow NO_2F$ step 2

The mechanism must agree with the overall chemical equation. This can be checked by adding the two equations (steps) together and cancelling the species that are on both sides.

$$\begin{array}{ll} NO_2 + F_2 \rightarrow NO_2F + \cancel{F} & \text{step 1} \\ NO2 + \cancel{F} \rightarrow NO2F & \text{step 2} \\ \hline 2NO_2 + F_2 \rightarrow 2NO_2F & \text{overall equation} \end{array}$$

F is an intermediate and is used up in step 2
Rate expression for each stage:

Step 1: rate = $k_1[NO_2][F_2]$
Step 2: rate = $k_2[NO_2][F]$

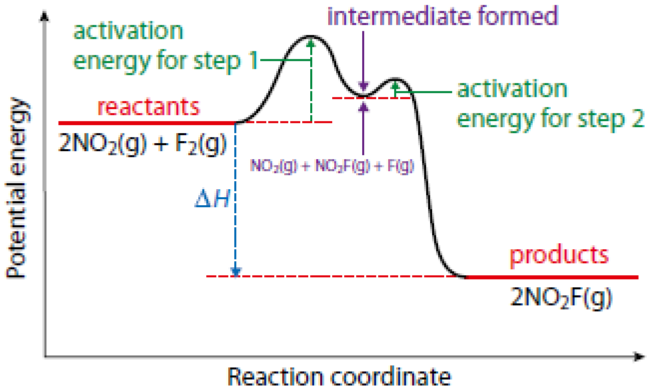
The rate equation for step 1 is the same as the experimental rate equation, and so it would seem that this step governs the overall rate of reaction.
The second step has no apparent effect on the rate. Step 1 is called the rate-determining step of the mechanism and occurs significantly more slowly than step 2.

slow
$NO_2 + F_2 \rightarrow NO2F + F$ **step 1 rate-determining step**

fast
$NO_2 + F \rightarrow NO_2F$ **step 2**

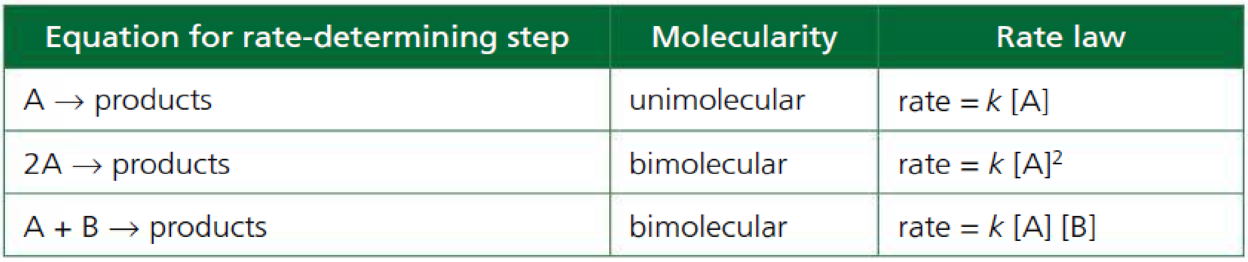
This means that changing the concentrations of the species present in the fast second step does not affect the rate of the reaction to any great extent.
The slowest step in a reaction mechanism is called the rate-determining step.

The potential energy profile for this reaction shows that the rate-determining step (step 1) has a much higher activation energy than the other step.



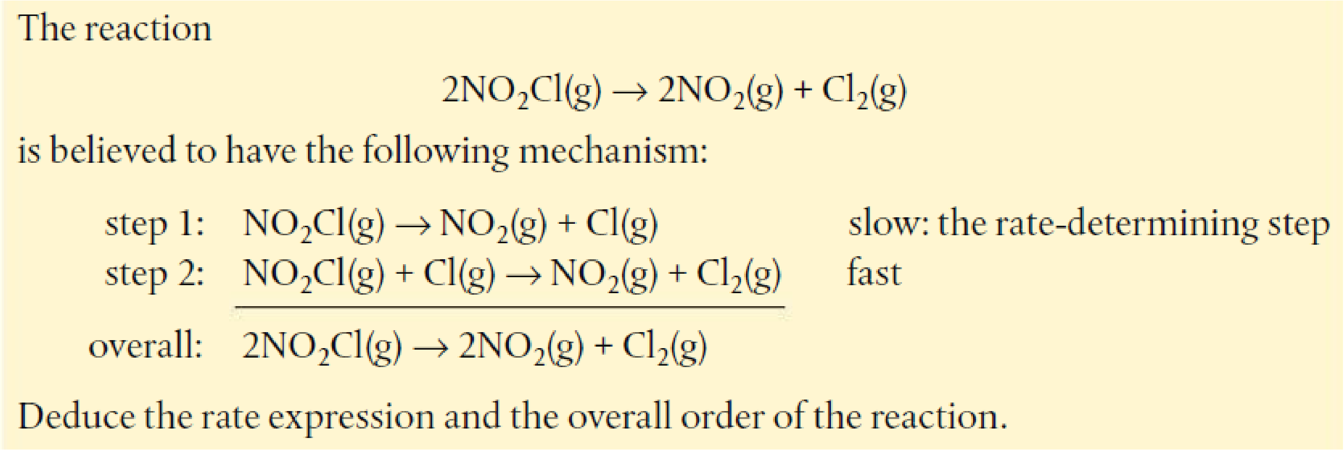
Potential energy profile for a two-step reaction. The formation of an intermediate is shown by the potential energy well in the profile.

The term **molecularity** is used in reference to an elementary step to indicate the number of reactant species involved. So **unimolecular** refers to an elementary step that involves a single reactant particle, **bimolecular** refers to an elementary step with two reactant particles. In the reactions above both steps are bimolecular. **Termolecular** reactions (those that involve three reactant particles) are rare (collision theory supports).



Equation for rate-determining step	Molecularity	Rate law
A → products	unimolecular	rate = k [A]
2A → products	bimolecular	rate = k $[A]^2$
A + B → products	bimolecular	rate = k [A] [B]

Example 1



The reaction

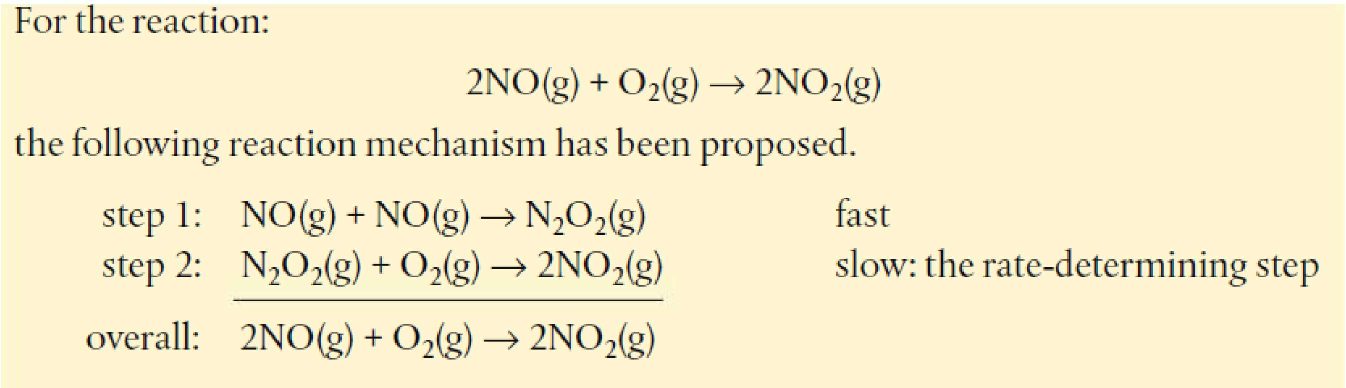
$$2NO_2Cl(g) \rightarrow 2NO_2(g) + Cl_2(g)$$

is believed to have the following mechanism:

step 1: $NO_2Cl(g) \rightarrow NO_2(g) + Cl(g)$ slow: the rate-determining step
step 2: $NO_2Cl(g) + Cl(g) \rightarrow NO_2(g) + Cl_2(g)$ fast

overall: $2NO_2Cl(g) \rightarrow 2NO_2(g) + Cl_2(g)$

Deduce the rate expression and the overall order of the reaction.



For the reaction:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

the following reaction mechanism has been proposed.

step 1: $NO(g) + NO(g) \rightarrow N_2O_2(g)$ fast
step 2: $N_2O_2(g) + O_2(g) \rightarrow 2NO_2(g)$ slow: the rate-determining step
overall: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

a. What is the rate expression and the overall order for the reaction?
b. From the examples, what does it mean for a reaction to be zero order with respect to a particular reactant?

TOK

Reaction mechanisms can be supported by indirect evidence but cannot be observed. What evidence would be needed to accept a proposed reaction mechanism as certain?

Reactions involving a catalyst

Consider;

CH3COCH3(aq) + I2(aq) → CH3COCH2I(aq) + HI(aq)

This reaction is acid (H^+) catalysed. The experimental rate equation is:
rate = k[CH3COCH3][H^+]

The rate equation does not include I2, so this must be involved only after the rate-determining step.
The mechanism could be proposed as:
CH3COCH3 + **H^+** → X **rate-determining step (**X is an intermediate).
X + I2 → CH3COCH2I + HI + **H^+** **fast**

H^+ will cancel out when the equations are added together.
The catalyst is involved in the rate-determining step but is regenerated in the second step and therefore does not appear in the overall chemical equation.

Catalysts change a reaction mechanism, allowing the reaction to occur via an alternative pathway that has a lower activation energy.

Nature of science

The principle of Occam's (Ockham's) razor is often used in science to decide between different theories.It involves the idea that if there are two theories that give equally acceptable explanations of experimental data, the simpler one should be adopted.

This is often used to decide between different reaction mechanisms.

We should seek the simplest possible mechanism that is consistent with the rate equation and the stoichiometric equation.

6.3 Activation energy: The rate constant *k* is temperature dependent.

The Arrhenius equation

Learning objectives

- Understand that increasing the temperature causes the rate constant to increase
- Work out values of activation energy and the frequency factor (pre-exponential factor) using the Arrhenius equation

In a rate equation such as rate = *k*[A][B],as the temperature increases, the rate constant increases exponentially.

The temperature dependence of the rate constant is expressed in the Arrhenius equation.

Svante Arrhenius showed that the fraction of molecules with energy greater than activation energy, *E*a, at temperature *T* is proportional to the expression:

$$e^{-\frac{Ea}{RT}}$$

where *R* is the gas constant (= 8.31 J K–1 mol–1) and *T* is the absolute temperature (in K). This must mean that the reaction rate, and therefore also the rate constant, are also proportional to this value.

So we can write;

k $\alpha\ e^{-\frac{Ea}{RT}}$ and k$= A\ e^{-\frac{Ea}{RT}}$

where;

- *A* is called the frequency factor (also called the pre-exponential factor, *A*-factor **or Arrhenius constant**) and takes account of the **frequency** of collisions and the **orientation** of the collisions.
- $e^{-\frac{Ea}{RT}}$ represents the fraction of collisions that have *E* ≥ *E*a. However, not all collisions with *E* ≥ *E*a result in reaction and **A** contains a factor that allows for this to be considered.

Using the Arrhenius equation to calculate activation energy

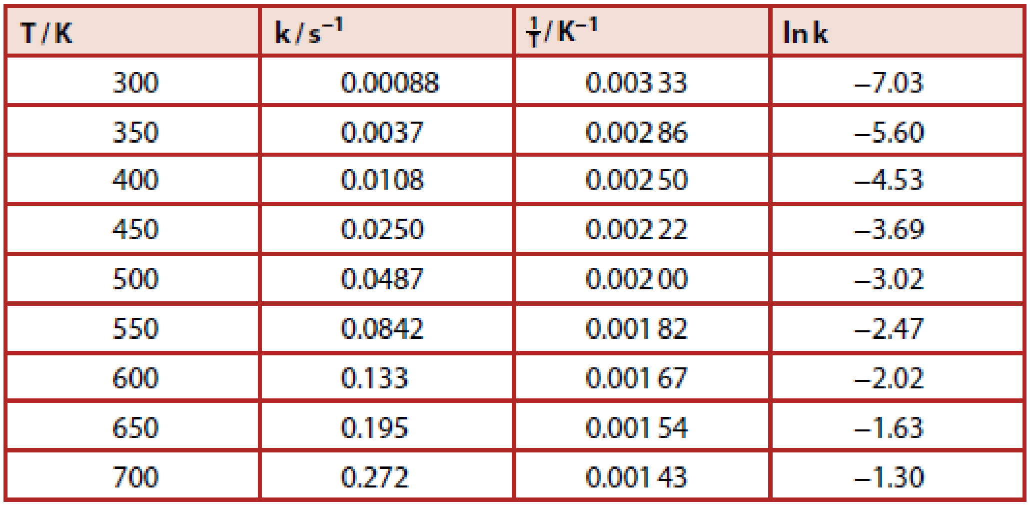
If we take the natural logarithm (logarithm to base e) of both sides of the equation above, we find that

$$\text{Ink} = -\frac{Ea}{RT}\times\frac{1}{T} + \text{InA}$$

This is a form of the equation for a straight line $y = mx + c$. So a graph of ln_k (y-axis) against $1/T$ (x-axis) will give a straight line with gradient (m) = $-Ea/R$. This is known as an **Arrhenius plot.**
R is the gas constant (8.31$JK^{-1}mol^{-1}$) and so

Gradient =-$\frac{Ea}{R}$ and – Ea = gradient x R

Example



T / K	k / s^{-1}	$\frac{1}{T}$ / K^{-1}	ln k
300	0.00088	0.003 33	−7.03
350	0.0037	0.002 86	−5.60
400	0.0108	0.002 50	−4.53
450	0.0250	0.002 22	−3.69
500	0.0487	0.002 00	−3.02
550	0.0842	0.001 82	−2.47
600	0.133	0.001 67	−2.02
650	0.195	0.001 54	−1.63
700	0.272	0.001 43	−1.30

Graph

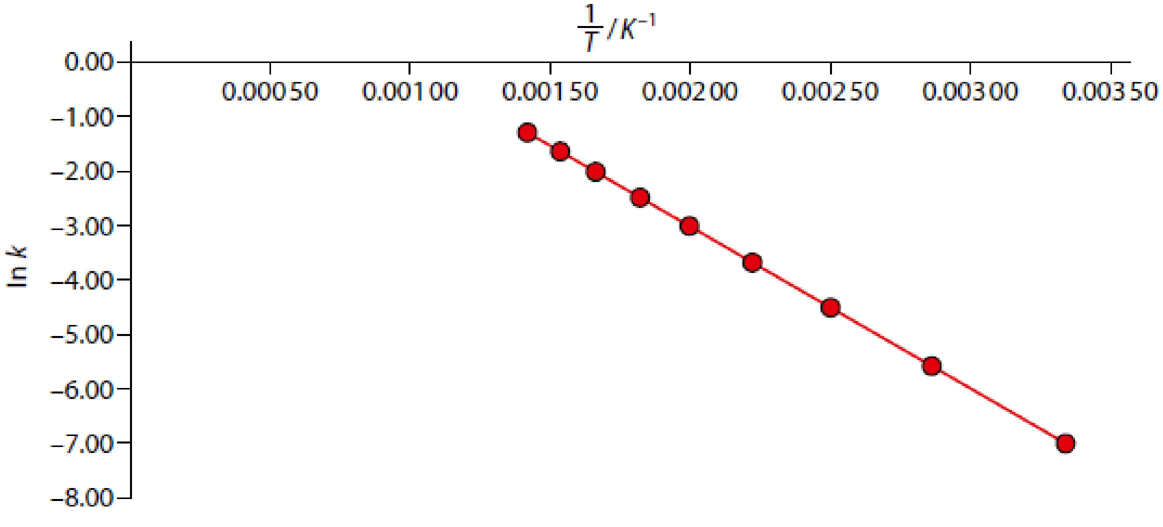


Figure 6.32 ln k (y-axis) against $\frac{1}{T}$ (x-axis).

By comparing the Arrhenius equation with the equation of a straight line ($y = mx + c$, where m is the gradient and b is the intercept on the y-axis) we see why the graph is a straight line.

$$\begin{array}{ccccccc} \ln k & = & \dfrac{-E_a}{R} & \times & \dfrac{1}{T} & + & \ln A \\ y & = & m & & x & + & c \end{array}$$