

Chemistry³

introducing inorganic, organic and physical chemistry

second edition

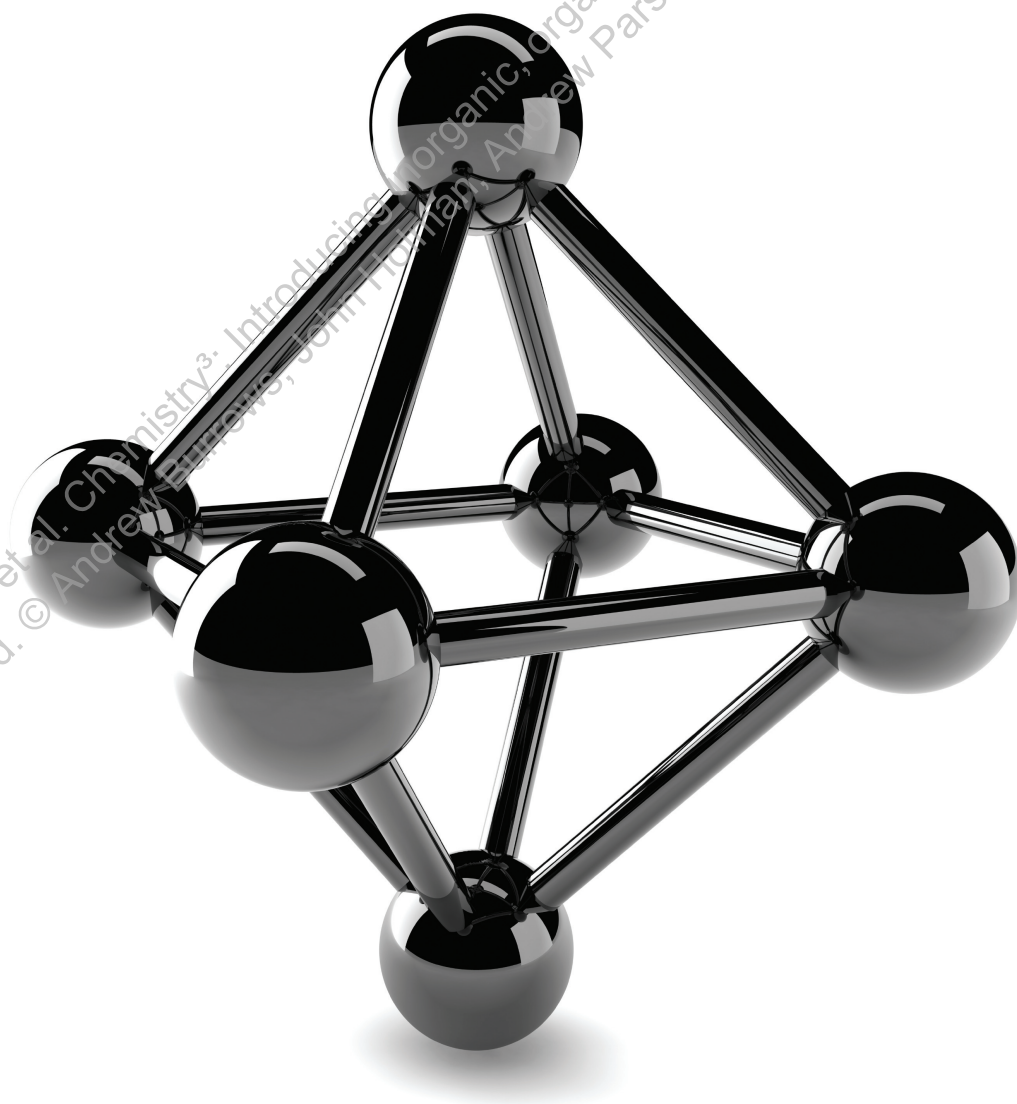
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Impression: 1

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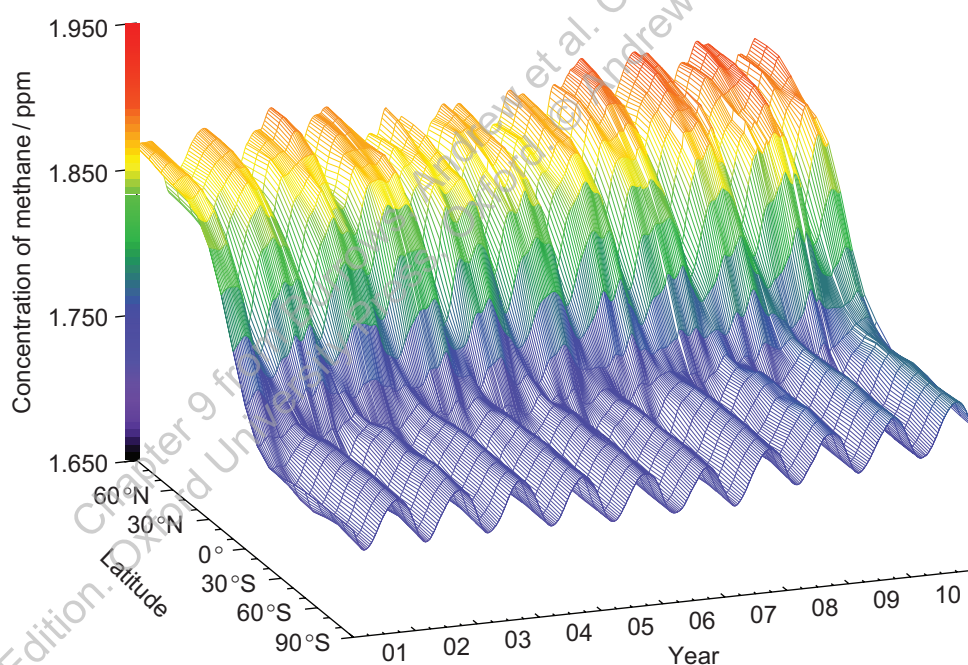
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9

Reaction kinetics

▼ A global plot of methane concentrations in the troposphere showing the variation with time and latitude. (The colours show the concentration ranges indicated on the vertical axis.) The concentration is higher in the Northern Hemisphere than it is in the Southern Hemisphere, because more methane is emitted in the Northern Hemisphere and the transfer of air across the Equator is slow. © NOAA



Three-dimensional representation of the latitudinal distribution of atmospheric methane in the marine boundary layer. Data from the Carbon Cycle cooperative air sampling network were used. The surface represents data smoothed in time and latitude. Contact: Dr. Ed Dlugokencky, NOAA ESRL Carbon Cycle, Boulder, Colorado, (303) 497-6228, ed.dlugokencky@noaa.gov, <http://www.esrl.noaa.gov/gmd/ccgg/>.

This chapter builds on the following topics:

- Measurement, units, and nomenclature Section 1.2, p.7
- Amount of substance and molar mass Section 1.3, p.18
- Balancing equations Section 1.4, p.21
- Concentrations of solutions Section 1.5, p.34
- Enthalpy profiles for exothermic and endothermic processes Section 1.6, p.45
- Chemical equilibrium: how far has a reaction gone? Section 1.9, p.56
- Kinetic molecular theory and the gas laws Section 8.4, p.354
- The distribution of molecular speeds Section 8.5, p.359

◀ Note that the peaks in the Northern Hemisphere coincide with the troughs in the Southern Hemisphere.

Increased concentrations of methane in the troposphere are thought to be due to melting permafrost in regions of Arctic tundra. ▶

Methane in the troposphere

Methane absorbs infrared radiation and is an important greenhouse gas. To investigate the link between increased concentrations of greenhouse gases and climate change, scientists need information about the processes that release methane into the atmosphere and about what happens to the methane once there. In particular, they need to know *how quickly* the methane is removed and what is its *average lifetime* in the troposphere (the lower atmosphere). (Box 9.3 on p.396 discusses the significance of the average lifetime of emitted methane.)

Methane is emitted from a variety of natural and human-related sources. It is produced when bacteria living in airless (anaerobic) places break down carbohydrates. The biggest emissions come from wetlands, ruminant animals (such as cattle), and biomass burning. The average concentration of methane in the troposphere in 2010 was 1.79 ppm (by volume). This is a substantial increase from its pre-industrial (1750–1800) concentration of around 0.7 ppm.

The main way methane is removed from the troposphere is by reaction with hydroxyl radicals, $\bullet\text{OH}$. The first step of this process is



in which the $\bullet\text{OH}$ radical removes a hydrogen atom from methane to form a molecule of water and a $\text{CH}_3\bullet$ radical. (You can read about the formation of radicals in Section 19.1, p.860.) The rate of the reaction of methane with $\bullet\text{OH}$ is crucial in determining the lifetime of methane molecules in the troposphere. The reaction is a simple elementary reaction (Section 9.4) and the rate of reaction is governed by the following rate equation

$$\text{rate of reaction} = k[\text{CH}_4][\bullet\text{OH}]$$

where k is the rate constant. The value of the rate constant, k , is related to how fast the reaction proceeds and is obtained from laboratory experiments.

In the troposphere, the concentration of methane is approximately constant (at least on a day to day basis—it is increasing but only slowly), which means methane must be removed at roughly the same rate as it is being emitted. So,

$$\begin{aligned} \text{the average rate of emission} &= \text{the average rate of removal} \\ &= k[\text{CH}_4][\bullet\text{OH}] \end{aligned}$$

where $[\text{CH}_4]$ and $[\bullet\text{OH}]$ are the average concentrations of CH_4 and $\bullet\text{OH}$, respectively.

Rearranging this equation, the average concentration of methane in the troposphere is given by

$$[\text{CH}_4] = \frac{\text{average rate of emission}}{k[\bullet\text{OH}]}$$

so that the concentration of methane depends inversely on the concentration of $\bullet\text{OH}$ radicals.

The three-dimensional figure opposite shows methane concentrations in the troposphere over a 10 year period. There is a seasonal variation because the reactions that generate $\bullet\text{OH}$ radicals from water require sunlight, so concentrations of $\bullet\text{OH}$ are higher in the summer months. Methane is, therefore, removed more rapidly in the summer and its concentration is lower.

Methane concentrations have been rising sharply since 2007, after a decade or so of holding fairly steady. There is concern that this may be due to the melting of permafrost in regions of Arctic tundra, which releases previously trapped methane into the atmosphere.



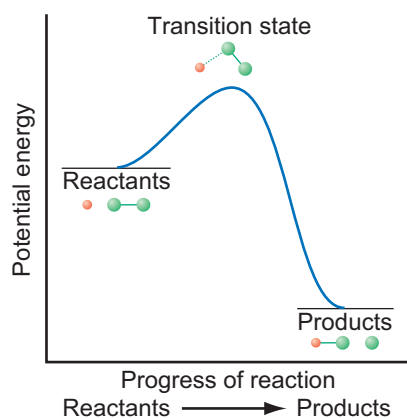


Figure 9.1 A general reaction profile showing the progress of an elementary reaction from reactants to products, via a transient, high-energy transition state.

Enthalpy profiles for exothermic and endothermic reactions are shown in Section 1.6 (p.46). Energy and enthalpy profiles are often called **reaction profiles**.



Paul Crutzen, Mario Molina, and F. Sherwood Rowland were awarded the Nobel Prize in Chemistry in 1995 for their work concerning the formation and removal of ozone in the stratosphere. You can read about some of the reactions involved in the ozone layer and the role of CFCs in ozone depletion in Box 27.6 (p.1227).



Much of chemistry is about reactions, so a knowledge of the rates at which they occur is of central importance. The study of rates of reactions is called **reaction kinetics**.

Kinetic studies provide information about the **mechanisms** of reactions—the detailed routes by which they take place. Most of the reactions you encounter are **complex reactions** in which an overall reaction takes place by a series of simple steps, called **elementary reactions**. The elementary reactions combine together to give the overall reaction. In this chapter, elementary reactions are discussed first in Section 9.4, followed by complex reactions in Section 9.5.

9.1 Why study reaction kinetics?

The study of reaction kinetics falls into two major areas. The first is a search for fundamental information about the interactions and energy changes that take place at a molecular level during an elementary reaction. The progress of a reaction can be charted by constructing an energy profile such as the one shown in Figure 9.1. At the highest energy on the curve is a transient structure, formed from the reactants, that can either return to the reactants, or go on to form the products. This is the *transition state* for the reaction. Detailed information about the structure of transition states contributes to an understanding of how the reactants are transformed into the products. Theories of how reactions take place are discussed in Section 9.8.

The second area of reaction kinetics involves the study of complex reactions, and the elementary reactions that make them up. Experimental studies on a reaction in solution might lead to the determination of a rate equation, which shows how the rate of a reaction depends on the concentrations of the reactants, and to a value of the rate constant for the reaction. Such experiments have provided much of the evidence for the mechanisms of chemical reactions, and examples of this are described in Section 9.6.

Rate constants are related to how fast a reaction proceeds at a particular temperature and compilations of rate constants are widely used in applications of gas phase reaction kinetics. Rate constants are the key to deciding on the relative importance of reactions in a system of interconnected reactions, such as exists in the atmosphere. A knowledge of rate constants of elementary reactions allowed, for example, the mechanism for ozone depletion in the stratosphere (upper atmosphere) to be worked out by Paul Crutzen.

In industry, the rates at which reactions occur are linked to profitability and safety. Understanding the factors that govern the rates, particularly temperature (Section 9.7), is essential. In the pharmaceutical industry, a knowledge of kinetics can help chemists maximize the formation of a desired product and minimize competing side-reactions.

An understanding of the role of catalysts in speeding up reactions, including the action of enzymes in living organisms, comes from kinetic studies. This is discussed in Section 9.9. First, though, the chapter starts by defining what is meant by the rate of a reaction (Section 9.2) and looks at ways of monitoring concentrations as a reaction proceeds (Section 9.3).

◀ Helium-filled balloons are sent up into the stratosphere carrying instruments to measure ozone concentrations, which can be used to study the kinetics of reactions in the stratosphere. This balloon is being launched near McMurdo Station, in Antarctica.

The rates of the reactions involved in food degradation are important in determining the shelf life of foods. ▶



9.2 What is meant by the rate of a reaction?

The **rate of a reaction** is the rate at which reactants are converted into products. You can measure this by monitoring either the consumption of a reactant or the formation of a product.



Iron powder burning—a chemical reaction with a fast rate.



Iron rusting—a chemical reaction with a slow rate.

i Unlike in a car, which has a speedometer to measure speed, reaction rate cannot be measured directly. Instead, you measure the concentration of a reactant or product at different times—just as you could measure the speed of a car by measuring the distance travelled after different times.

Consider first a simple reaction in which a single reactant is converted into a single product, for example, in an isomerization reaction

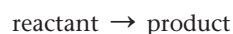


Figure 9.2 plots the concentration of the reactant against time. It shows how the rate of the reaction changes as the reaction proceeds and is called a **kinetic profile**. The curve is steepest at the start, when $t = 0$, and becomes progressively less steep as the reaction proceeds. At the end of the reaction, the plot becomes horizontal because the concentration of the reactant is no longer changing. The steepness of the curve tells you how fast the reaction is taking place. The rate of reaction at a particular instant can be found by drawing a tangent to the curve at that time and measuring the gradient of the tangent. The rate at the start of the reaction, when $t = 0$, is called the **initial rate** of the reaction.

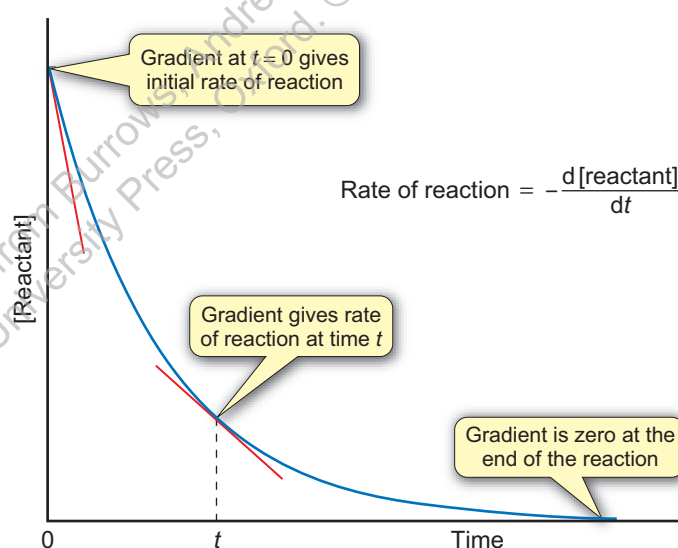
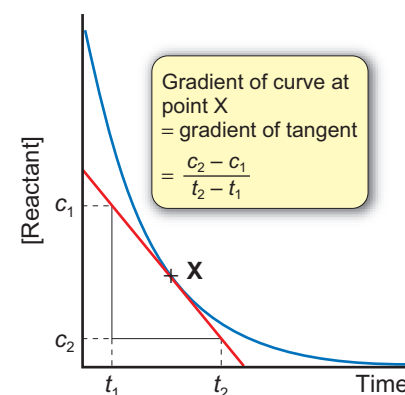


Figure 9.2 The concentration of the reactant plotted against time.

Σ Drawing tangents and measuring gradients

A **tangent** is a straight line drawn so that it just touches the curve at the point of interest. It has the same slope (**gradient**) as the curve at that point.



In this case, the gradient has a negative value because the concentration decreases with time (c_2 is smaller than c_1). You can find more information about gradients in Maths Toolkit, MT4 (p.1312).

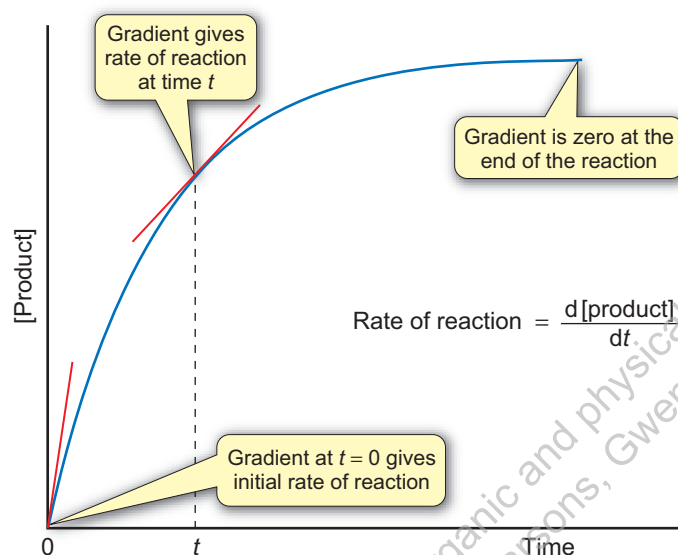


Figure 9.3 The concentration of the product plotted against time.

Σ The gradient of a plot of $[A]$ against t is the **differential** of $[A]$ with respect to t and is denoted by $\frac{d[A]}{dt}$.

If you need help with differentials, look in Maths Toolkit, MT6 (p.1318).

$\rightarrow$ The relationship between the amounts of reactants and products in the balanced chemical equation is known as the **stoichiometry** of the reaction; see Section 1.4 (p.23).

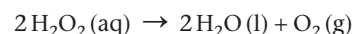
i The more rigorous definition of the rate of a reaction on p.386 takes into account the stoichiometry of the reaction and ensures that the rate of reaction has the same value whether given in terms of consumption of a reactant or the formation of a product.

You can express the gradient at a particular time as the differential, $\frac{d[\text{reactant}]}{dt}$. The value of the gradient is negative in Figure 9.2, because the reactant is being used up, so the rate of reaction = $-\frac{d[\text{reactant}]}{dt}$. The minus sign is included because rates are always quoted as positive quantities.

Now look at the plot of the concentration of the *product* against time in Figure 9.3. This time the gradient of the curve has positive values because the product is being formed in the reaction. At any time, t , the rate of formation of the product in this reaction is the same as the rate of consumption of the reactant, so

$$\text{rate of reaction} = \frac{d[\text{product}]}{dt} = -\frac{d[\text{reactant}]}{dt}$$

The relationship between the rate of removal of reactant and the rate of formation of product isn't always this simple and depends on the stoichiometry of the reaction. Take, for example, the decomposition of hydrogen peroxide to give water and oxygen.



In this case, 2 mol of hydrogen peroxide decompose to form 2 mol of water and 1 mol of oxygen. So, at any time, t , the rate in terms of the formation of oxygen will be half the rate in terms of the consumption of H_2O_2 , and half the rate in terms of the formation of H_2O , as shown in Figure 9.4. Another example is given in Worked example 9.1.

In some reactions, the kinetic profile may be a straight line rather than a curve as shown in Figure 9.5. In this case, the rate of consumption of the reactant is constant and is given by the gradient of the line. This kind of kinetic profile is explained in Section 9.5 (p.401).

Factors affecting the rate of reaction

The rate of a chemical reaction may be affected by a number of factors, including:

- the concentrations of the reactants;
- the temperature of the reaction;

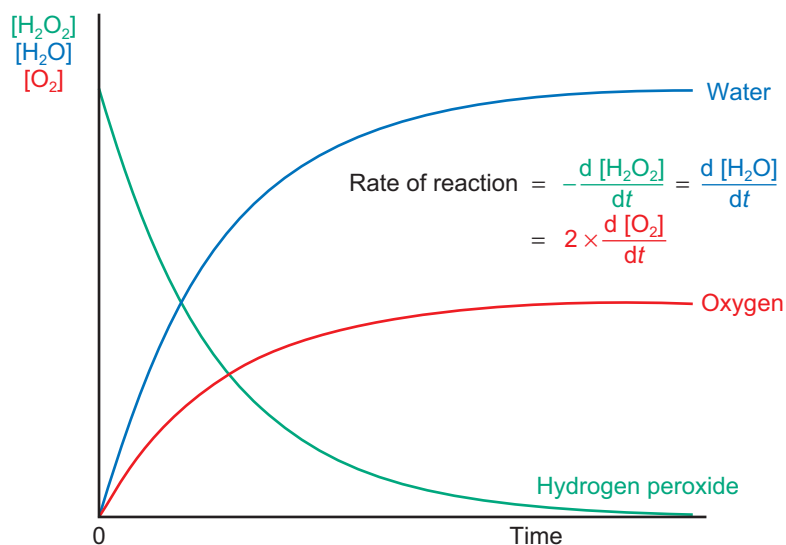


Figure 9.4 The decomposition of hydrogen peroxide.

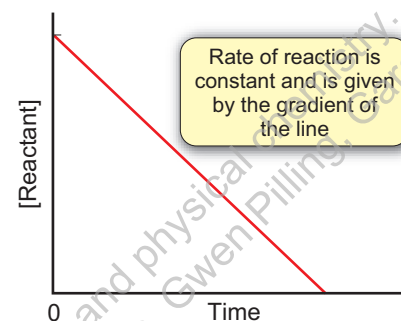


Figure 9.5 The plot of reactant concentration against time may sometimes be a straight line.

- the intensity of radiation (if the reaction involves radiation such as light);
- the particle size of a solid (related to the surface area of the solid particles);
- the polarity of a solvent (for reactions in solution involving ions);
- the presence of a catalyst.

The next four sections (Sections 9.3–9.6) are concerned with the effects of concentration.

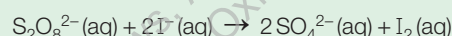
Units of rate of reaction

Concentrations are normally measured in mol dm^{-3} , so the units for rate of reaction are usually $\text{mol dm}^{-3} \text{s}^{-1}$.



Worked example 9.1 The rate of a reaction

For the following reaction, the initial rate of formation of $\text{I}_2(\text{aq})$ was found to be $2.5 \times 10^{-3} \text{ mol dm}^{-3} \text{s}^{-1}$



What was:

- the initial rate of formation of $\text{SO}_4^{2-}(\text{aq})$;
- the initial rate of consumption of $\text{S}_2\text{O}_8^{2-}(\text{aq})$?

Strategy

Use the stoichiometric equation to find the relationship between the number of moles of $\text{I}_2(\text{aq})$ formed and the number of moles of $\text{SO}_4^{2-}(\text{aq})$ formed in the reaction, and the number of moles of $\text{S}_2\text{O}_8^{2-}(\text{aq})$ consumed. This gives the relation between the rates of reaction.

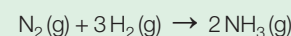
Solution

1 mol of $\text{S}_2\text{O}_8^{2-}(\text{aq})$ reacts to form 2 mol of $\text{SO}_4^{2-}(\text{aq})$ and 1 mol of $\text{I}_2(\text{aq})$.

- The initial rate of formation of $\text{SO}_4^{2-}(\text{aq})$
 $= 2 \times \text{initial rate of formation } \text{I}_2(\text{aq})$
 $= 5.0 \times 10^{-3} \text{ mol dm}^{-3} \text{s}^{-1}$.
- The initial rate of consumption of $\text{S}_2\text{O}_8^{2-}(\text{aq})$
 $= \text{initial rate of formation } \text{I}_2(\text{aq})$
 $= 2.5 \times 10^{-3} \text{ mol dm}^{-3} \text{s}^{-1}$.

Question

For the reaction between nitrogen and hydrogen



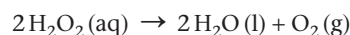
the rate of formation of ammonia was measured as $10 \text{ mmol dm}^{-3} \text{s}^{-1}$. What was the rate of consumption of hydrogen?

9.3 Monitoring the progress of a reaction

The method used to monitor the concentration of a reactant or product as the reaction proceeds depends very much on the nature of the reaction, the substances involved, and the speed with which the reaction takes place.

You need to look for a measurable property of either a reactant or a product, or of the system as a whole, that changes with time as the reaction proceeds and from which the concentrations of the reactants can be determined.

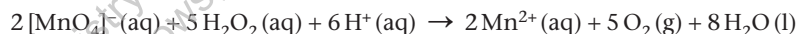
Physical properties are often the best because measuring them is non-intrusive and does not disturb the reaction. For example, you may have followed a reaction, such as the decomposition of hydrogen peroxide or the reaction of marble chips with acid, by collecting and measuring the *volume of gas* given off at different times during the reaction.



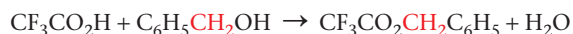
Alternatively, you may have carried out the reaction in an open conical flask on a balance and measured the *change in mass* as the reaction proceeded. Figure 9.6 shows some typical results for these types of experiments.

For reactions taking place in the gas phase (in a closed container of constant volume), it is often possible to follow the reaction by monitoring the *change in pressure* as the reaction proceeds.

Spectroscopic methods are useful where a reactant or product has a strong absorption in an accessible part of the spectrum. The intensity of absorption can then be used to measure the concentration of that substance. When the reaction involves a coloured compound, a *spectrophotometer* (sometimes called a colorimeter) can be conveniently used to monitor the concentration of that substance. For example, the reaction of purple $[\text{MnO}_4]^-$ ions with hydrogen peroxide in acidic solution can be monitored in this way



Sometimes it is possible to follow a reaction using *NMR spectroscopy* if there is a characteristic signal that changes during the reaction. For example, in the esterification of trifluoroethanoic acid ($\text{CF}_3\text{CO}_2\text{H}$) with benzyl alcohol ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$)



the consumption of benzyl alcohol can be monitored by the change in the signal from the CH_2 hydrogens in the ^1H NMR spectrum.

Spectroscopic techniques based on the use of *flow tubes and lasers* have allowed faster and faster reactions to be monitored. These techniques are discussed at the end of Section 9.4 (p.397) and in Box 9.5 (p.402).

i Marble is a form of calcium carbonate, CaCO_3 .

The relationship between gas pressures, gas volumes, and the amount in moles is described in Section 8.1 (p.341).

Spectroscopic techniques, including spectrophotometric analysis, are described in Section 11.4 (p.540). The theory underlying the techniques can be found in Chapter 10. NMR spectroscopy is discussed in Sections 10.7 (p.492) and 12.3 (p.576).

i Lasers that produce a flash of visible or ultraviolet radiation on a femtosecond timescale ($1 \text{ fs} = 1 \times 10^{-15} \text{ s}$) have allowed chemists to probe the mechanisms of very fast reactions.

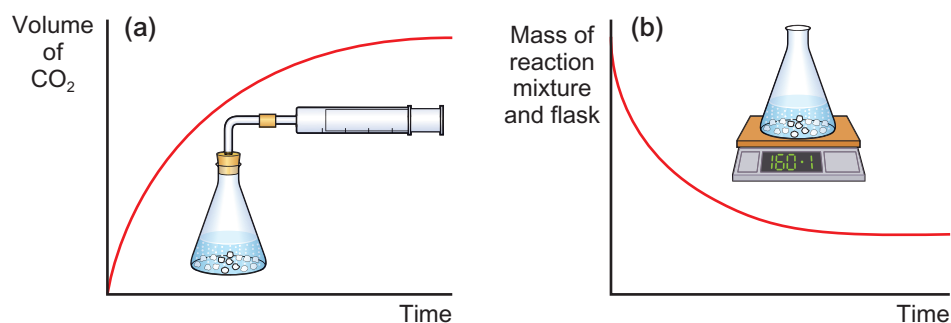


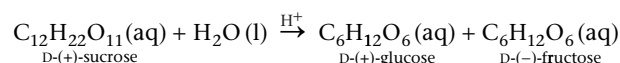
Figure 9.6 Monitoring the reaction of marble chips with dilute hydrochloric acid by (a) measuring the volume of CO_2 given off, and (b) measuring the mass of the reaction mixture and flask as the reaction proceeds.

If there is a change in the number or type of ions present in the solution, their concentration can be monitored by measuring the *conductivity* of the solution. For example, the hydrolysis of 2-chloro-2-methylpropane generates ionic products



Reactions in which the concentration of $\text{H}^+(\text{aq})$ ions changes can be measured by using a glass electrode to follow the *pH of the solution* during the reaction. This would provide another way of following this hydrolysis reaction.

For reactions of chiral compounds, where there is a *change in optical activity*, a polarimeter can be used to measure the rotation of the plane of polarized light as a function of time. An early example of the use of this method, first carried out in 1850, was to follow the rate of the acid-catalysed conversion of sucrose into a mixture of glucose and fructose



Since D-(-)-fructose has a larger specific rotation than D-(+)-glucose, the resulting mixture is laevorotatory (rotates plane-polarized light in an anticlockwise direction).

Titration is sometimes used to measure concentrations in rate studies, but you need to withdraw a small sample to carry out the titration and this disturbs the reaction. It is also a slow method and there needs to be some way of quenching (stopping or slowing down) the reaction as soon as you withdraw the sample.

The key to success in all the methods is to ensure that there is rapid mixing at the start (compared to the time the reaction takes) and that the temperature is kept constant. The rates of many reactions are dependent on temperature so, if the temperature varies, your results will be meaningless. This is particularly important for exothermic or endothermic reactions where there are heat changes during the reaction. There must be good thermal contact between the reaction vessel and the surroundings (for example, a water bath) to keep the temperature constant.

9.4 Elementary reactions

Rate equations

Elementary reactions are single-step reactions that involve one or two molecules or atoms. For example



There are two important features of elementary reactions. The first is that the equation represents the actual changes that take place at a molecular level during the reaction—in the case above, this involves the collision of an H atom with a Cl_2 molecule to produce a molecule of HCl and a Cl atom. For a complex reaction, which is made up of a series of elementary reactions, the chemical equation merely summarizes the overall stoichiometry of the reaction. It doesn't tell you about the changes that take place at a molecular level.

The second feature of an elementary reaction is that you can use the chemical equation to write a **rate equation** for the reaction. A rate equation expresses the rate of the reaction at a particular instant in terms of concentrations of the reactants at that instant.

For the reaction in Equation 9.1, the rate equation is

$$\text{rate of reaction} = k[\text{H}^\bullet][\text{Cl}_2]$$

where k is the **rate constant** for the reaction. The value of k is characteristic of the reaction and is constant for a particular temperature. The rate constant is related to how fast the reaction proceeds at that temperature. Figure 9.7 shows plots of the concentration of reactant against time for different temperatures, that is, for different values of k .

For the elementary reaction



Measurement of the conductivity of ionic solutions is discussed in Section 16.2 (p.726). The use of a glass electrode to measure pH is described in Section 11.2 (p.520). The definition of pH and calculations involving pH are in Section 7.2 (p.306).

You can find out about chiral compounds and the use of a polarimeter to measure optical activity in Section 18.4 (p.832). The D/L nomenclature for sugars is explained in Box 18.6 (p.836).

i In Equation 9.1, the hydrogen and chlorine atoms, $\text{H}^\bullet$ and $\text{Cl}^\bullet$, are both radicals.

A **radical** is an atom or molecule containing an unpaired electron; see Section 5.1 (p.217) and Section 19.1 (p.860).

i Fast reactions involving a radical reactant (and their reverse reactions) are generally single-step **elementary reactions**. A **complex reaction** consists of a series of elementary steps (see Section 9.4). You should always assume that a reaction is complex unless there is evidence otherwise.

i A rate equation is sometimes called a **rate law**.

Dependence of the rate of reaction on temperature is discussed in Section 9.7 (p.421).

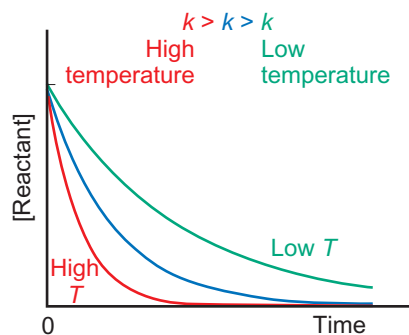


Figure 9.7 Plots of the concentration of a reactant against time at three different temperatures, that is, for different values of the rate constant, k .

Expressing the rate of consumption of a reactant or the rate of formation of a product as a differential is described in Section 9.2 (p.381).

the rate equation is

$$\text{rate of reaction} = k[\text{C}_2\text{H}_6]$$

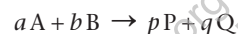
Defining the rate of a reaction

For the reaction of $\text{H}^\bullet$ with Cl_2 in Equation 9.1, the rate of reaction has the same value whether you consider the rate of consumption of a reactant or the rate of formation of a product. For the reaction of ethane to form two methyl radicals in Equation 9.2, this is not the case. The rate of formation of methyl radicals is twice the rate of consumption of ethane (see p.382). In the reverse process, shown in Equation 9.3



the rate of consumption of methyl radicals is twice the rate of formation of ethane.

It would be helpful to have a definition for the rate of a reaction that gives the same value of the rate whether you are monitoring the rate of consumption of any of the reactants or the rate of formation of any of the products. This is done as follows. For a general reaction



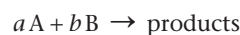
$$\text{rate of reaction} = -\frac{1}{a} \frac{d[\text{A}]}{dt} = -\frac{1}{b} \frac{d[\text{B}]}{dt} = \frac{1}{p} \frac{d[\text{P}]}{dt} = \frac{1}{q} \frac{d[\text{Q}]}{dt} \quad (9.4)$$

This corresponds to the expressions for the rates given in Section 9.2 (p.381), except that the terms $\frac{1}{a}$, $\frac{1}{b}$, etc. have been added to take account of the stoichiometry of the reaction.

This definition is used to write the differential rate equations for elementary reactions in the rest of the chapter.

Reaction order

In general, for an elementary reaction



the rate equation takes the form

$$\text{rate of reaction} = k[\text{A}]^a [\text{B}]^b \quad (9.5)$$

where k is the rate constant and a and b are the stoichiometric coefficients in the chemical equation. In the rate equation they give the **order of the reaction**:

- a is the order of the reaction with respect to A;
- b is the order of the reaction with respect to B.

The **overall order** of the reaction is given by $a + b$.

Why do rate equations take this form? If the elementary reaction involves two molecules A and B, these molecules must collide in order to react. The rate of collision of A and B depends on how many A and B molecules are present in a given volume—in other words, on their concentrations. There is more about collision theory of reaction in Section 9.8 (p.429).

- For Equation 9.1, the reaction is first order with respect to $\text{H}^\bullet$ and first order with respect to $[\text{Cl}_2]$. Overall, the reaction is second order ($a + b = 2$).
- For Equation 9.2, the reaction is first order with respect to $[\text{C}_2\text{H}_6]$. Overall, the reaction is first order. (There is only one reactant, so no substance B in the rate equation.)

i The **order of a reaction** with respect to a reactant (in an elementary reaction) gives the power to which the concentration of that substance is raised in the rate equation.

i The number 1 is assumed, rather than written, in the rate equation, as is the case for stoichiometric coefficients in chemical equations.

- For Equation 9.3, the reaction is second order with respect to $[\text{CH}_3^\bullet]$. Overall, the reaction is second order.

In practice, elementary reactions involve either one or two reactants, and a and b can only take the values 1 or 2. So, the overall order of an elementary reaction can only be first order or second order.

Differential rate equations

A rate equation where the rate of consumption of a reactant, or the rate of formation of a product, is written as a differential (see p.381) is known as a **differential rate equation**. Using the definition for the rate of reaction in Equation 9.4, you can now write differential rate equations for the reactions in Equations 9.1–9.3. These are shown in Table 9.1, expressed in terms of both the consumption of reactants and the formation of products.

For example, for



$$\text{rate of reaction} = -\frac{1}{2} \frac{d[\text{CH}_3^\bullet]}{dt} = \frac{d[\text{C}_2\text{H}_6]}{dt} = k[\text{CH}_3^\bullet]^2$$

So

$$-\frac{d[\text{CH}_3^\bullet]}{dt} = 2 \times k[\text{CH}_3^\bullet]^2$$

You can practise writing differential rate equations in Worked example 9.2.

Units of k

Rates of reaction are expressed in $\text{mol dm}^{-3} \text{s}^{-1}$ (see p.383). The units of k depend on the order of the reaction. For a first order reaction

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

so $k = \text{rate} / [\text{A}]$, and the units of k are given by

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

For a second order reaction

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

so $k = \text{rate} / [\text{A}]^2$ and the units of k are given by

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

Table 9.1 Rate equations expressed in terms of differentials showing the relationship between the rate of consumption of reactants and the rate of formation of products

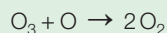
Reaction	Rate of consumption of reactants	Rate of formation of products
(9.1) $\text{H}^\bullet + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}^\bullet$	$-\frac{d[\text{H}^\bullet]}{dt} = -\frac{d[\text{Cl}_2]}{dt} = k[\text{H}^\bullet][\text{Cl}_2]$	$\frac{d[\text{HCl}]}{dt} = \frac{d[\text{Cl}^\bullet]}{dt} = k[\text{H}^\bullet][\text{Cl}_2]$
(9.2) $\text{C}_2\text{H}_6 \rightarrow 2 \text{CH}_3^\bullet$	$-\frac{d[\text{C}_2\text{H}_6]}{dt} = k[\text{C}_2\text{H}_6]$	$\frac{d[\text{CH}_3^\bullet]}{dt} = 2 \times k[\text{C}_2\text{H}_6]$
(9.3) $2 \text{CH}_3^\bullet \rightarrow \text{C}_2\text{H}_6$	$-\frac{d[\text{CH}_3^\bullet]}{dt} = 2 \times k[\text{CH}_3^\bullet]^2$	$\frac{d[\text{C}_2\text{H}_6]}{dt} = k[\text{CH}_3^\bullet]^2$

Equations involving differentials are called **differential equations**, see Maths Toolkit MT6 (p.1318).



Worked example 9.2 Writing differential rate equations for elementary reactions

The following elementary reaction between ozone and oxygen atoms occurs in the atmosphere.



- (a) Write down an expression for the rate of the reaction.
- (b) What is the order of the reaction with respect to (i) O_3 , and (ii) O ? What is the overall order of the reaction?
- (c) Use differential expressions, as in Table 9.1 (p.387), to write rate equations in terms of the rates of consumption of reactants and the rate of formation of the product.

(Note that both O_2 and O atoms have two unpaired electrons and are *biradicals*; see Section 4.10, p.194. The dots are omitted here for simplicity.)

Strategy

The reaction is an elementary process, so you can use the chemical equation to write the rate equation. The stoichiometric coefficients in the chemical equation give the orders of reaction with respect to each reactant. Use Equation 9.4 and Table 9.1 to help you write the rate equation in terms of differentials.

Solution

- (a) Rate of reaction = $k[\text{O}_3][\text{O}]$.
- (b) The reaction is first order with respect to O_3 and first order with respect to O . The overall order of the reaction is $1 + 1 = 2$.
- (c) From Equation 9.4

$$\text{rate of reaction} = -\frac{d[\text{O}_3]}{dt} = -\frac{d[\text{O}]}{dt} = \frac{1}{2} \frac{d[\text{O}_2]}{dt}$$

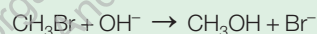
Combining this equation with the rate equation in (a)

$$\text{rate of consumption of reactants: } -\frac{d[\text{O}_3]}{dt} = -\frac{d[\text{O}]}{dt} = k[\text{O}_3][\text{O}]$$

$$\text{rate of formation of products: } \frac{d[\text{O}_2]}{dt} = 2 \times k[\text{O}_3][\text{O}]$$

Question

The alkaline hydrolysis of bromomethane is an elementary reaction



- (a) Write a rate equation for the reaction in terms of the differential for consumption of CH_3Br .
- (b) What is the overall order of the reaction?



Differentiation and integration

When you differentiate an expression for a variable, y , with respect to a second variable, x , the result (a differential $\frac{dy}{dx}$) tells you the rate at which y changes with respect to x . Integration is the opposite of differentiation. In this case, you start with an expression describing the rate of change, that is, the gradient of a plot (a curve or a straight line) and integrate it to find an expression for the curve or straight line itself.



An **integrated rate equation** gives the concentration of a reactant as a function of time.



This screencast explains the difference between differential and integrated rate equations and walks you through Box 9.1 to demonstrate how the integrated rate equation for a first order reaction is derived from the differential rate equation for the reaction.

$$y = mx + c$$

$$\ln[A]_t = -kt + \ln[A]_0$$

Integrated rate equations

Rate equations tell you the rate of reaction at a particular instant during the reaction. However, you can't measure rates of reaction directly—experimental data usually consist of measurements of concentration of a reactant or product at different times. It would be useful to have an expression that shows how the concentration varies with time. This information comes from the **integrated rate equation** for the reaction.

The integrated rate equation is derived mathematically from the differential rate equation for the reaction. You can see how this is done for a first order elementary reaction in Box 9.1. The resulting equation, and how it is used, are described below.

A first order elementary reaction

For a first order elementary reaction



the integrated rate equation (Equation 9.6a) is an expression linking the concentration of the reactant A at a particular time, $[A]_t$, to the time, t , the concentration of A at the start of the reaction, $[A]_0$, and the rate constant, k .

$$\ln [A]_t = \ln [A]_0 - kt \quad (9.6a)$$

So, if you know the concentration of A at the start and a value for the rate constant, the integrated rate equation allows you to work out the concentration of a reactant or product at any time during the reaction.

Alternatively, if you can measure the concentrations during the reaction, the integrated rate equation can be used to find a value for the rate constant, k . This is easily done because

Equation 9.6a corresponds to the equation for a straight line ($y = mx + c$), so a plot of $\ln[A]_t$ against t is a straight line with a gradient $-k$ (Figure 9.8). The plot also helps you to determine the order of the reaction. If the experimental results plotted in this way lead to a straight line, then the reaction is first order.

Equations 9.6b and 9.6c are two useful alternative ways of writing Equation 9.6a (see Box 9.1). Equation 9.6c is an equation for **exponential decay** and tells you about the shape of the plot of $[A]$ against time. A common feature of all first order reactions is that the concentration of the reactant decays exponentially with time as shown in Figure 9.9.



Straight line graphs

The equation for a straight line is

$$y = mx + c$$

You can find help with plotting and interpreting straight line graphs in Maths Toolkit MT4 (p.1312).



Natural logarithms

'ln' means 'logarithm to the base e', where $e = 2.7183$.

So, $\ln x = \log_e x$ and is known as a natural logarithm. Natural logarithms are explained in Maths Toolkit MT3 (p.1310).

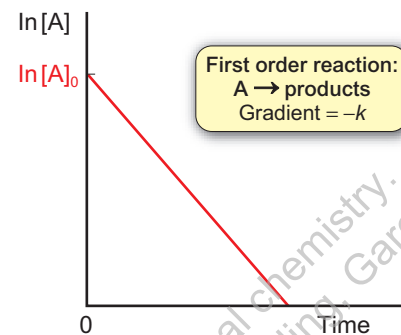
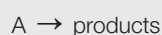


Figure 9.8 For the first order reaction, $A \rightarrow \text{products}$, a plot of $\ln[A]$ against t is a straight line. The rate constant k can be found from the gradient.



Box 9.1 Deriving the integrated rate equation for a first order reaction

From Equation 9.4 (p.386) the differential rate equation for the first order elementary reaction



is given by

$$\text{rate of reaction} = -\frac{d[A]}{dt} = k[A]$$

To solve this differential equation to obtain a relationship between $[A]$ and t , first separate these two variables so that $[A]$ is on one side of the equation and t is on the other.

$$\frac{d[A]}{[A]} = -kdt$$

Now integrate both sides of the equation from $[A] = [A]_0$ at $t = 0$, to $[A] = [A]_t$ at time t . (Note. Go to Maths Toolkit MT7 (p.1321) if you need help with carrying out integration.)

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_0^t dt$$

To do this you need to use the standard integral

$$\int_{x_1}^{x_2} \frac{dx}{x} = [\ln x]_{x_1}^{x_2} = \ln x_2 - \ln x_1$$

Then

$$[\ln[A]]_{[A]_0}^{[A]_t} = -k[t]_0^t$$

$$\ln[A]_t - \ln[A]_0 = -k(t - 0)$$

which can be rearranged to give

$$\ln[A]_t = \ln[A]_0 - kt \quad (9.6a)$$

Using the expression, $\ln \frac{a}{b} = \ln a - \ln b$, Equation 9.6a can be written as

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad (9.6b)$$

A third way of writing this equation makes use of the fact that $\ln y = x$ can be written as $y = e^x$, so Equation 9.6b becomes

$$\frac{[A]_t}{[A]_0} = e^{-kt}$$

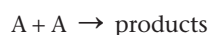
so that

$$[A]_t = [A]_0 e^{-kt} \quad (9.6c)$$

Equation 9.6c has the form of an **exponential decay**, which is an important feature of first order reactions. (The properties of exponential functions, e^x (also written $\exp(x)$), are described in Maths Toolkit MT3 (p.1310) and MT4 (p.1312).)

A second order elementary reaction

For a second order elementary reaction



the integrated rate equation is given by

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + 2kt \quad (9.7b)$$

$$\frac{y}{[A]_t} = mx + \frac{c}{[A]_0}$$

You can see how this is derived from the differential rate equation in Box 9.2. In this case, a plot of $\frac{1}{[A]_t}$ against t is a straight line with gradient $2k$ (Figure 9.10). Equations 9.7a and 9.7c are alternative ways of writing Equation 9.7b (see Box 9.2).

Figure 9.11 shows plots of $[A]$ against t for a first order and for a second order reaction

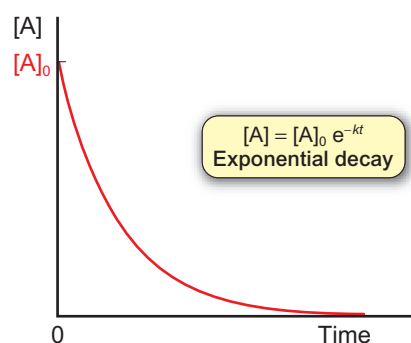


Figure 9.9 For the first order reaction, $A \rightarrow \text{products}$, a plot of $[A]$ against t is an exponential decay curve.

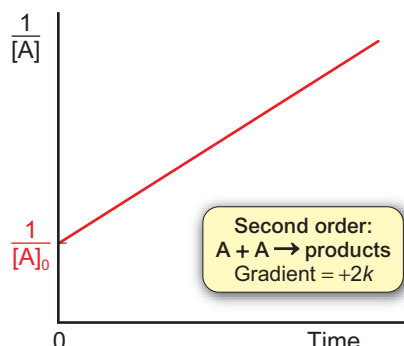


Figure 9.10 For a second order reaction, $A + A \rightarrow \text{products}$, a plot of $1/[A]$ against t is a straight line. The rate constant k can be found from the gradient.

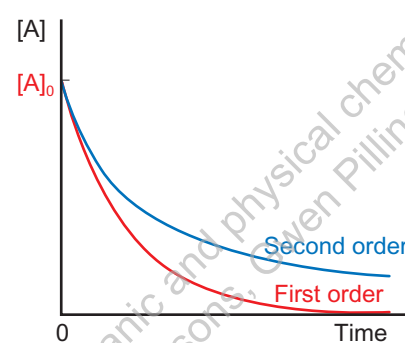


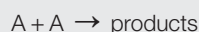
Figure 9.11 A comparison of decay curves for a first order and a second order reaction with the same initial decay rate.



Box 9.2 Deriving the integrated rate equation for a second order reaction

This follows the general procedure given for deriving the integrated rate equation for a first order reaction in Box 9.1.

From Equation 9.4 (p.386) the differential rate equation for the second order elementary reaction



is given by

$$\text{rate of reaction} = -\frac{1}{2} \frac{d[A]}{dt} = k[A]^2$$

so

$$-\frac{d[A]}{dt} = 2 \times k[A]^2$$

Separating the variables, the equation can be rewritten as

$$\frac{d[A]}{[A]^2} = -2k dt$$

To obtain a relationship between $[A]$ and t , integrate both sides of the equation from $[A] = [A]_0$ at $t = 0$, to $[A] = [A]_t$ at time t .

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -2k \int_0^t dt$$

(Note that $2k$ is constant, so goes outside the integral.)

To do this you need to use the standard integral

$$\int_{x_1}^{x_2} \frac{dx}{x^2} = \left[-\frac{1}{x} \right]_{x_1}^{x_2} = \left(-\frac{1}{x_2} \right) - \left(-\frac{1}{x_1} \right) = -\frac{1}{x_2} + \frac{1}{x_1}$$

Then

$$\left[-\frac{1}{[A]} \right]_{[A]_0}^{[A]_t} = -2k[t]_0^t$$

$$-\frac{1}{[A]_t} + \frac{1}{[A]_0} = -2k(t - 0)$$

which can be rearranged to give

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = 2kt \quad (9.7a)$$

Here are two useful alternative forms of Equation 9.7a

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + 2kt \quad (9.7b)$$

$$[A]_t = \frac{[A]_0}{1 + 2kt[A]_0} \quad (9.7c)$$

Equation 9.7c allows you to predict the concentration of A at any time after the start of the reaction.

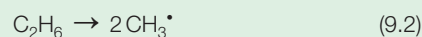
with the same initial rate. Note that, for the second order reaction, $[A]$ approaches zero more slowly than for the first order reaction.

Worked example 9.3 illustrates the use of integrated rate equations.



Worked example 9.3 Writing integrated rate equations

Write an integrated rate equation for the decomposition of ethane to give two methyl radicals in Equation 9.2 (p.385). Explain how a value of the rate constant k can be found from experimental measurements of concentration of ethane at different times during the course of the reaction.



Strategy

The reaction is a first order elementary reaction, so the integrated rate equations are given by Equations 9.6(a–c) in Box 9.1.

Solution

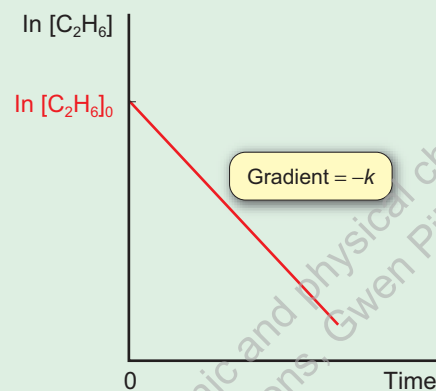
Use Equation 9.2 to write the differential equation.

$$-\frac{d[\text{C}_2\text{H}_6]}{dt} = k[\text{C}_2\text{H}_6]$$

Use Equation 9.6a on p.388 to write the integrated rate equation.

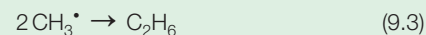
$$\ln [\text{C}_2\text{H}_6]_t = \ln [\text{C}_2\text{H}_6]_0 - kt$$

This is the most useful form of the integrated rate equation in this case because it is the equation of a straight line that can be used to find the rate constant. A plot of $\ln [\text{C}_2\text{H}_6]$ against t is a straight line, with gradient equal to $-k$.



Question

Write an integrated rate equation for reaction of two methyl radicals to form ethane in Equation 9.3 (p.386). Explain how a value of the rate constant k can be found from experimental measurements of concentration of the methyl radical at different times during the course of the reaction.



Pseudo-first order reactions

In elementary reactions where there is more than one reactant, such as $\text{A} + \text{B} \rightarrow \text{products}$, the concentrations of *both* A and B change during the reaction and affect the rate. A useful method used to study the kinetics involves isolating one reactant at a time by having the other reactant in large excess. Suppose B is in large excess: this means that the concentration of B is effectively constant throughout the reaction and any changes in the rate are due to changes in the concentration of A alone.

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

If $[\text{A}] \ll [\text{B}]$, you can assume that $[\text{B}]$ hardly changes in the reaction and is equal to its initial value $[\text{B}]_0$. Then

$$\text{rate of reaction} = k'[\text{A}], \quad \text{where } k' = k[\text{B}]_0$$

The differential rate equation can now be written as a first order process

$$-\frac{d[\text{A}]}{dt} = k'[\text{A}]$$

Using Equation 9.6a (p.388) to write the integrated rate equation

$$\ln [\text{A}]_t = \ln [\text{A}]_0 - k't \quad (9.8a)$$

so substituting for k'

$$\ln [\text{A}]_t = \ln [\text{A}]_0 - k[\text{B}]_0 t \quad (9.8b)$$

i This is called the **isolation technique**. Its use in the study of the kinetics of complex reactions is described in Section 9.5 (p.403).

i For example, if $[\text{B}]_0 = 1.00 \text{ mol dm}^{-3}$ and $[\text{A}]_0 = 0.01 \text{ mol dm}^{-3}$, then the concentration of B at the end of the reaction when A is all used up is $(1.00 - 0.01) \text{ mol dm}^{-3} = 0.99 \text{ mol dm}^{-3}$. So, $[\text{B}]$ is almost constant.

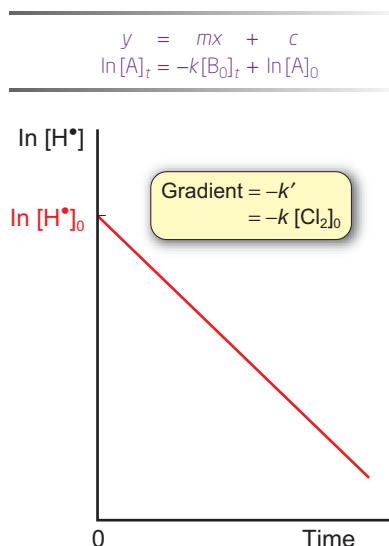


Figure 9.12 Plot of $\ln [H^*]$ against t for the pseudo-first order reaction, $H^* + Cl_2 \rightarrow HCl + Cl^*$, when Cl_2 is in large excess.

i The **half life** of a reactant is the time taken for its concentration to fall to half its initial value.

In the presence of a large excess of B, the reaction has all the appearance of a first order reaction. The reaction is said to show **pseudo-first order** kinetics under these conditions and k' is called the **effective rate constant** for a fixed concentration of B, $[B]_0$. A plot of $\ln [A]$ against t is a straight line with gradient $-k[B]_0$.

The reaction of chlorine molecules with hydrogen atoms in Equation 9.1 (p.385) can be studied in this way.



Under the reaction conditions, H^* is present in only very small concentrations, so $[H^*] \ll [Cl_2]$, and you can assume $[Cl_2] = [Cl_2]_0$ throughout the reaction. The differential rate equation is

$$-\frac{d[H]}{dt} = k'[H^*], \quad \text{where } k' = k[Cl_2]_0$$

The integrated rate equation is then

$$\ln [H^*] = \ln [H^*]_0 - k[Cl_2]_0 t$$

Figure 9.12 shows a plot of $\ln [H^*]$ against time.

Half lives

An important characteristic of a first order reaction is the **half life**, $t_{1/2}$, of the reactant. This is the time taken for the concentration of the reactant to fall to half its initial value. You can use half lives to decide whether a reaction is first order, and to get a value for the rate constant, k . For a first order reaction, $A \rightarrow$ products, you can find the half life of A by substituting $[A]_t = [A]_0/2$ at $t = t_{1/2}$ into the integrated rate equation.

Using the integrated rate equation in the form of Equation 9.6b (Box 9.1, p.389)

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad (9.6b)$$

For $[A]_t = [A]_0/2$

$$\ln \frac{[A]_0}{2[A]_0} = -kt_{1/2}$$

Rearranging this to give an expression for $t_{1/2}$

$$t_{1/2} = \frac{-\ln \frac{1}{2}}{k}$$

$$t_{1/2} = \frac{\ln 2}{k} \quad (9.9)$$

Since $\ln 2 = 0.693$

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

The key point is that, since Equation 9.9 does not contain the term $[A]_0$,

the half life of the reactant in a first order reaction is independent of its initial concentration, so $t_{1/2}$ is constant through the course of the reaction.

If the concentration of A at any time, t , is $[A]_t$, it will fall to $\frac{1}{2}[A]_t$ after an interval of $t_{1/2}$.

Σ Since $\ln \frac{a}{b} = \ln a - \ln b$,
 $-\ln \frac{1}{2} = -(\ln 1 - \ln 2) = (\ln 2 - \ln 1)$
 $= \ln \frac{2}{1} = \ln 2$

i The half life provides a useful indication of the rate constant for a first order reaction. A reaction with a large rate constant has a short half life.

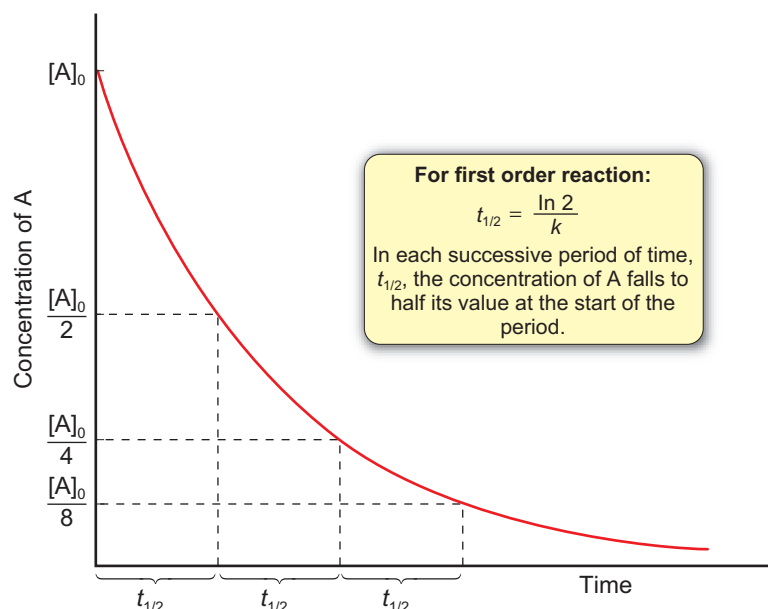
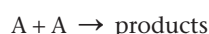


Figure 9.13 For a first order reaction, $A \rightarrow \text{products}$, the half life of A is independent of its initial concentration.

Figure 9.13 shows three successive half lives, when the concentration of A falls from $[A]_0 \rightarrow \frac{[A]_0}{2} \rightarrow \frac{[A]_0}{4} \rightarrow \frac{[A]_0}{8}$. After n successive half lives, the concentration of A will be $\frac{[A]_0}{2^n}$.

In contrast to a first order reaction, the half life of a second order reaction does depend on the initial concentration of the reactant. For the second order reaction



you can find the half life of A by substituting $[A]_t = [A]_0/2$ at $t = t_{1/2}$ into the integrated rate equation.

Using the integrated rate equation in the form of Equation 9.7a (Box 9.2, p.390)

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = 2kt \quad (9.7a)$$

For $[A]_t = [A]_0/2$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = \frac{1}{[A]_0} = 2kt_{1/2}$$

Rearranging this to give an expression for $t_{1/2}$

$$t_{1/2} = \frac{1}{2k[A]_0} \quad (9.10)$$

In this case, the half life gets longer as the concentration of the reactant falls.

A constant half life indicates a first order reaction. If you inspect a set of data of concentration against time for a reaction and see that the initial concentration falls to half its value in a certain time as in Figure 9.13, and that another concentration falls to half its value in the same time, the reaction is likely to be first order. To be sure, you would need to plot a graph of $\ln[A]$ against t to show that this gives a straight line.

In Worked example 9.4, you can use both the half life method and the integrated rate equation to find the order of a reaction and a value for the rate constant. The significance of the lifetimes of molecules in the atmosphere is discussed in Box 9.3.



This screencast walks you through Figure 9.13 and explains how to find the half life of a reaction.



Photochromic sunglasses darken or lighten in response to light intensity. This is achieved by incorporating a light-sensitive dye into the lenses. The fading of the dye in the presence of light is a first order process. Manufacturers publish half lives of the different coloured dyes used.

The decay of a radioactive isotope follows an exponential curve and is a first order process. Its half life is a characteristic property of a radioactive isotope. Examples are discussed in various parts of the book: ^{14}C in Box 3.8 (p.159), ^3H (tritium) in Box 25.7 (p.1156), ^{40}K in Box 27.9 (p.1243), and ^{98}Tc in Box 28.1 (p.1251).

i In fact, *any* fractional life remains constant during a first order reaction. So, for example, if you measure the 'quarter' life, $t_{1/4}$, the time for the concentration of a reactant to fall to a quarter of its initial value, you find it is independent of the initial concentration and remains constant through the course of the reaction.

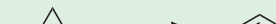
Σ This is a common way of tabulating data. The concentration of cyclopropane at $t=0$ is $1.50 \times 10^{-3} \text{ mol dm}^{-3}$. So, [cyclopropane] has been divided by $10^{-3} \text{ mol dm}^{-3}$ to give the numbers in the table. Remember: quantity = number $\times$ unit, so number = quantity / unit (see Section 1.2, p.7).



Worked example 9.4 Isomerization of cyclopropane

When cyclopropane is heated to 750 K in a closed container, it isomerizes to form propene.

The reaction was monitored using infrared spectroscopy and the following data obtained.




 cyclopropane


 propene

t / min	0	5.0	10	20	30	40	50	60
$[\text{cyclopropane}] / 10^{-3} \text{ mol dm}^{-3}$	1.50	1.23	1.01	0.68	0.46	0.31	0.21	0.14

Show that the reaction is first order and find a value for the rate constant, k , at 750 K.

Strategy

This worked example illustrates two ways of tackling the problem.

1 Using half lives. Plot a graph of [cyclopropane] against time and measure successive half lives. If the reaction is first order, the half life will be independent of the concentration of

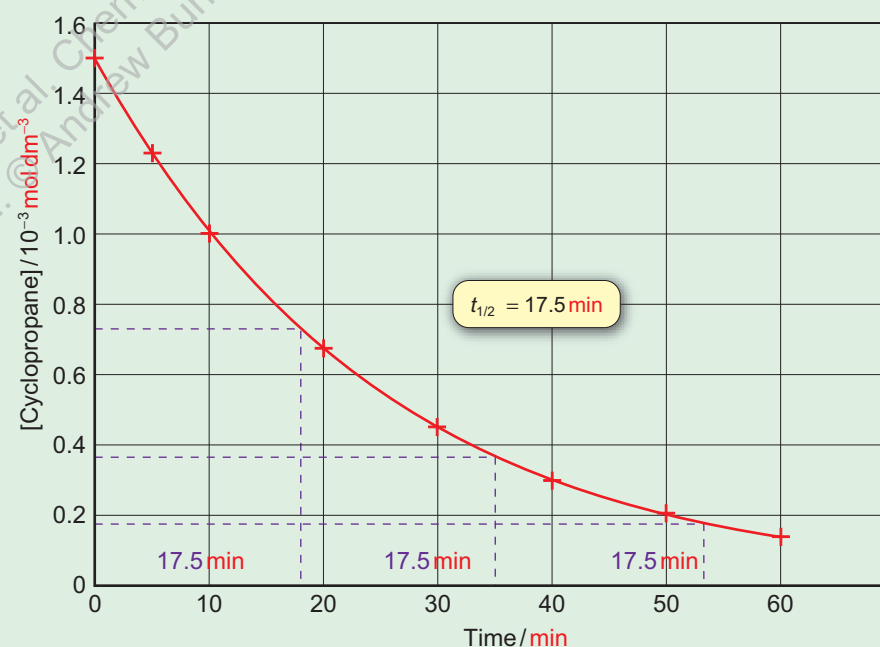
cyclopropane. Then use $t_{1/2} = \frac{\ln 2}{k}$ (Equation 9.9) to find a value for the rate constant.

2 Using an integrated rate equation. Use the integrated rate equation for a first order reaction: $\ln [A]_t = \ln [A]_0 - kt$ (Equation 9.6b) and plot a graph of $\ln [\text{cyclopropane}]_t$ against t . (Remember $\ln = \log_e$.) For a first order reaction, the plot is a straight line with gradient $-k$.

Solution

1 Using half lives

Plot a graph of [cyclopropane] against t , as shown below. Measure at least three half lives.



The measured half lives have a constant value showing that the reaction is first order.

To find k , substitute an average value for the half life into Equation 9.9





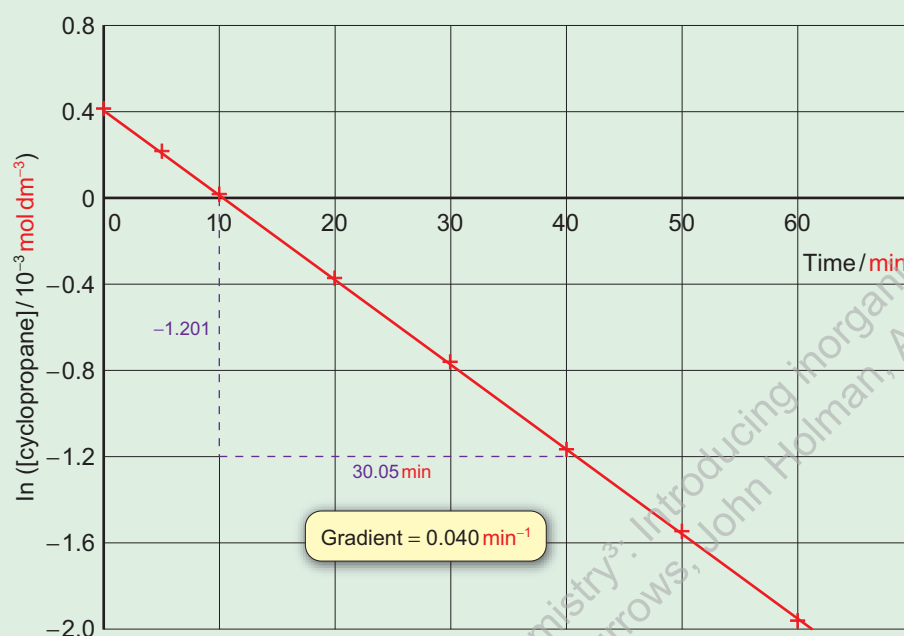
$$t_{1/2} = \frac{\ln 2}{k} \quad (9.9)$$

$$\text{so } k = \frac{0.693}{17.5 \text{ min}} = 0.040 \text{ min}^{-1} = 6.6 \times 10^{-4} \text{ s}^{-1} \quad (1 \text{ min}^{-1} = \frac{1}{60} \text{ s}^{-1})$$

2 Using an integrated rate equation

The data give the following plot for $\ln [\text{cyclopropane}]$ against t .

t/min	0	5.0	10	20	30	40	50	60
$\ln ([\text{cyclopropane}]/10^{-3} \text{ mol dm}^{-3})$	0.405	0.207	0.001	-0.386	-0.777	-1.171	-1.561	-1.966



Σ Note that [cyclopropane] is divided by its units so that you are finding the logarithm of a number (rather than a quantity with units). Here the units of [cyclopropane] are $10^{-3} \text{ mol dm}^{-3}$. You could have plotted the graph using units of mol dm^{-3} for [cyclopropane] and obtained the same

gradient. This is because, when you find the gradient, you are subtracting two values of $\ln [\text{cyclopropane}]$:

$$\ln a_1 - \ln a_2 = \ln \frac{a_1}{a_2} \text{ and } \ln 10^{-3}a_1 - \ln 10^{-3}a_2 = \ln \frac{a_1}{a_2}$$



See Maths note on p.381 about finding the gradient of a straight line.

The plot is a straight line showing that the reaction is first order.

The gradient of the line = -0.040 min^{-1} , so

$$k = 0.040 \text{ min}^{-1} = 6.6 \times 10^{-4} \text{ s}^{-1}$$

which agrees with the value from the half life method.

Generally speaking, it is preferable to use the integrated rate equation and plot a straight-line graph to determine k , rather than use the half life method, because it is difficult to find half lives accurately from experimental data.

Question

The reaction of methyl radicals to form ethane was investigated using the flash photolysis technique described on p.398. The following results were obtained at 295 K.

$t/10^{-4} \text{ s}$	0	3.00	6.00	10.0	15.0	20.0	25.0	30.0
$[\text{CH}_3\cdot]/10^{-8} \text{ mol dm}^{-3}$	1.50	1.10	0.93	0.74	0.55	0.45	0.41	0.35

Show that the reaction is second order and find a value for the rate constant at 295 K.



Box 9.3 Atmospheric lifetime of methane

The impact of methane on climate change (see p.379) depends on the amount emitted from the Earth's surface, the length of time it stays in the troposphere, and its ability to absorb infrared radiation. This box is about calculating the lifetime of methane in the troposphere.

Methane is removed from the troposphere by reaction with $\cdot\text{OH}$ radicals. These radicals act as scavengers and are responsible for removing many of the compounds we emit



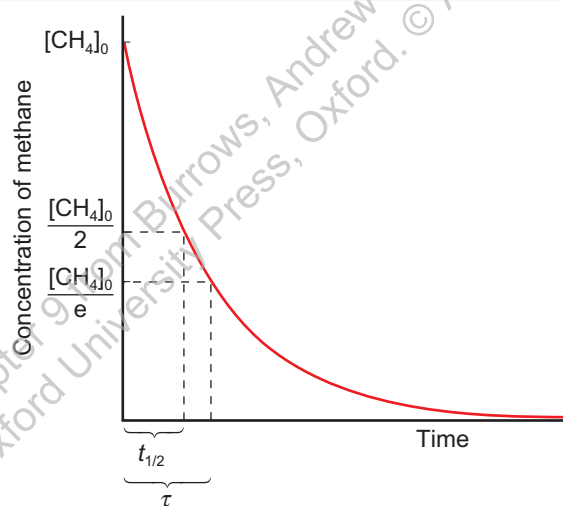
This is a second order elementary reaction and the rate of reaction = $k[\text{CH}_4][\cdot\text{OH}]$.

The kinetics of reactions in the troposphere are different from those in laboratory experiments, because the reactions are not taking place in a closed container. In the troposphere, $\cdot\text{OH}$ radicals are constantly being produced and removed. As a result, the concentration of $\cdot\text{OH}$ is approximately constant, $[\cdot\text{OH}]_{\text{constant}}$, and you can treat its reaction with CH_4 as a pseudo-first order reaction (see p.391).

$$\text{Rate of reaction} = k'[\text{CH}_4], \text{ where } k' = k[\cdot\text{OH}]_{\text{constant}}$$

The total concentration of methane in the troposphere is also approximately constant, but to work out a lifetime you need to consider the fate of specific emitted methane molecules. The **lifetime**, τ , of methane molecules in the troposphere is the *average time* between emission of a molecule of CH_4 and its removal by reaction with $\cdot\text{OH}$.

By this definition, τ is equal to the time it takes for an initial concentration $[\text{CH}_4]_0$ to fall to $[\text{CH}_4]_0/e$ —approximately a third of its initial value, while in the presence of a constant $[\cdot\text{OH}]$. (The lifetime is related to the probability of a molecule still being present after emission. This falls exponentially with time, which explains the presence of 'e' in the expression for τ .) On the decay curve below, compare τ with the half life, $t_{1/2}$, which is the time it takes for the concentration to fall to half of its initial value.



▲ Decay curve of emitted methane showing lifetime, τ , and half life, $t_{1/2}$ ($e = 2.7183$)

Using the integrated rate equation for a first order reaction in the form of Equation 9.6b (Box 9.1, p.389)

$$\ln \frac{[\text{CH}_4]_t}{[\text{CH}_4]_0} = -k't \quad (9.6b)$$

When $t = \tau$, $[\text{CH}_4]_t = [\text{CH}_4]_0/e$, so

$$\ln \frac{[\text{CH}_4]_0}{e[\text{CH}_4]_0} = -k'\tau, \text{ so } \ln \frac{1}{e} = -k'\tau$$

Rearranging to give an expression for τ

$$\tau = \frac{-\ln \frac{1}{e}}{k'} = \frac{\ln e}{k'}$$

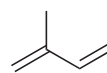
But $\ln e = 1$, and $k' = k[\cdot\text{OH}]_{\text{constant}}$, so

$$\tau = \frac{1}{k[\cdot\text{OH}]_{\text{constant}}}$$

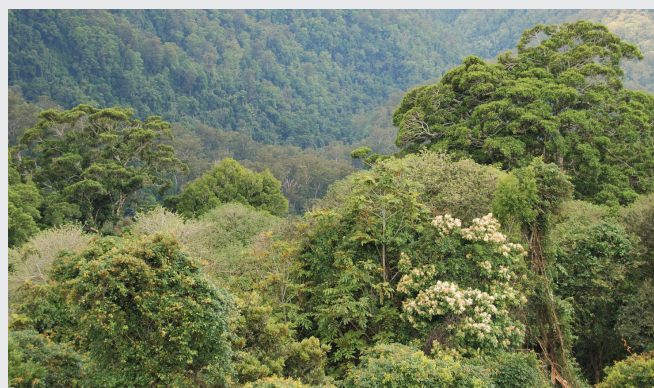
In the troposphere, the average concentration of $\cdot\text{OH}$ radicals is $1 \times 10^{-15} \text{ mol dm}^{-3}$ and $k = 3.9 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Substituting these values in the expression above gives a value for τ of ~ 8 years.

The long lifetime of 8 years means that methane travels large distances from where it was emitted and becomes broadly distributed throughout the troposphere (see p.379). For a given emission rate, the tropospheric concentration is larger if the lifetime is long.

Now contrast this with another hydrocarbon, isoprene, which is released into the troposphere in huge quantities from vegetation. It absorbs infrared radiation, but is not a significant greenhouse gas. Its emission rate on a global scale is of the same order of magnitude as that of methane, but it has a short lifetime (τ about 1 hour) so it is only found close to its emission source and its tropospheric concentration is small.



isoprene
[2-methylbuta-1,3-diene]



▲ Tropical rainforests are a source of isoprene.

Question

Calculate a value for the half life (in years) of methane under the conditions in the troposphere.

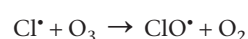
Kinetic techniques used to study elementary reactions

Elementary reactions often involve atoms and other radicals and occur very rapidly, so that special techniques are needed to study them. Two of the most widely used are *flow techniques* and *flash photolysis*. Both methods are designed to produce well-mixed reactants on a very short timescale. The concentration of one of the reactants is then measured after a short time interval, often using a spectroscopic technique. A series of experiments is carried out, varying the time interval in each experiment, to give values of concentration at different times after the start of the reaction. The conditions are usually chosen so that one reactant is in large excess so that the reaction follows pseudo-first order kinetics (see p.391).

➞ A third method of studying fast reactions uses a stopped-flow technique and is described for complex reactions in Box 9.5 (p.402).

The discharge flow method

This is commonly used to study the reactions of atoms with molecules, such as the reaction of chlorine radicals with ozone, an important reaction in the stratosphere.



The chlorine radicals are formed by flowing chlorine gas (Cl_2), diluted in N_2 , through a microwave discharge, which causes some of the Cl_2 molecules to dissociate to form $\text{Cl}^\bullet$ radicals. The experimental setup is shown in Figure 9.14.

O_3 (also diluted in N_2) is then introduced through an injector and mixes rapidly with the $\text{Cl}^\bullet/\text{Cl}_2/\text{N}_2$ mixture already flowing through the apparatus. The whole mixture then flows down a tube at a constant speed, u . The $\text{Cl}^\bullet$ radicals are monitored by a detector at a distance x along the tube, which corresponds to the time ($t = x/u$) since the reactants were mixed and the reaction started. The experiment is then repeated and the time varied by changing the position of the injector. In this way, the concentration of $\text{Cl}^\bullet$ radicals can be measured for a series of reaction times.

The conditions are arranged so that $[\text{Cl}^\bullet] \ll [\text{O}_3]$ and the reaction shows pseudo-first order kinetics. Using Equations 9.8(a) and (b) on p.391

$$\ln [\text{Cl}^\bullet] = \ln [\text{Cl}^\bullet]_0 - k't \quad \text{where } t = x/u \text{ and } k' = k[\text{O}_3]_0$$

A plot of $\ln [\text{Cl}^\bullet]$ against t gives a straight line with a gradient of $-k'$ (the pseudo-first order rate constant). The whole set of experiments is then repeated for different $[\text{O}_3]_0$. The value of k' is plotted against $[\text{O}_3]_0$, which gives a straight line with gradient k (the overall, second order rate constant for the reaction).

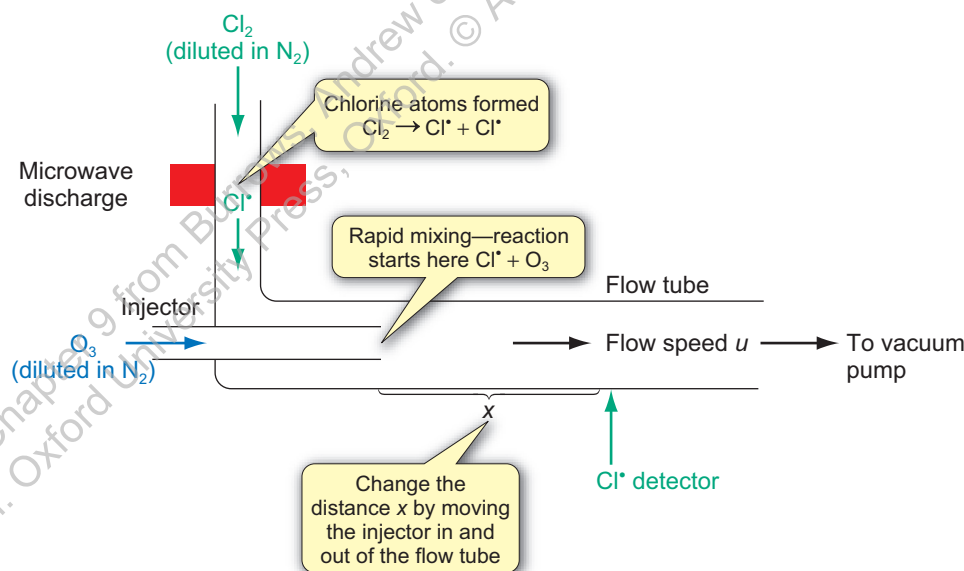


Figure 9.14 The discharge flow method for investigating fast reactions.

i **Photolysis** is the breaking of bonds in a molecule by the absorption of light.

➞ The thermodynamics of the formation of vapour trails (contrails) from jet aircraft is discussed in Box 15.4 (p.705).

i There is a wide variety of flash photolysis techniques using different energy sources and with different methods of monitoring the reaction. The technique can also be adapted to study reactions in solution.

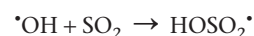


This screencast walks you through Figure 9.15 to explain the stages in a flash photolysis experiment to find the rate constant for the reaction of $\cdot\text{OH}$ radicals with SO_2 .

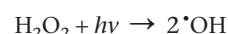
Flash photolysis

In one example of this technique, a brief intense flash of light from a laser is used to produce radicals very rapidly by photolysis of a precursor molecule. The radicals generated react with a second reactant already in the reaction cell. The concentration of the radical rises rapidly during the flash and then decays as it reacts. Its concentration is monitored in a series of experiments as a function of time.

For example, the reaction of $\cdot\text{OH}$ radicals with SO_2 molecules has been studied in this way. (This reaction is important in the formation of vapour trails from jet aircraft.)



In this case, the reaction cell initially contains a mixture of H_2O_2 and SO_2 . A laser operating at 248 nm photolyses the H_2O_2 molecules to produce $\cdot\text{OH}$ radicals



The conditions are arranged so that $[\cdot\text{OH}] \ll [\text{SO}_2]$ and the reaction shows pseudo-first order kinetics. The concentration of hydroxyl radicals is measured spectroscopically. The sequence of events in the investigation is shown in Figure 9.15.

A series of experiments is carried out with several delay times after the flash, using a constant value of $[\text{SO}_2]_0$. The results (Graph 1) give a kinetic profile of $[\cdot\text{OH}]$ against time. A first order plot of $\ln[\cdot\text{OH}]$ against time (Graph 2) is a straight line with gradient $-k'$ (the pseudo-first order rate constant). The whole set of experiments is then repeated for different $[\text{SO}_2]_0$ and the overall rate constant found from a plot of k' against $[\text{SO}_2]_0$ (Graph 3) as described on p.397 for the $\text{Cl}\cdot + \text{O}_3$ reaction.

The length of the initial laser pulse must be significantly shorter than the timescale of the reaction being studied. Gas phase reactions of radicals occur on microsecond and millisecond timescales and are studied using lasers with pulse lengths ~ 10 ns (nanosecond, 1×10^{-9} s). Faster reactions, such as the reactions involved in photosynthesis, require lasers with shorter pulse lengths ~ 1 ps (picosecond, 1×10^{-12} s). Even shorter laser pulses on the femtosecond timescale (1 fs = 1×10^{-15} s) have been used to observe the vibrations and

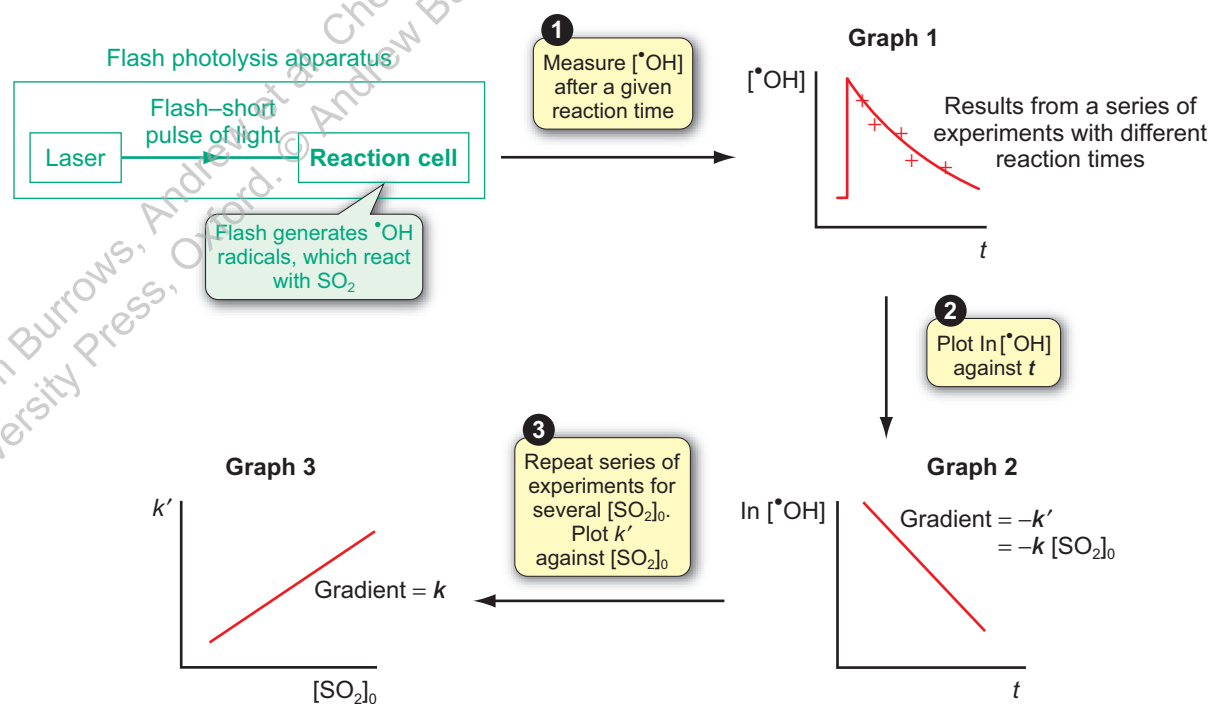


Figure 9.15 Stages in a flash photolysis experiment, for example the reaction of $\cdot\text{OH}$ radicals with SO_2 .



Femtosecond lasers are being used to investigate the rapid transfer of solar energy between molecules in photosynthesis.



The Egyptian born chemist, Ahmed Zewail, was awarded the Nobel Prize in 1999 for his development of femtochemistry, the probing of chemical reactions on the femtosecond ($1 \text{ fs} = 1 \times 10^{-15} \text{ s}$) timescale. His technique has been called the world's fastest camera.

rotations of chemical bonds, and their rearrangements, as product molecules are formed from the reactants. The laser is effectively 'freezing' the molecules in time and taking a snapshot. This new area of chemistry is called **femtochemistry**.

Box 9.4 describes one of the earliest uses of flash photolysis and the significance of the results almost 50 years later.

i Femtochemistry allows chemists to observe the transition state for a reaction (see Section 9.8, p.430).

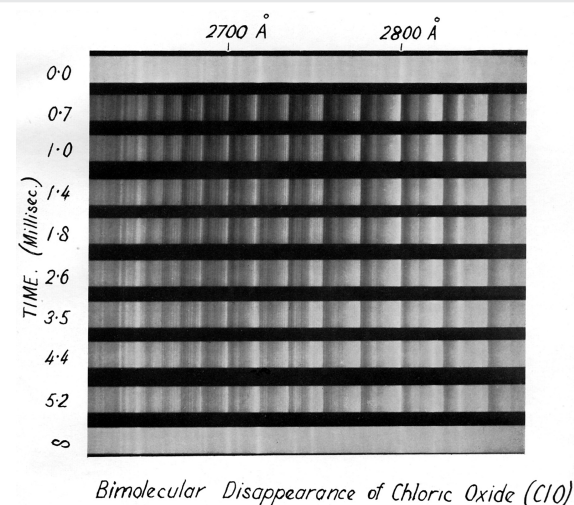


Box 9.4 Using flash photolysis to monitor $\text{ClO}^\bullet$ radicals

Ronald Norrish and George Porter were awarded the Nobel Prize in 1967 for their invention of flash photolysis in the late 1940s. One of the earliest publications using the new technique described the photochemical reaction between Cl_2 and O_2 and the observation of an absorption spectrum due to the short-lived intermediate, $\text{ClO}^\bullet$. Porter then used this spectrum to monitor the concentration of $\text{ClO}^\bullet$ at different times to study the kinetics of its decay.

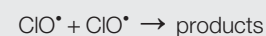
The absorption spectrum was obtained by first firing a photolytic flash lamp (causes photolysis) to produce $\text{ClO}^\bullet$ radicals and then firing a second flash lamp a measured time delay after the first. Light from the second flash passed through the reaction cell and then through a spectrometer. The spectrum was recorded on a photographic plate. A series of experiments was conducted with different time delays between the two flashes.

Figure 1 is a photograph from Porter's 1952 paper and shows a series of spectra recorded at different times after the photolytic flash. Each spectrum contains a series of bands corresponding to the vibrational structure of the absorption spectrum in the region of 270 nm. The strength of the $\text{ClO}^\bullet$ absorption decreases with time as the $\text{ClO}^\bullet$ reacts. The concentration of $\text{ClO}^\bullet$ was determined from the fraction of light absorbed at a specific wavelength (see Section 10.3, p.454).



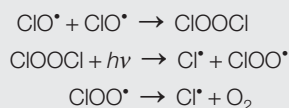
▲ Figure 1 $\text{ClO}^\bullet$ spectra recorded at different times after the photolytic flash.

By plotting $1/[\text{ClO}^\bullet]$ against time and obtaining a straight line, Porter showed that the decay of $\text{ClO}^\bullet$ is a second order process and obtained the rate constant for the reaction

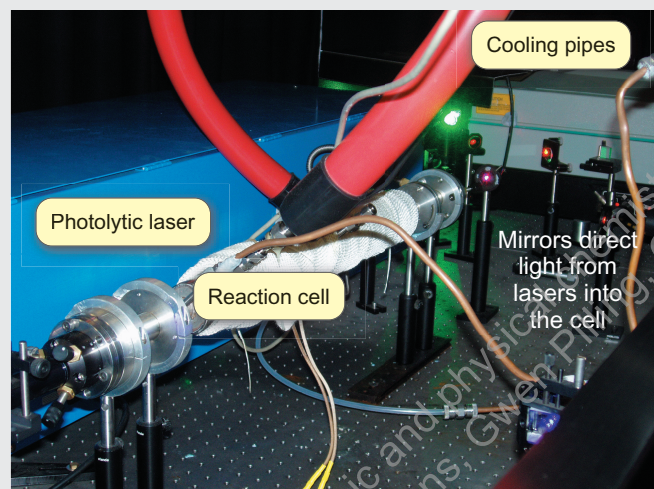


→ Fifty years later, interest in this reaction was reawakened and new studies, based essentially on the same technique as that used by Porter, were conducted using a modern instrument at the Jet Propulsion Laboratory in California. The impetus for the new investigation was the observation of the stratospheric ozone 'hole' by Joe Farman and his colleagues of the British Antarctic Survey at Halley Bay in Antarctica. $\text{ClO}^\bullet$ is involved in a catalytic cycle leading to ozone depletion (see Boxes 27.6, p.1227 and 27.8, p.1235).

However, the catalytic cycle cannot explain the dramatic reduction in ozone in the Antarctic spring when the concentration of oxygen atoms is very low. (In the cycle, $\text{ClO}^\bullet$ radicals react with O to regenerate $\text{Cl}^\bullet$ radicals.) An alternative mechanism for forming $\text{Cl}^\bullet$ from $\text{ClO}^\bullet$ was needed and the second order reaction of $\text{ClO}^\bullet$, first investigated by Porter, provided a possible route to $\text{Cl}^\bullet$, via its dimer, ClOOCi



Experiments (like the one in Figure 2) were designed to measure the yields of all the possible products from the reaction $\text{ClO}^\bullet + \text{ClO}^\bullet$. The results showed that dimer formation is the major route to the formation of $\text{Cl}^\bullet$ radicals from $\text{ClO}^\bullet$ in the Antarctic spring.



▲ **Figure 2** A modern flash photolysis apparatus set up to monitor the decay of radicals. The photolytic laser is on the left. The probe laser (which fires the second flash) is off to the right. Mirrors direct the light from the two lasers into the reaction cell. The red light being reflected by the mirrors is from the probe laser.

Question

Write a differential rate equation and an integrated rate equation for the formation of the $\text{ClO}^\bullet$ dimer from $\text{ClO}^\bullet$.



Summary

- An elementary reaction is a single step reaction involving one or two molecules or atoms.
- For a general reaction $aA + bB \rightarrow pP + qQ$
rate of reaction = $-\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{p} \frac{d[P]}{dt} = \frac{1}{q} \frac{d[Q]}{dt}$
- The rate equation for an elementary reaction can be written directly from the chemical equation for the reaction.
- A rate equation, in which the rate of consumption of a reactant, or the rate of formation of a product, is written as a differential, is called a differential rate equation.
- An integrated rate equation gives the concentration of a reactant as a function of time.
- The half life of a reactant is the time taken for its concentration to fall to half its initial value.
- Table 9.2 summarizes the equations for the first order, second order, and pseudo-first order elementary reactions that you have met in Section 9.4.

Table 9.2 A summary of equations for elementary reactions

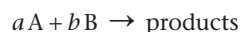
Type of reaction	Order of reaction	Differential rate equation	Integrated rate equation	Half life, $t_{1/2}$
$A \rightarrow \text{products}$	First order	$-\frac{d[A]}{dt} = k[A]$	$\ln [A]_t = \ln [A]_0 - kt$	$\frac{\ln 2}{k}$
$A + A \rightarrow \text{products}$	Second order	$-\frac{d[A]}{dt} = 2k[A]^2$	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + 2kt$	$\frac{1}{2k[A]_0}$
$A + B \rightarrow \text{products}$ where $[A] \ll [B]$	Pseudo-first order	$-\frac{d[A]}{dt} = k'[A]$ where $k' = k[B]_0$	$\ln [A]_t = \ln [A]_0 - k't$ $= \ln [A]_0 - kt[B]_0$	$\frac{\ln 2}{k'} = \frac{\ln 2}{k[B]_0}$

? For practice questions on the topics in Sections 9.1–9.4, see questions 2, 3, 6, 8, 9, and 11–13 at the end of this chapter (pp.440–441).

9.5 Complex reactions: experimental methods

Most of the reactions you will meet are not simple elementary reactions. They are **complex reactions** in which the mechanism involves a series of elementary reactions. For a complex reaction, you cannot write down the overall rate equation directly from the stoichiometric equation for the reaction. The rate equation *must* be determined from experiments to investigate how the rate depends on the concentration of each of the reactants.

For a general reaction in which A and B are reactants



the overall rate equation is given by an equation of the form

$$\text{rate of reaction} = k[A]^m[B]^n \quad (9.11)$$

where k is the **overall rate constant** for the reaction and m and n are the **orders of the reaction**, with respect to A and B, respectively. The orders often have values of 0, 1, or 2, but sometimes can take higher, or even fractional, values. The **overall order** of the reaction is $(m + n)$.

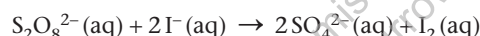
Note that the stoichiometric coefficients in the chemical equation, a and b , do not appear in the overall rate equation. It may sometimes turn out that m and n take the values of a and b , but you cannot assume this.

Sometimes a substance that does not appear among the reactants in the stoichiometric equation can appear in the rate equation. This might be a product of the reaction or a catalyst. If the rate of the overall reaction is found experimentally to be unaffected by the concentration of a reactant, the reaction is said to be **zero order** with respect to that reactant ($m = 0$) and it does not appear in the overall rate equation.

Here are some examples of complex reactions.

Example 1 The reaction of iodide ions (I^-) with peroxodisulfate ions ($S_2O_8^{2-}$)

The equation for the reaction is



Experiments show that the rate equation for the reaction is

$$\text{rate of reaction} = k[S_2O_8^{2-}(\text{aq})][I^-(\text{aq})]$$

so this reaction is first order with respect to $S_2O_8^{2-}$, first order with respect to I^- , and second order overall.

Example 2 The reaction of propanone (CH_3COCH_3) with iodine (I_2)

The equation for the reaction is



The reaction is catalysed by acids.

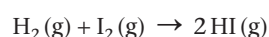
Experiments show that the rate equation for the reaction is

$$\text{rate of reaction} = k[CH_3COCH_3(\text{aq})][H^+(\text{aq})]$$

so this reaction is first order with respect to both CH_3COCH_3 and H^+ . Note that the catalyst, H^+ , appears in the rate equation even though it is not used up in the reaction. In contrast, I_2 does not appear in the rate equation, even though it is a reactant. The reaction is zero order with respect to I_2 . The overall order of the reaction is two.

Example 3 The reaction between hydrogen (H_2) and iodine (I_2)

The equation for the reaction is



Experiments show that the rate equation for the reaction is

$$\text{rate of reaction} = k[H_2(\text{g})][I_2(\text{g})]$$

How do I know if a reaction is an elementary process or a complex reaction?

Fast reactions involving a radical reactant (and their reverse reactions) are generally elementary reactions. You should always assume that a reaction is a complex reaction unless you read otherwise. Reactions of the type $A + B + C$ or $A + 2B$ must be complex because the probability of more than two reactant molecules colliding simultaneously is very low.



This screencast explains the difference between elementary and complex reactions.

 The mechanism of the acid-catalysed reaction of propanone with halogens is discussed in Section 23.3 (p.1079).

so this reaction is first order with respect to H_2 and first order with respect to I_2 and second order overall. (Further experiments show that this is not an elementary reaction, but a complex reaction involving I atoms.)

Example 4 The reaction between hydrogen (H_2) and bromine (Br_2)

The equation for the reaction is



Experiments show that the rate equation for the reaction is

$$\text{rate of reaction} = k[\text{H}_2(\text{g})][\text{Br}_2(\text{g})]^{1/2}$$

so this reaction is first order with respect to H_2 , but has an order of $\frac{1}{2}$ with respect to bromine. The overall order is $\frac{3}{2}$.

Compare this with Example 3. Similar looking reactions do not always have the same kinetics.

 The experimentally determined orders for complex reactions give chemists an insight into the **mechanisms** by which reactions occur (see Section 9.6, p.412). The mechanism of the reaction $\text{H}_2 + \text{Br}_2$ involves a series of four elementary reactions and is described in more detail in Section 9.6 (p.419).

 In all kinetics experiments, it is important to carry out the reactions at a constant temperature (for example, in a thermostatically controlled water bath). Otherwise, the results will be meaningless.

Choosing an experimental method

To investigate the kinetics of a complex reaction, you need to determine how the rate of the reaction depends on the concentration of each of the reactants—and also on the concentration of any catalyst involved. From these experiments you can find the order of the reaction with respect to each of these components, then construct an overall rate equation and find the overall rate constant for the reaction.

The first step is to decide on an experimental method for monitoring the concentration of one of the reactants (or a product) as a function of time. This is discussed in Section 9.3. Box 9.5 describes a method for studying fast reactions in solution.

Having decided how you are going to monitor the reaction, you then need to think about how to carry out the experiments and analyse the results. There is a range of procedures available. Which one to choose depends on the particular reaction, what information you require, and the accuracy needed.



Box 9.5 The stopped-flow technique

The stopped-flow technique is used for studying fast reactions in solution. It is essentially a way of rapidly mixing the reactants.

Two solutions, containing the separate reactants, are contained in syringes, which are mechanically driven to force the solutions into the mixing chamber and then down a short tube and into a third syringe. The solutions enter the mixing chamber turbulently and this promotes rapid mixing. After a short time, the plunger in the third syringe hits a stop and the flow is immediately halted. The concentration of one of the reactants, or of a product, is then monitored as a function of time using, for example, absorption spectroscopy, and a kinetic profile is determined.

The kinetics of the reaction (order and rate constant) are determined by measuring kinetic profiles for a range of initial concentrations. Typical reaction timescales are ~20 ms.

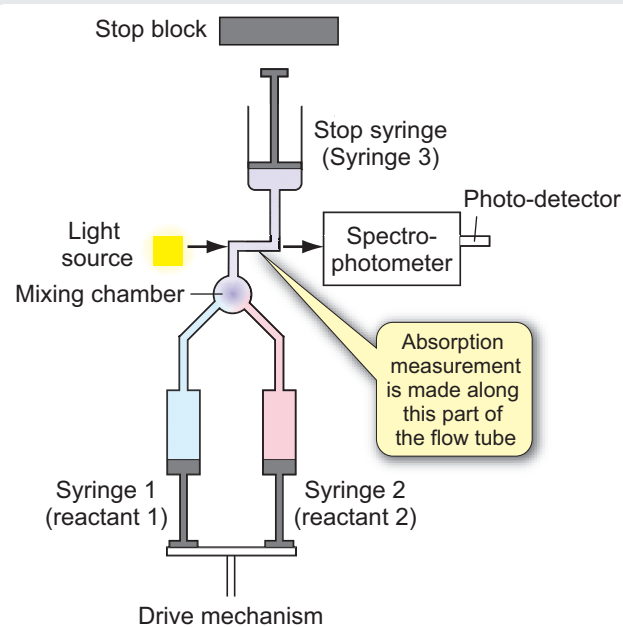


Diagram of a stopped-flow apparatus. ➤

The isolation technique

The most common type of reaction involves more than one reactant. The trouble is that, as the reaction proceeds, the concentrations of *all* the reactants decrease and affect the overall rate of the reaction. This problem is overcome by isolating one reactant at a time, by having all the other reactants in large excess. As a result, their concentrations can be assumed to be constant throughout the reaction and the effect of a single reactant on the rate of reaction can be studied. This is sometimes called the **isolation technique**.

For a reaction of the type, $A + B \rightarrow \text{products}$, where the rate of reaction $= k[A]^m[B]^n$, you would need to conduct two sets of experiments. In the first set, the concentration of B is in large excess, so that the order with respect to A can be determined. Rate of reaction $= k'_A[A]^m$, where k'_A is an effective rate constant for the reaction of A, and $k'_A = k[B]^n_0$.

In a second set of experiments, the concentration of A is in large excess, and the order with respect to B is determined. Rate of reaction $= k'_B[B]^n$, where k'_B is an effective rate constant for the reaction of B, and $k'_B = k[A]^m_0$.

The next task is to decide what method to use in each set of experiments to determine the order with respect to a single reactant. There are a number of options:

- drawing tangents to the concentration–time curve;
- initial rates method;
- using integrated rate equations;
- using half lives.

Drawing tangents to the concentration–time curve

First, the readings of concentration of the reactant A against time are used to plot a kinetic profile. If the plot is a straight line, the rate of reaction is independent of the concentration of A and the reaction is zero order with respect to A. In this case, rate of reaction $= k$ and the rate constant can be found from the gradient of the straight line.

More likely, the kinetic profile will be a curve of the type shown in Figure 9.16. Finding the rate of reaction at different values of [A] involves drawing tangents to the curve at different points and calculating the gradient of the tangent at each point. The gradient of each tangent is a measure of the rate of the reaction at that concentration of A.

i The **isolation technique** is introduced in Section 9.4 (p.391) where pseudo-first order elementary reactions are discussed. It is used in conjunction with one of the methods listed below (except the initial rates method where it is unnecessary).

 This may seem odd. How can the rate of reaction be independent of one of the reactants? This is explained on p.413.

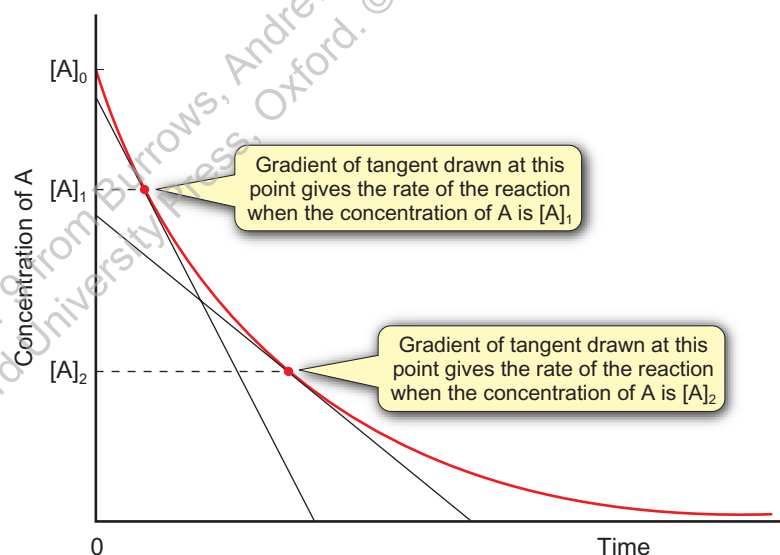


Figure 9.16 Drawing tangents to a concentration–time curve.

$\Sigma \log ab = \log a + \log b$ and
 $\log a^b = b \log a$
 Further help with logarithms can be
 found in Maths Toolkit MT3 (p.1310).

$$y = mx + c$$

$$\log(\text{rate}) = m \log[A] + \log k'$$

(here m is the order with respect to A)

- You can then use the values of the rates of reaction determined from the tangents to plot a graph of the rate against $[A]$. If this graph is a straight line, the rate of reaction is directly proportional to $[A]$ and the reaction is pseudo-first order with respect to A.
- If the plot is a curve, the reaction is not first order. You cannot, however, assume it must then be second order with respect to A—it might be third order, or fractional. You must now plot a graph of the rate against $[A]^2$. If this plot is a straight line, the reaction is second order with respect to A. If this plot is also a curve, the reaction is neither first nor second order with respect to A.

A less laborious and more general method of analysing the data involves plotting the *logarithms* of the rate and the concentration (called a **log-log plot**).

$$\text{rate of reaction} = k'[A]^m$$

Taking logarithms (either $\log_{10}$ or $\log_e$) of each side of the equation gives $\log(\text{rate}) = \log(k'[A]^m)$, so that

$$\log(\text{rate}) = m \log[A] + \log k' \quad (9.12)$$

This equation has the form of a straight line, $y = mx + c$, where m is the gradient and c the intercept. A plot of $\log(\text{rate})$ against $\log[A]$ is *always* a straight line, whatever the order of the reaction with respect to A. The order is found from the gradient of the line and the rate constant is found from the intercept. The sequence of reasoning is summarized in Figure 9.17.

It is difficult to draw accurate tangents to a curve—particularly if there is some scatter in the experimental data that do not fit on to a smooth curve. To help, there are software packages that allow you to feed in the concentration–time data to obtain the gradient as a

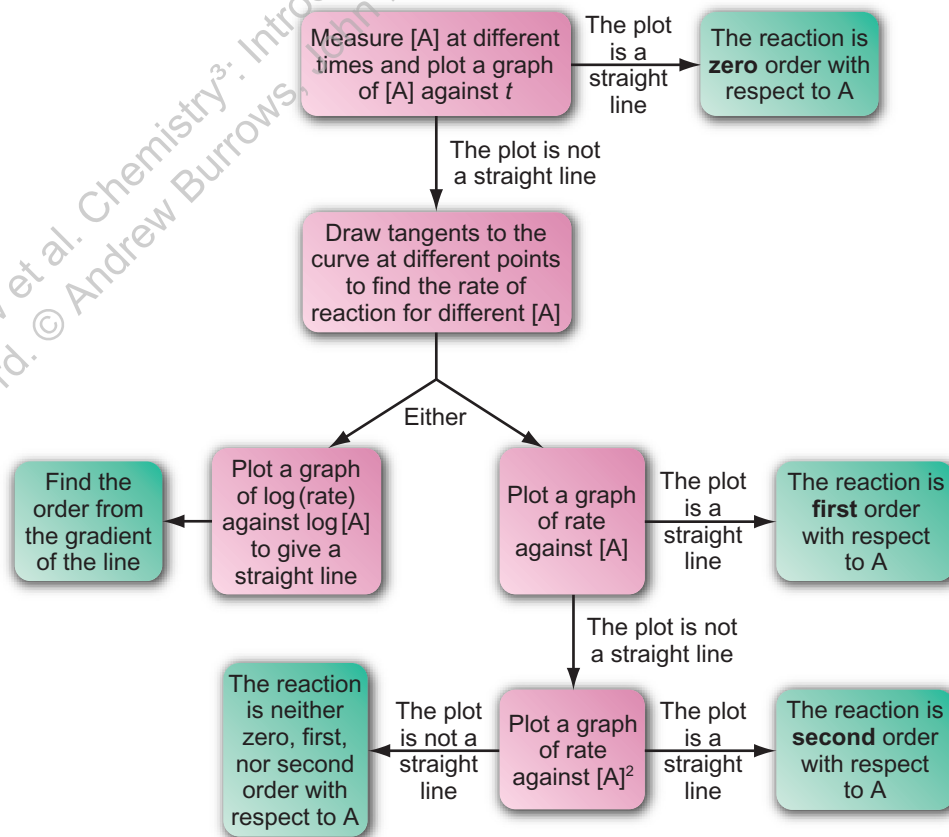


Figure 9.17 A summary of the sequence of reasoning to determine the order with respect to A by drawing tangents to a concentration–time curve and subsequent graphical methods.

function of concentration. Even so, the method is not used in accurate work. Log–log plots are quite good for determining reaction orders, but tend to give large errors on the values of rate constants.

Initial rates method

The initial rates method provides a more accurate variant of the previous method. As before, readings of concentration of a reactant (or product) at different times are used to plot a kinetic profile, but this time only one tangent is drawn to the curve at $t = 0$. The gradient of the tangent gives the rate of reaction at the start of the reaction. The experiment is then repeated several times using different initial concentrations.

For example, to investigate the decomposition of dinitrogen pentoxide



a series of separate experiments is carried out, each with a different initial concentration of N_2O_5 . In each experiment, the concentration of N_2O_5 is monitored as the reaction proceeds and a graph of $[\text{N}_2\text{O}_5]$ against time is plotted to give a kinetic profile. For each graph, only the tangent at $t = 0$ is drawn, so the reaction need only be followed long enough to allow an accurate tangent to be drawn at this point. The gradients of the tangents give the initial rate of the reaction for different initial concentrations of N_2O_5 .

The way to process and interpret the initial rate data to assign a reaction order follows the reasoning in Figure 9.17. You can often get a preliminary idea of the orders by inspecting the tabulated data as described in Worked example 9.5. The most reliable method is to plot a graph of $\log(\text{initial rate})$ versus $\log(\text{initial concentration})$ for each reactant (see p.404).

Figure 9.18(a) shows the tangents drawn to find the initial rates in five separate experiments. Figure 9.18(b) shows a plot of initial rate against initial concentration. This is a straight line, showing that the rate is proportional to $[\text{N}_2\text{O}_5]$ and the reaction is first order.

The initial rate method still has the disadvantage of drawing a tangent to a curve, and the tangent at $t = 0$ is particularly difficult to draw accurately. This problem can be overcome by measuring $\Delta[\text{N}_2\text{O}_5]$, the amount of reactant consumed in a given time Δt , instead of drawing the tangent. Provided $\Delta[\text{N}_2\text{O}_5]$ is less than about 10% of $[\text{N}_2\text{O}_5]_0$, $\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$ is a good approximation to the initial rate. This is illustrated in Figure 9.19.

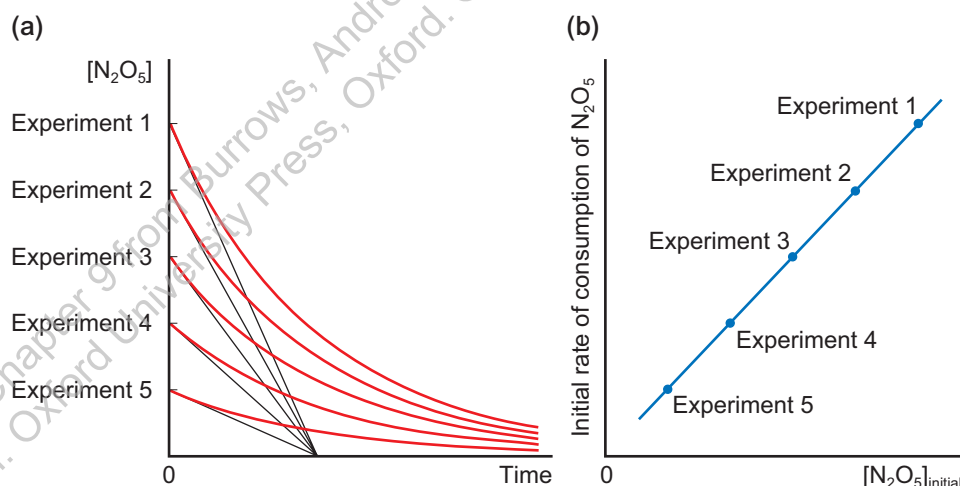


Figure 9.18 (a) The initial rate of reaction for each experiment (1–5) is found by drawing a tangent to the curve at the start of the reaction. (b) A plot of the five initial rates obtained in (a) against the initial concentration of N_2O_5 for each experiment.

i The **initial rate** of a reaction is the instantaneous rate of change in concentration of a reactant at the instant the reaction starts.

i For a reaction involving more than one reactant, the isolation technique is not necessary when using the initial rates method, since the concentrations of all the reactants are approximately constant (at their initial values) for the time interval of the initial rate.

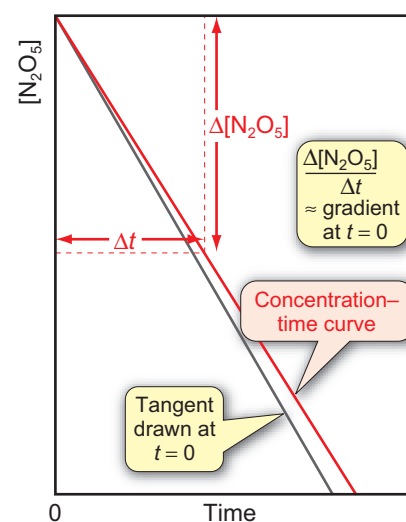
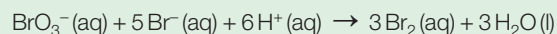


Figure 9.19 This is the first part of one of the curves in Figure 9.18a, near $t = 0$. It shows $\Delta[\text{N}_2\text{O}_5]$ for a 10% change in concentration. The error introduced by approximating the gradient to $\Delta[\text{N}_2\text{O}_5]/\Delta t$ is 4.8%.


Worked example 9.5 Using the initial rate method to investigate the reaction between bromate ions and bromide ions

Bromate ions (BrO_3^-) react with bromide ions (Br^-) in acid solution to form bromine (Br_2)



The concentration of $\text{BrO}_3^-(\text{aq})$ was monitored at 298 K in four separate experiments, each with different initial concentrations of the reactants as shown in the following table.

Experiment	Initial concentration / mol dm^{-3}			Initial rate / $10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$
	$[\text{BrO}_3^-(\text{aq})]$	$[\text{Br}^-(\text{aq})]$	$[\text{H}^+(\text{aq})]$	
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.6
4	0.20	0.10	0.20	9.6

(a) Determine the order of reaction with respect to each reactant and give the overall order of reaction.

(b) Write the overall rate equation for the reaction and find a value of the rate constant, k , at 298 K.

Strategy

By inspecting the data, find how the initial rate varies for each reactant as its concentration changes. To isolate the effect of each reactant, compare experiments that differ in the concentration of one substance at a time.

Solution

(a) Finding the orders of reaction

- Order with respect to BrO_3^- . Comparing experiments 1 and 2, $[\text{BrO}_3^-]$ doubles and the rate doubles, so the reaction is first order with respect to BrO_3^- .
- Order with respect to Br^- . Comparing experiments 1 and 3, $[\text{Br}^-]$ increases by a factor of 3 and the rate increases by a factor of 3, so the reaction is first order with respect to $[\text{Br}^-]$.
- Order with respect to H^+ . Comparing experiments 2 and 4, $[\text{H}^+]$ increases by a factor of 2, but the rate increased by a factor of 4 (2^2). The rate of reaction in this case is proportional to $[\text{H}^+]^2$, so the reaction is second order with respect to H^+ .

The overall order of the reaction = $1 + 1 + 2 = 4$.

(b) The rate equation and determination of the rate constant.

The rate equation for the overall reaction is

$$\text{rate of consumption of } \text{BrO}_3^- = -\frac{d[\text{BrO}_3^-]}{dt} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

Find a value for k by substituting the values from one of the experiments into the rate equation. For example, using experiment 2

$$2.4 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1} = k \times (0.20 \text{ mol dm}^{-3}) \times (0.10 \text{ mol dm}^{-3}) \times (0.10 \text{ mol dm}^{-3})^2$$

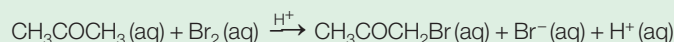
$$k = 12 \text{ dm}^9 \text{ mol}^{-3} \text{ s}^{-1}$$

The average value of k calculated from the four experiments is $12 \text{ dm}^9 \text{ mol}^{-3} \text{ s}^{-1}$.



→ Question

The acid-catalysed bromination of propanone was investigated using the initial rate method at 298 K



The concentration of Br_2 was monitored in five separate experiments. By inspection of the following data, determine the order of the reaction with respect to each of the substances in the table.

Experiment	Initial concentration / mol dm^{-3}			Initial rate / $10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$
	$[\text{CH}_3\text{COCH}_3(\text{aq})]$	$[\text{Br}_2(\text{aq})]$	$[\text{H}^+(\text{aq})]$	
1	0.30	0.05	0.05	5.60
2	0.30	0.10	0.05	5.60
3	0.30	0.05	0.10	11.1
4	0.40	0.05	0.20	30.5
5	0.40	0.05	0.05	7.55

Using integrated rate equations

Integrated rate equations provide the most accurate method of determining reaction orders and rate constants, and are widely used in experimental work in chemical kinetics. The integrated rate equations derived in Section 9.4 for first and second order elementary reactions can be applied to complex reactions, when considering the order with respect to a single reactant. This is achieved using the isolation technique described on p.403, in which all reactants except the one under investigation are in excess. The rate constant in the integrated rate equation is then an effective rate constant and the order determined is called a **pseudo-order**.

For a pseudo-first order reaction, the integrated rate equation is

$$\ln [A]_t = \ln [A]_0 - k't \quad (\text{where } k' \text{ is the effective rate constant}) \quad (\text{from 9.6a})$$

so a plot of $\ln [A]$ against t is a straight line with a gradient of $-k'$.

For a second order reaction, the integrated rate equation is

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + 2k't \quad (\text{from 9.7b})$$

so a plot of $\frac{1}{[A]}$ against t is a straight line with a gradient of $+2k'$.

The integrated rate equation for a zero order reaction is derived in Box 9.6 and is given by

$$[A]_t = [A]_0 - k't \quad (9.13)$$

so a plot of $[A]_t$ against t is a straight line with a gradient of $-k'$. Box 9.7 describes an example of a zero order reaction.

The advantage of integrated rate equations is they allow you to plot your experimental readings of concentration and time directly as straight lines, without having to calculate the rate of reaction from the gradient of a tangent to the concentration–time plot. (They also allow you to make good use of all of your data as it becomes harder to draw tangents towards the end of a reaction.)

Worked example 9.6 illustrates the use of integrated rate equations in the analysis of the kinetics of a complex reaction.

Integrated rate equations are derived and explained for first and second order elementary reactions in Section 9.4 (p.388). The same equations apply for complex reactions when investigating the order with respect to a single reactant.

i The '2' in Equation 9.7b arises from the stoichiometric equation for the reaction (see p.386 and p.389). When using Equation 9.7b for a complex reaction, check whether the '2' is appropriate for the particular reaction being studied.

$$y = mx + c$$

$$[A]_t = -k't + [A]_0$$

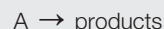
i For a zero order reaction, $\text{rate} = k$, so the units of k are the same as the units of rate: $\text{mol dm}^{-3} \text{ s}^{-1}$.



Box 9.6 Deriving the integrated rate equation for a zero order reaction

This follows the general procedure given for deriving the integrated rate equation for a first order reaction in Box 9.1 (p.389).

The differential rate equation for a pseudo-zero order reaction



is given by

$$\begin{aligned} \text{rate of reaction} &= -\frac{d[A]}{dt} \\ &= k' \end{aligned}$$

Separating the variables, the equation can be rewritten as

$$d[A] = -k' dt$$

Integrate both sides of the equation from $[A] = [A]_0$ at $t = 0$, to $[A] = [A]_t$ at time t .

$$\int_{[A]_0}^{[A]_t} d[A] = -k' \int_0^t dt$$

This gives

$$\begin{aligned} [A]_t - [A]_0 &= -k' t \\ ([A]_t - [A]_0) &= -k'(t - 0) \end{aligned}$$

which can be rearranged to

$$[A]_t = [A]_0 - k' t \quad (9.13)$$



Box 9.7 Pharmacokinetics

The study of how a drug reaches its target and what happens to it in the body is known as **pharmacokinetics**. This information is important in the pharmaceutical industry when a new drug is being developed. There is no point in perfecting the structure of a new compound to bind to a specific receptor site, if the compound has no chance of reaching it.

There are four stages to consider:

- **drug absorption:** this is the route by which the drug reaches the bloodstream from the point of administration;
- **drug distribution:** once absorbed, the drug is distributed around the body in the blood supply and then more slowly from there to the tissues and organs;
- **drug metabolism:** this is the breaking down of the drug in the body due to the action of enzymes;
- **drug excretion:** the main route for excretion is via the kidneys and bladder.

The aim is to design a drug with an optimum lifetime in the body—one that is long enough for it to reach its target and be effective, but short enough to ensure it does not build up in the body.

The pharmacokinetics of ethanol have been studied and the results used to set the legal limits for alcohol in the blood and urine. Ethanol is rapidly absorbed into the bloodstream from the stomach and small intestine, and is quickly distributed to all parts of the body. Its metabolism in the liver is catalysed by a dehydrogenase enzyme (see Box 23.3 (p.1060)) and the degradation process follows zero order kinetics with respect to ethanol. This is because all the active sites in the enzyme molecules become filled with ethanol molecules. The slow step in the degradation takes place in the active sites and



▲ The degradation of ethanol in the body follows zero order kinetics.

the kinetics of this step governs the overall kinetics. The concentration of active sites with bound ethanol molecules is constant, so the rate of reaction is independent of the concentration of unbound ethanol. (The kinetics of enzyme-catalysed reactions is explained more fully in Box 9.8, p.436.)

Question

The breakdown in the body of the chemotherapy drug, cisplatin, is found to follow first order kinetics. The rate constant at body temperature is $1.87 \times 10^{-3} \text{ min}^{-1}$. The concentration of the drug in the body of a cancer patient is $5.16 \times 10^{-4} \text{ mol dm}^{-3}$. What will the concentration be after 24 hours?

Using half lives

The expressions for half lives, $t_{1/2}$, derived in Section 9.4 for first order and second order elementary reactions can be applied to complex reactions when considering the order with respect to a single reactant. The most useful half life is the one for first order reactions, which is a constant, and so independent of the concentration of A

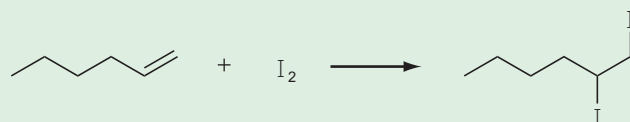
$$t_{1/2} = \frac{\ln 2}{k} \quad (9.9)$$

Half lives for first and second order elementary reactions are discussed in Section 9.4 (p.392). The same expressions for half lives apply for complex reactions when investigating the order with respect to a single reactant (see Table 9.2, p.400).



Worked example 9.6 Using integrated rate equations to investigate the reaction of iodine with hex-1-ene

Hex-1-ene reacts with I_2 in an addition reaction to give 1,2-diiodohexane. (The addition of halogens to alkenes is discussed in Section 21.3, p.968.)



The reaction was carried out in solution at 298 K using a large excess of hex-1-ene. Use the data in the following table to find the order of the reaction with respect to I_2 .

t/s	0	500	1500	2500	3500	4500	5500	6500	7500
$[I_2]/10^{-3} \text{ mol dm}^{-3}$	20.0	17.5	14.1	11.7	10.1	8.9	7.9	7.1	6.5

Strategy

The aim of this worked example is to demonstrate the use of integrated equations in finding the order of the reaction with respect to I_2 .

Assuming no other substances are involved, the overall rate equation for the reaction can be written as

$$\begin{aligned} \text{rate of reaction} &= -\frac{d[I_2]}{dt} \\ &= k[I_2]^m[\text{hex-1-ene}]^n \end{aligned}$$

Since hex-1-ene is in large excess, $[\text{hex-1-ene}]$ is constant throughout the reaction, so

$$-\frac{d[I_2]}{dt} = k'[I_2]^m$$

where k' is an effective rate constant.

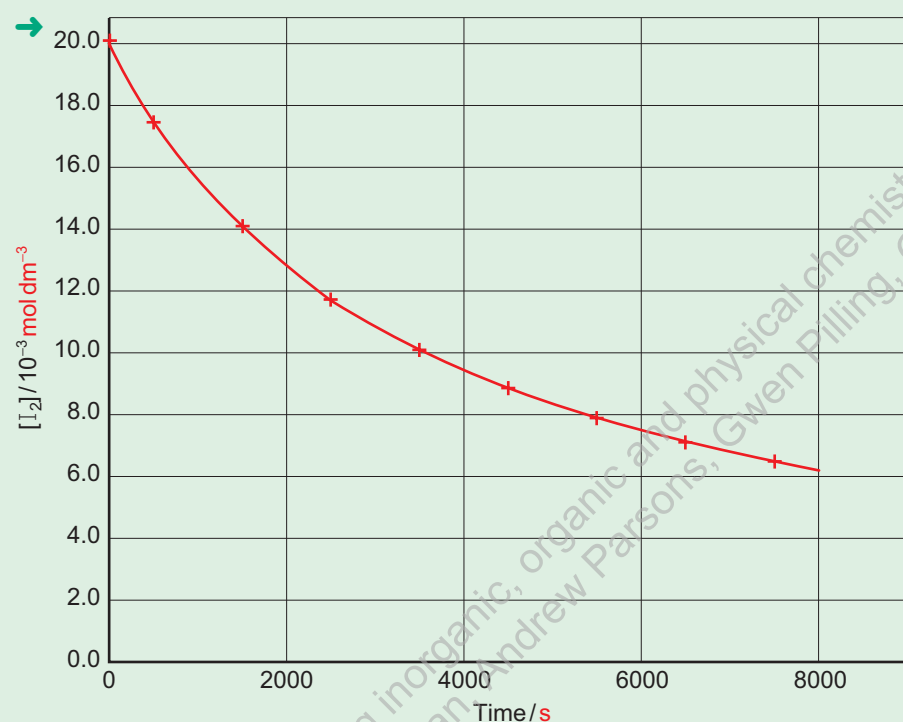
To find m , use integrated rate equations for zero, first, and second order reactions to plot $[I_2]$ against t , $\ln[I_2]$ against t , and $1/[I_2]$ against t , respectively. Whichever plot gives a straight line corresponds to the integrated rate equation for the reaction.

Solution

- To test for zero order kinetics, use the integrated rate equation

$$[A]_t = [A]_0 - k't \quad (9.13)$$

Use the data in the question to plot a graph of $[I_2]$ against time. →



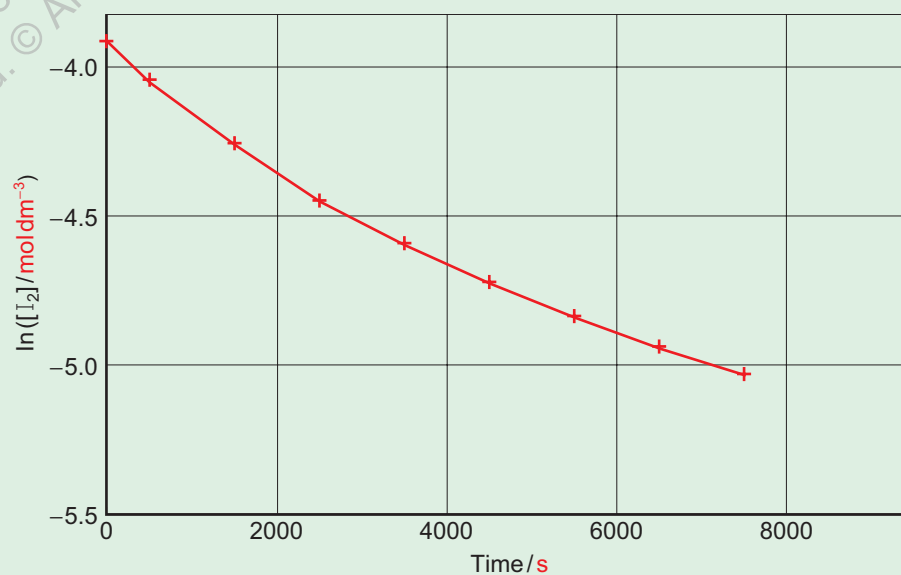
The plot is not a straight line, so the reaction is **not** zero order with respect to I_2 .

- To test for *first order kinetics*, use the integrated rate equation

$$\ln[A]_t = \ln[A]_0 - k't \quad (9.6a)$$

and plot a graph of $\ln[I_2]$ against time.

t/s	0	500	1500	2500	3500	4500	5500	6500	7500
$\ln([I_2]/\text{mol dm}^{-3})$	-3.91	-4.05	-4.26	-4.45	-4.60	-4.72	-4.84	-4.95	-5.04



The plot is not a straight line, so the reaction is **not** first order with respect to I_2 .

Σ The logarithm of $([I_2]/\text{mol dm}^{-3})$ is plotted here. You could have plotted the logarithm of $([I_2]/10^{-3} \text{ mol dm}^{-3})$ and this would also give a curve (see the maths note in Worked example 9.4 (p.395)). A logarithm has no units, but you should always indicate on the y-axis the units you have used for the concentration in calculating the logarithm.

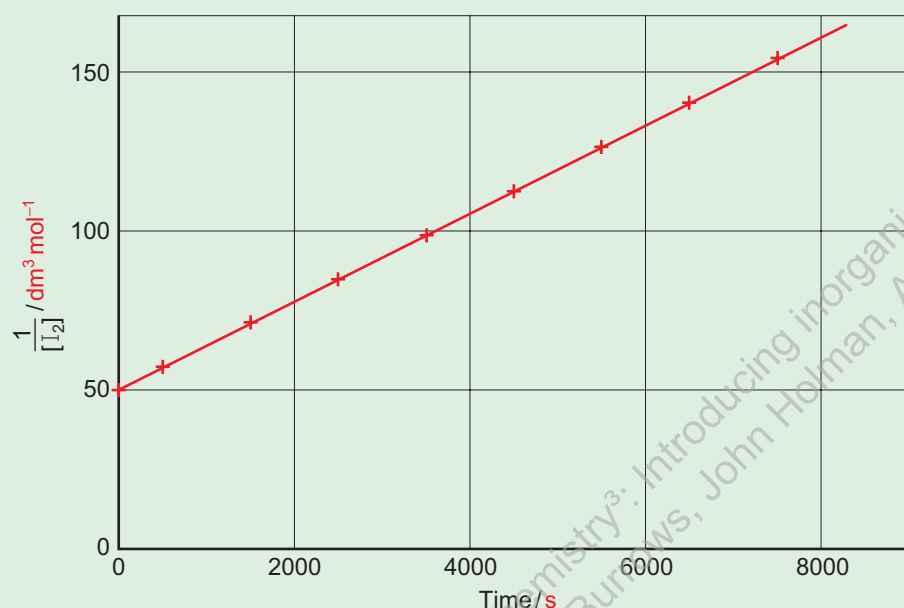
→ To test for *second order kinetics*, use the integrated rate equation

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + k't \quad (\text{from 9.7b})$$

and plot a graph of $\frac{1}{[I_2]}$ against time.

(The factor of 2 is omitted in Equation 9.7b because the stoichiometry for I_2 is 1; see pp.386–387.)

t/s	0	500	1500	2500	3500	4500	5500	6500	7500
$\frac{1}{[I_2]}/\text{dm}^3\text{mol}^{-1}$	50.0	57.1	70.9	85.5	100	112	127	141	154



This plot is linear and confirms that the reaction is second order with respect to I_2 . The pseudo-second order rate equation is then

$$\frac{d[I_2]}{dt} = k'[I_2]^2$$

Question

Suggest an alternative way of showing that the reaction is not first order with respect to I_2 that would have saved you plotting $\ln[I_2]$ against time.



Summary

- A complex reaction takes place by a series of elementary reactions.
- The overall rate equation of a complex reaction cannot be predicted from the stoichiometric equation. It *must* be determined experimentally.
- For the complex reaction, $aA + bB \rightarrow \text{products}$:

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

where k is the overall rate constant, and m and n are the orders with respect to A and B, respectively. The overall order of the reaction is $m + n$.





- The rate of a reaction can also depend on the concentration of a substance that does not appear as a reactant in the chemical equation, such as a catalyst.
- Orders of complex reactions often have values of 0, 1, or 2, but sometimes can take higher, or fractional, values.
- For reactions involving more than one reactant, the effect of the concentration of each reactant on the rate of reaction is studied using the isolation technique for each reactant in turn.
- Experimental methods for investigating the kinetics of complex reactions include: drawing tangents to a concentration–time curve; the initial rate method; using integrated rate equations; using half lives.
- Integrated rate equations provide the most accurate and reliable method for determining reaction orders and rate constants. Table 9.3 summarizes the characteristics for reaction orders 0, 1, and 2.

Table 9.3 Using integrated rate equations to study complex reactions

	Order		
	0	1	2
Rate equation	Rate = k'	Rate = $k'[A]$	Rate = $k'[A]^2$
Integrated rate equation	$[A]_t = [A]_0 - k't$	$\ln [A]_t = \ln [A]_0 - k't$	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + 2k't^*$
Plot of $[A]$ vs. t	Straight line	Curve	Curve
Plot of $\ln [A]$ vs. t	Curve	Straight line	Curve
Plot of $\frac{1}{[A]}$ vs. t	Curve	Curve	Straight line
Half life, $t_{1/2}$	Not constant	Constant	Not constant

* The multiplication factor before k' depends on the stoichiometry of the reaction.



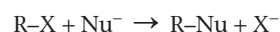
For practice questions on these topics, see questions 5, 7, 10, 14, and 21 at the end of this chapter (pp.440–442).

9.6 Complex reactions: reaction mechanisms

The series of elementary steps that make up a complex reaction is known as the **mechanism** of the reaction. Each step has its own rate constant—some steps may take place quickly; others more slowly. Sometimes there are very large differences between the timescales of the individual steps. For example, the timescale for the overall reaction may be minutes or hours, whereas an individual elementary step may take place on a timescale of only microseconds or nanoseconds.

Working out organic reaction mechanisms from kinetic studies

Kinetic studies of the type described in this section are the main source of evidence for the mechanisms of many organic reactions. For example, the kinetics of nucleophilic substitution reactions of halogenoalkanes were extensively studied by Sir Christopher Ingold and co-workers at University College, London, in the 1930s.

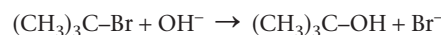


where $X = Cl, Br, \text{ and } I$ and Nu^- is a nucleophile, such as OH^- .

The researchers showed that there are two extreme types of kinetics for these reactions. In some cases, the rate of nucleophilic substitution was found to be first order with respect to the halogenoalkane, but zero order with respect to the nucleophile—that is, the rate of

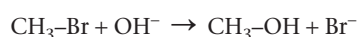
The mechanisms of nucleophilic substitution reactions of halogenoalkanes are discussed in Section 20.3 (p.924).

reaction does not depend on the concentration of the nucleophile. The overall order of the reaction is then one. The alkaline hydrolysis of 2-bromo-2-methylpropane (*tert*-butyl bromide) shows this type of kinetics



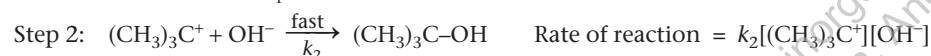
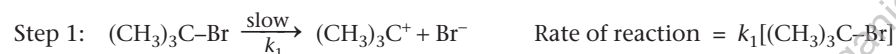
$$\text{rate of reaction} = k[(\text{CH}_3)_3\text{CBr}]$$

In other reactions, the rate of nucleophilic substitution was found to be first order with respect to the halogenoalkane and first order with respect to the nucleophile. The overall order of the reaction is then two. The alkaline hydrolysis of bromomethane shows this type of kinetics



$$\text{rate of reaction} = k[\text{CH}_3\text{Br}][\text{OH}^-]$$

So, how can these experimental observations be linked to a reaction mechanism in each case? Why is the rate of hydrolysis of $(\text{CH}_3)_3\text{C-Br}$ independent of the concentration of OH^- ions? This was explained by proposing the two-step mechanism shown below. Each step is an elementary reaction with its own rate constant. Step 1 proceeds much more slowly than step 2.



Step 1 acts as a bottleneck for the reaction—rather like an exit gate acting as a bottleneck for a crowd pushing its way out of a stadium. It doesn't matter how fast people move away from the gate—once they are through it, the rate of emptying the stadium is governed by the rate people pass through the gate. The rate of step 1 determines the rate of the overall reaction, so step 1 is called the **rate-determining step**. The rate equation for step 1 becomes the rate equation for the overall reaction. The rate-determining step in this case involves only a single molecule of the reactant and is said to be **unimolecular**. This type of mechanism is known as an **$\text{S}_\text{N}1$ mechanism** (substitution, nucleophilic, unimolecular).

In contrast, the hydrolysis of bromomethane is second order. To explain this, a one-step mechanism was proposed



This is an elementary reaction and the rate equation is given by

$$\text{rate of reaction} = k[\text{CH}_3\text{Br}][\text{OH}^-]$$

In the reaction, the OH^- ion starts to form a bond with the carbon atom in bromomethane at the same time as the bond between the carbon atom and bromine starts to lengthen and break. The transition from reactants to products takes place smoothly in a single step (called a **concerted process**).

In this case, the mechanism for the reaction involves a single step, which is rate-determining. Since this step involves two molecules, the reaction is said to be **bimolecular**. This type of mechanism is known as an **$\text{S}_\text{N}2$ mechanism** (substitution, nucleophilic, bimolecular).

Once a mechanism has been proposed for an organic reaction, chemists look carefully at the features of the reaction, particularly any stereochemical implications, and design experiments to test the theory. A mechanism can never be proved absolutely. A valid mechanism must consist of one or more elementary reactions, the sum of which gives the overall equation for the reaction. It must correctly predict the experimentally determined rate equation and be consistent with all related kinetic experimental data and stereochemical observations.

The two important points to note at this stage are, firstly, the link between kinetics experiments and theoretical reaction mechanisms and, secondly, the idea of a slow, rate-determining step governing the kinetics of a complex reaction. These ideas are taken further in Section 9.8.

i For many halogenoalkanes, the kinetics are more complex, suggesting that the reactions are taking place by mechanisms that lie somewhere between the two.

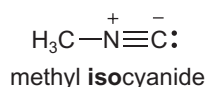
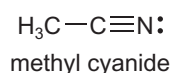
 The use of bromomethane as a pesticide is discussed at the start of Chapter 20 (p.911).

i Explaining zero order
The idea of a rate-determining step explains why it is possible to have a rate equation that is zero order for a particular reactant. If the reactant is not involved in the rate-determining step, its concentration won't affect the rate of the reaction. But the reactant is still involved in the reaction and gets used up.

i A reaction in which the reactants are converted to products in a single step is said to be a **concerted reaction**.

i The **molecularity** of a reaction is the number of molecules taking part in the rate-determining step of the reaction. It applies only to elementary reactions. The idea of molecularity is developed further in Section 9.8 (p.428).

 The detailed mechanisms of these nucleophilic substitution reactions, and the stereochemical implications, are described in Section 20.3 (p.924). The effect of solvent polarity on the rate of reaction is also discussed.



➞ The IUPAC name for methyl cyanide is ethanenitrile; see Section 2.6 (p.98). It is a polar aprotic solvent often known by its common name, acetonitrile; see Section 20.3 (p.931).

i Methyl cyanide and methyl isocyanide are functional group isomers; see Section 18.1 (p.810).

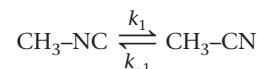
➞ Dynamic equilibrium and basic ideas about chemical equilibrium and K_c are discussed in Section 1.9 (p.56). The thermodynamics of equilibrium is developed in Chapter 15.

i Both O_2 and O have two unpaired electrons and are biradicals. The dots have been omitted here for simplicity.

Kinetics of reversible reactions

All the examples in the previous sections involve reactions that essentially go to completion in one direction. For many reactions, this is not the case and the reaction comes to an equilibrium position. As the reaction approaches equilibrium, the forward reaction is opposed by the reverse (back) reaction.

For example, in the isomerization of methyl isocyanide to methyl cyanide



the forward and reverse reactions are first order elementary reactions and k_1 and k_{-1} are the rate constants for the forward and reverse reactions, respectively.

As soon as CH_3CN is formed in the reaction, some of it reacts to reform CH_3NC , so the measured rate of reaction involves not only the rate of consumption of CH_3NC , but also the rate of formation of CH_3NC . The rate equation is given by

$$-\frac{d[\text{CH}_3\text{NC}]}{dt} = k_1[\text{CH}_3\text{NC}] - k_{-1}[\text{CH}_3\text{CN}]$$

At equilibrium, the net rate of consumption of CH_3NC is zero, because the rates of the forward and reverse reactions are equal. So, at equilibrium

$$k_1[\text{CH}_3\text{NC}]_{\text{eqm}} = k_{-1}[\text{CH}_3\text{CN}]_{\text{eqm}}$$

Rearranging this equation

$$\frac{k_1}{k_{-1}} = \frac{[\text{CH}_3\text{CN}]_{\text{eqm}}}{[\text{CH}_3\text{NC}]_{\text{eqm}}}$$

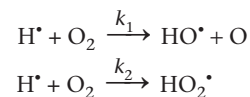
This corresponds to the equilibrium constant, K_c , for the reaction, so the ratio of the rate constants for the forward and reverse reactions is equal to the equilibrium constant for the reaction. (Remember the idea of dynamic equilibrium.)

$$\frac{k_1}{k_{-1}} = K_c \quad (9.14)$$

This is an important relationship, which links kinetics and equilibrium for an elementary reaction. It is a general expression for an elementary reaction and does not just apply to first order reactions. (But remember, it does not apply to a complex reaction involving several elementary steps, where the equilibrium constant is written for the overall reaction.) If the forward rate constant is much larger than the reverse rate constant, then $K_c \gg 1$. The position of equilibrium is well over to the right and the products predominate in the equilibrium mixture. If the opposite is true, then $K_c \ll 1$ and the reactants predominate in the equilibrium mixture.

Kinetics of parallel reactions

Sometimes more than one set of products can be obtained from the same reactants. For example, the reaction of a hydrogen atom with an oxygen molecule can proceed by two independent elementary reactions (these reactions take place when hydrogen burns in oxygen)



The reactions take place in parallel, and the ratio of products formed from each reaction depends on the relative magnitudes of the rate constants, k_1 and k_2 . It is analogous to the situation in Figure 9.20 on p.415 when the water can leave the tank by two exit pipes of differing diameters. The ratio of the volumes of water leaving by each pipe depends on the relative cross-sectional areas of the pipes.

The rate of consumption of $\text{H}^\bullet$ atoms is the sum of the rates of the two individual reactions

$$-\frac{d[\text{H}^\bullet]}{dt} = k_1[\text{H}^\bullet][\text{O}_2] + k_2[\text{H}^\bullet][\text{O}_2] = (k_1 + k_2)[\text{H}^\bullet][\text{O}_2]$$

$$\text{The rate of the overall reaction} = -\frac{d[\text{H}^\bullet]}{dt} = k[\text{H}^\bullet][\text{O}_2]$$

where k is the overall rate constant for the consumption of $\text{H}^\bullet$ atoms, so

$$k = (k_1 + k_2)$$

Under pseudo-first order conditions when $[\text{H}^\bullet] \ll [\text{O}_2]$ (see pp.391 and 403)

$$-\frac{d[\text{H}^\bullet]}{dt} = k[\text{H}^\bullet][\text{O}_2]_0 = k'[\text{H}^\bullet], \quad \text{where } k' = (k_1 + k_2)[\text{O}_2]_0$$

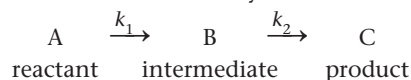
and $[\text{O}_2]_0$ is the initial concentration of O_2 .

Kinetics of consecutive reactions

Many chemical reactions occur in a sequence—the product of one reaction becomes the reactant for the next reaction in the sequence, and so on. This is true for many reactions in the atmosphere, for many biochemical processes that proceed by a cascade of reactions, and for many industrial processes.

Earlier in this section, you saw that complex reactions take place by a series of elementary steps. How can the kinetics of such a sequence of consecutive reactions be understood?

Consider the sequence of first order elementary reactions:



The first step is a first order reaction and the concentration of A decays exponentially, but the behaviour of B and C depends on the relative magnitudes of the rate constants k_1 and k_2 .

- If k_1 is much larger than k_2 (that is, if the first step is much faster than the second step), there is a considerable time lag between the loss of A and the formation of C. The first reaction takes place quickly and the intermediate B builds up to a concentration comparable to the starting concentration of A, before reacting slowly to form C.
- If k_2 is much larger than k_1 (that is, if the first step is much slower than the second step), B reacts rapidly once it is formed so its concentration is always small. The formation of C then follows closely the decay of A. The concentration of B is always small, so the rate of change of the concentration, $\frac{d[\text{B}]}{dt}$, is also small.

These two situations are illustrated in Figures 9.21(a) and (b). In each case, the rate constants, k_1 and k_2 , differ by a factor of 5. In (a) $k_1 = 5k_2$ and in (b) $k_2 = 5k_1$. The dashed curves in (b) show what happens if B is even more reactive and $k_2 = 50k_1$. The maximum concentration reached by B is then very small, as is the rate of change of B. In general, if B is a highly reactive species, such as a reactive radical, then $[\text{B}]$ and $\frac{d[\text{B}]}{dt}$ are very small. This is the basis of the steady state approximation.

Steady state approximation

One way to simplify the mathematical analysis of a series of reactions involving highly reactive species, such as the intermediate B above, is to make use of the **steady state approximation**. This states that the rate of change of concentration of a reactive species, X, in a sequence of consecutive reactions is approximately zero. X gets used up as fast as it is formed, so its concentration stays constant—it reaches a **steady state**.

$$\frac{d[\text{X}]}{dt} \approx 0$$

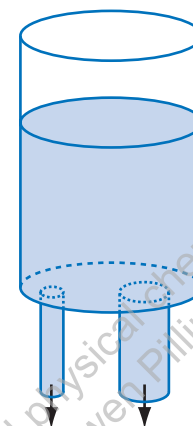


Figure 9.20 Water flowing out of a tank with two exit pipes is analogous to a reaction mechanism containing two parallel reactions.

➞ You can see an example of a biochemical cascade process in Box 19.2 (p.858).

➞ Exponential decay in a first order reaction is described in Section 9.4 (p.389).

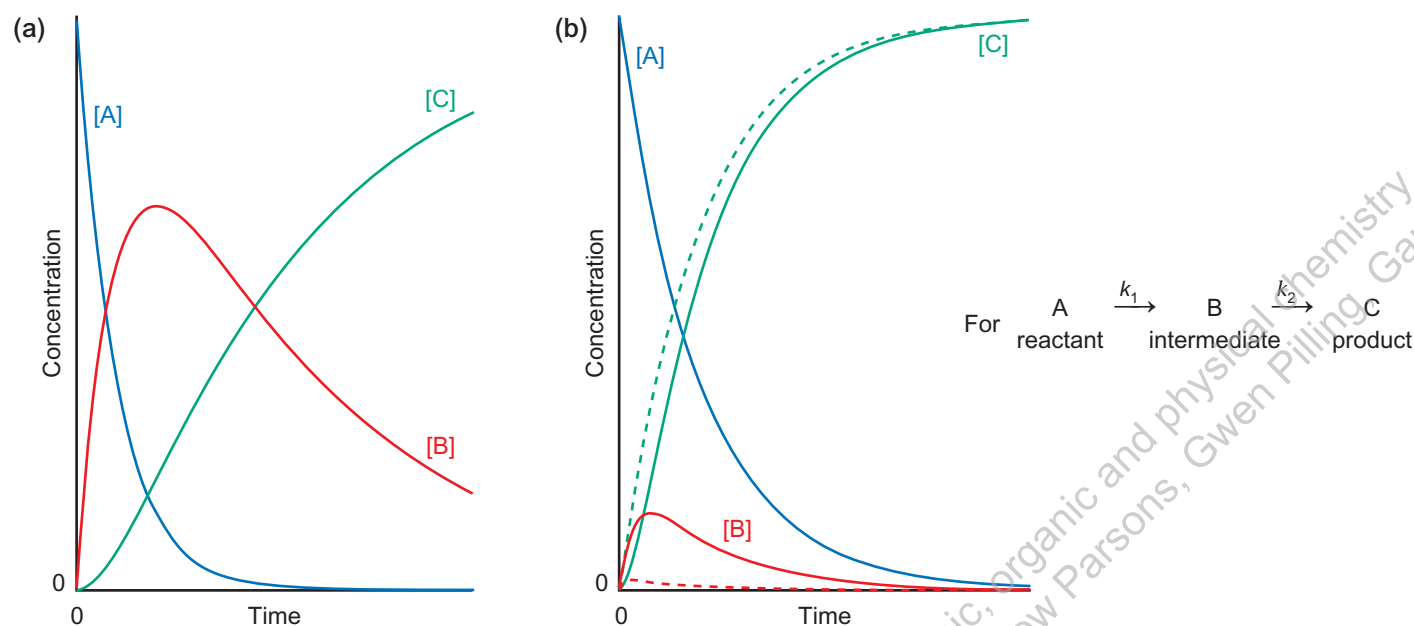


Figure 9.21 Plots showing the concentrations of A, B, and C in the sequence of reactions $A \rightarrow B \rightarrow C$. (a) $k_1 = 5k_2$, (b) $k_2 = 5k_1$ (solid lines) and $k_2 = 50k_1$ (dashed lines).

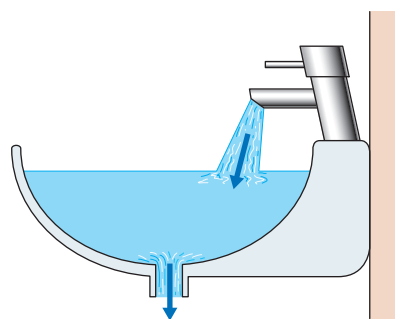


Figure 9.22 One example of a steady state situation.

 You can practise using the steady state approximation in Worked example 9.7 (p.418). It is used in the next subsection to explain the kinetics of a series of reactions involving a reversible step and is applied to the reaction of H_2 and Br_2 on p.420.



The reactions in a natural gas flame reach a steady state. Gas and air flow into the flame and the combustion products move away from the flame. The concentration of radical intermediates in the flame is approximately constant.

The steady state approximation is usually a very good approximation for reactions involving radicals because many radicals have high reactivity. When a steady state is reached, $[X]$ is constant and

$$\frac{d[X]}{dt} = (\text{rate of formation of } X - \text{rate of consumption of } X) = 0 \quad (9.15)$$

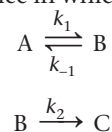
It is rather like the situation in Figure 9.22, where water is running into a washbasin with the plug out of the waste pipe. Before long, it gets to a point where water is running out as fast as it is running in, and the level of water in the basin stays the same. If you turned the tap on more, the level of the water would rise, but that would make the water run out faster because of the higher pressure. Before long it would reach a steady state again, but with a higher water level in the basin.

Equilibrium and steady state

At equilibrium, the concentrations of reactants and products are constant because the rates of the forward and reverse reactions in the equilibrium are the same. A series of reactions reaches a steady state when the rate of formation of an intermediate is the same as its rate of removal—but these two processes are not the reverse of one another and they don't come to equilibrium.

A mechanism with a reversible step

Sometimes in a sequence of consecutive reactions, some of the steps are reversible. Consider the following reaction sequence in which the first step is reversible.



There are two types of kinetics depending on the relative magnitudes of the rate constants.

(a) Pre-equilibrium

If the reaction from $B \rightarrow C$ is relatively slow, then A and B have time to equilibrate. This is known as a **pre-equilibrium**. Then

$$\frac{[B]}{[A]} = K_c$$

where K_c is the equilibrium constant for the first step. Using Equation 9.14 (p.414)

$$\frac{k_1}{k_{-1}} = K_c \quad (9.14)$$

But $K_c = \frac{[B]}{[A]}$, so you can write an expression for [B] in terms of the rate constants for the forward and reverse reactions

$$[B] = K_c [A] = \frac{k_1}{k_{-1}} [A]$$

The overall rate of reaction is the rate of consumption of A, which is equal to the rate of formation of the product C. The conversion of B to C takes place slowly and is the rate-determining step. The rate equation for this step is the rate equation for the overall reaction

$$\text{rate of reaction} = -\frac{d[A]}{dt} = \frac{d[C]}{dt} = k_2[B] = k_2 \frac{k_1}{k_{-1}} [A] \quad (9.16)$$

(b) Short-lived intermediate

If B is very short-lived (either k_{-1} or k_2 is much larger than k_1), then the steady state approximation can be applied to B (Equation 9.15, p.416).

When a steady state is reached

$$\frac{d[B]}{dt} = (\text{rate of formation of B} - \text{rate of consumption of B}) = 0$$

$$\frac{d[B]}{dt} = k_1[A] - (k_{-1}[B] + k_2[B]) = 0$$

$$\text{so, } k_1[A] = (k_{-1} + k_2)[B]$$

Rearranging to give an expression for [B]

$$[B] = \frac{k_1[A]}{(k_{-1} + k_2)}$$

and

$$\text{rate of reaction} = \frac{d[C]}{dt} = k_2[B] = \frac{k_1 k_2 [A]}{(k_{-1} + k_2)} \quad (9.17)$$

There are two extreme cases.

- If k_{-1} is much larger than k_2 (that is, the conversion of B back to A is much faster than the conversion of B to C), k_2 can be omitted from the bottom line in Equation 9.17 and then

$$\frac{d[C]}{dt} = k_2 \frac{k_1}{k_{-1}} [A]$$

This is the same result as in Equation 9.16. A pre-equilibrium occurs that then leads to formation of C. Because k_{-1} is much larger than k_1 , the concentration of B in this pre-equilibrium is very small.

i In fact, B is being removed from the pre-equilibrium, but very slowly compared to the rate at which the equilibrium is established—so the approximation that the first step comes to equilibrium is a good one.

In this case

$$k_{-1} \gg k_1 \text{ and } k_{-1} \gg k_2.$$



This screencast walks you through Worked example 9.7 to illustrate the use of the steady state approximation in deriving a rate equation to test a proposed mechanism.

In this case

$$k_2 \gg k_1 \text{ and } k_2 \gg k_{-1}.$$

i O_2 has two unpaired electrons and is a biradical. NO and NO_2 both have an unpaired electron and are radicals. The dots have been omitted in Worked example 9.7 for simplicity.

- If k_2 is much larger than k_{-1} (that is, the conversion of B to C is much faster than the conversion of B back to A), k_{-1} can be omitted from the bottom line in Equation 9.17 and then

$$\frac{d[\text{C}]}{dt} = k_1[\text{A}]$$

which means that the conversion of $\text{A} \rightarrow \text{B}$ is the rate-determining step and equilibrium is not established.

You can use the steady state approximation to derive a rate equation in Worked example 9.7.

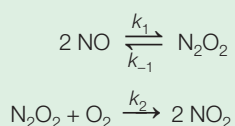


Worked example 9.7 The steady state approximation: deriving a rate equation to test a proposed reaction mechanism

A sample of the colourless gas, NO , rapidly turns brown when exposed to air due to the formation of NO_2 . The overall reaction is



Kinetic studies show that the reaction is second order with respect to NO and first order with respect to O_2 . The following mechanism has been proposed



in which N_2O_2 is a short-lived intermediate. Show that the proposed mechanism is compatible with the observed kinetics.

Strategy

To test whether the proposed mechanism is plausible, work out an expression for the overall rate equation that follows from the mechanism and compare it with the experimentally determined rate equation. (Remember that the steps in the proposed mechanism are elementary reactions.)

Step 1 Write down the experimentally determined rate equation.

Step 2 The intermediate, N_2O_2 , is short lived so you can apply the steady state approximation (Equation 9.15, p.416) to find an expression for $[\text{N}_2\text{O}_2]$.

Step 3 Use this to work out a rate equation from the mechanism in terms of $[\text{NO}]$ and $[\text{O}_2]$, and compare this with the experimentally determined rate equation.

Step 4 Think about the relative magnitude of the rate constants for the individual steps and decide which reaction is the rate-determining step and so governs the overall kinetics.

Solution

Step 1 Experimentally determined rate equation.

$$\text{Rate of reaction} = k[\text{NO}]^2[\text{O}_2]$$

Step 2 Using the steady state approximation to find an expression for $[\text{N}_2\text{O}_2]$.

From Equation 9.15 (p.416) when a steady state is reached

$$\frac{d[\text{N}_2\text{O}_2]}{dt} = (\text{rate of formation of } \text{N}_2\text{O}_2 - \text{rate of consumption of } \text{N}_2\text{O}_2) = 0$$

$$\frac{d[\text{N}_2\text{O}_2]}{dt} = k_1[\text{NO}]^2 - (k_{-1}[\text{N}_2\text{O}_2] + k_2[\text{N}_2\text{O}_2][\text{O}_2]) = 0$$

$$\text{so, } k_1[\text{NO}]^2 = (k_{-1} + k_2[\text{O}_2]) \times [\text{N}_2\text{O}_2]$$

Rearranging to give an expression for $[\text{N}_2\text{O}_2]$

$$[\text{N}_2\text{O}_2] = \frac{k_1[\text{NO}]^2}{(k_{-1} + k_2[\text{O}_2])} \quad (9.18)$$

Step 3 Deriving a rate equation from the mechanism.

From Equation 9.4 (p.386) for the rate of reaction

$$\text{rate of reaction} = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_2[\text{N}_2\text{O}_2][\text{O}_2]$$

so the rate of formation of NO_2 is given by the rate equation

$$\frac{d[\text{NO}_2]}{dt} = 2k_2[\text{N}_2\text{O}_2][\text{O}_2]$$

Substituting the expression for $[\text{N}_2\text{O}_2]$ in Equation 9.18 into the above equation

$$\begin{aligned} \frac{d[\text{NO}_2]}{dt} &= 2k_2 \times \frac{k_1[\text{NO}]^2}{(k_{-1} + k_2[\text{O}_2])} \times [\text{O}_2] \\ &= \frac{2k_1k_2[\text{NO}]^2[\text{O}_2]}{(k_{-1} + k_2[\text{O}_2])} \quad (9.19) \end{aligned}$$

This is the overall rate equation for the reaction in terms of measurable concentrations. It does not, however, fit the observed kinetics, which show that the reaction is second order with respect to NO and first order with respect to O_2 .

Step 4 Think about the relative magnitude of the rate constants.

Compare the relative magnitudes of k_{-1} and $k_2[\text{O}_2]$ in Equation 9.19. If $k_{-1} \gg k_2[\text{O}_2]$, the rate equation becomes

$$\frac{d[\text{NO}_2]}{dt} = \frac{2k_1k_2}{k_{-1}} [\text{NO}]^2[\text{O}_2] \rightarrow$$

→ which is now consistent with the observed kinetics (step 1). This would be the case if the second step is the rate-determining step for the reaction. The reaction is sufficiently slow that it does not disturb the pre-equilibrium between NO and N₂O₂, which is established quickly.

Note that this does not *prove* that the mechanism is correct—merely that it is consistent with the experimental observations.

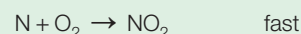
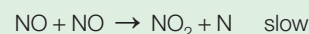
Question

(a) Show that the proposed mechanism is consistent with the overall equation for the reaction.

(b) Give the molecularity of each of the three elementary reactions in the proposed mechanism.

(c) Suggest why the reaction: $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ is unlikely to be an elementary reaction.

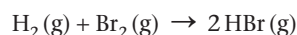
(d) An alternative mechanism that has been considered is



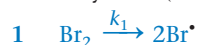
Explain why this mechanism can be discounted.

Chain reactions

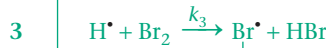
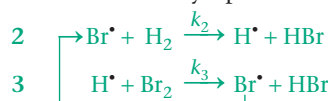
Radical chain reactions involve a sequence of reactions in which a radical reacts and then is regenerated in subsequent reactions. The overall reaction of hydrogen and bromine provides a good example of a chain reaction.



The first step involves the dissociation of Br₂ to form bromine radicals. This may be brought about by heat (**thermal dissociation**) or light (**photodissociation**)



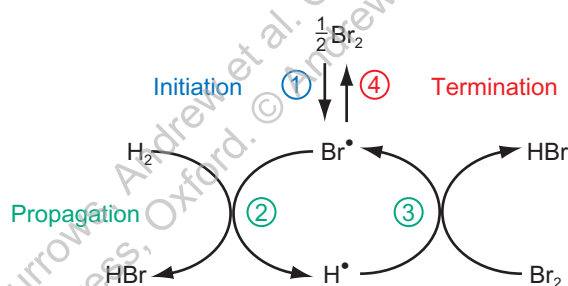
This is followed by a pair of reactions in which HBr is formed and Br[•] radicals are regenerated



The fourth step is the recombination of Br[•] radicals to form Br₂



The reaction sequence can be represented diagrammatically as follows



- Step 1 is called an **initiation reaction**—it leads to the net formation of radicals.
- Step 4 is a **termination reaction** and removes radicals from the system.
- Steps 2 and 3 are **propagation reactions** and keep the reaction going. They involve the replacement of one radical by another but do not change the overall concentration of radicals.

The experimentally determined rate equation obtained from kinetic studies is

$$\text{rate of reaction} = k[\text{H}_2(\text{g})][\text{Br}_2(\text{g})]^{1/2}$$

where k is the overall rate constant (see Section 9.5, p.402).

How can this be explained in terms of the mechanism for the reaction? How is it possible to have a fractional reaction order? The intermediate radicals in the mechanism proposed above are all very reactive and short lived, so you can use the steady state approximation

i In the atmosphere, the mechanism for the reaction of NO with O₂ described in Worked example 9.7 occurs only very slowly, because [NO] is so small and the rate depends on [NO]². NO from car exhausts, for example, is converted to NO₂ much more quickly by other processes, such as reaction with O₃.

i You might think that the reaction $\text{H}^\bullet + \text{H}^\bullet \rightarrow \text{H}_2$ would also be a termination reaction. In fact, $[\text{H}^\bullet] \ll [\text{Br}^\bullet]$ so this reaction proceeds very much more slowly than the recombination of Br[•] radicals to form Br₂ and has no significant effect.

(Equation 9.15 on p.416). There are three stages in the analysis and these are summarized below. The first stage gives an expression for the concentration of $\text{Br}^\bullet$ radicals. The second stage determines the relationship between the rates of the two propagation reactions. These expressions are then combined in the third stage to give a rate equation for the formation of HBr , which can be compared with the experimentally determined rate equation above.

Deriving a rate equation for the $\text{H}_2 + \text{Br}_2$ chain reaction

Stage 1 Finding an expression for $[\text{Br}^\bullet]$

Using the steady state approximation, you can say that when a steady state is reached the total radical concentration will be constant. The propagation reactions do not affect this concentration (they just convert one radical into another), so the rate of the initiation reaction (step 1: forms $\text{Br}^\bullet$) and the rate of the termination reaction (step 4: removes $\text{Br}^\bullet$) must be equal, and

$$2k_1[\text{Br}_2] = 2k_4[\text{Br}^\bullet]^2$$

(The '2' on each side of the equation is there because there are 2 $\text{Br}^\bullet$ involved in step 1 and step 4.) Rearranging this equation to give an expression for $[\text{Br}^\bullet]$

$$[\text{Br}^\bullet] = \left(\frac{k_1[\text{Br}_2]}{k_4} \right)^{1/2} \quad (9.20)$$

Stage 2 Finding the relationship between the rates of the propagation steps

In practice, the rates of the propagation reactions (steps 2 and 3) are much greater than the rates of the initiation and termination reactions (step 1 and step 4). As a result, the reaction cycles through the propagation reactions many times for each initiation and termination reaction—hence the name **chain reaction**. In order to maintain a steady state in radical concentrations, the rates of these two propagation reactions must be equal. If, for example, step 2 were faster than step 3, $[\text{H}^\bullet]$ would rise and $[\text{Br}^\bullet]$ would decline. So

$$\begin{aligned} \text{rate of step 2} &= \text{rate of step 3} \\ k_2[\text{Br}^\bullet][\text{H}_2] &= k_3[\text{H}^\bullet][\text{Br}_2] \end{aligned} \quad (9.21)$$

Stage 3 The rate of formation of HBr

HBr is formed in steps 2 and 3. Its total rate of formation is the sum of the rates of these steps. Since they are equal (Equation 9.21), you can write

$$\begin{aligned} \text{rate of formation of HBr} &= \frac{d[\text{HBr}]}{dt} = k_2[\text{Br}^\bullet][\text{H}_2] + k_3[\text{H}^\bullet][\text{Br}_2], \text{ and} \\ \frac{d[\text{HBr}]}{dt} &= 2k_2[\text{Br}^\bullet][\text{H}_2] \end{aligned} \quad (9.22)$$

Now, substitute the expression for $[\text{Br}^\bullet]$ from Equation 9.20 into Equation 9.22:

$$\frac{d[\text{HBr}]}{dt} = 2k_2 \left(\frac{k_1[\text{Br}_2]}{k_4} \right)^{1/2} [\text{H}_2]$$

so that

$$\frac{d[\text{HBr}]}{dt} = 2k_2 \left(\frac{k_1}{k_4} \right)^{1/2} \times [\text{Br}_2]^{1/2} [\text{H}_2] \quad (9.23)$$

Equation 9.23 is the rate equation from the proposed reaction mechanism. It gives the order with respect to Br_2 as 0.5 and the order with respect to H_2 as 1. The overall order is 1.5. This agrees with the experimentally determined rate equation. The rate constant k is given by

$$k = 2k_2 \left(\frac{k_1}{k_4} \right)^{1/2}$$

The kinetics of many chain reactions can be analysed in this way and often give fractional orders.



The reaction of H_2 and O_2 , initiated by a spark, is a chain reaction. The mechanism includes a branching reaction where one radical reacts to form two radicals. This leads to an exponential increase in the concentration of radicals, and in the rate of the reaction. The whole process occurs very rapidly—and the system explodes.

➞ Chain reactions involving organic radicals are discussed in Section 19.2 (p.901) and Section 20.2 (p.915).



Summary

- The series of elementary steps that make up a complex reaction is known as the mechanism of the reaction.
- A valid mechanism must correctly predict the experimentally determined rate equation and be consistent with all related kinetic experimental data and stereochemical observations. The sum of the elementary steps must give the overall equation for the reaction.
- Kinetic studies are the main source of evidence for the mechanism of many organic reactions.
- The rate equation for the slow rate-determining step is the rate equation for the overall reaction.
- For an equilibrium reaction where the forward and reverse reactions are elementary processes, the ratio of the rate constants for the forward and reverse reactions is equal to the equilibrium constant for the reaction.

$$\frac{k_1}{k_{-1}} = K_c$$

- The steady state approximation is used to simplify analysis of the kinetics of consecutive reactions involving a highly reactive intermediate, B. It is assumed that the concentration of B is very small, and that the rate of change of the concentration of B is zero.



For practice questions on these topics, see questions 17–19, 22, and 23 at the end of this chapter (pp.441–442).

9.7 Effect of temperature on the rate of a reaction

The Arrhenius equation

The rates of most chemical reactions increase as the temperature is raised. Applications of this are all around you. Food is cooked to speed up desirable reactions between chemical compounds in the food, whereas food is refrigerated to slow down chemical reactions that lead to decomposition and decay.

The rate constant, k , changes with temperature and determines the way in which the rate of reaction varies with temperature. This behaviour is summarized by the **Arrhenius equation**

$$k = Ae^{-\frac{E_a}{RT}} \quad (9.24a)$$

where k is the rate constant for the reaction

A is called the A factor (pre-exponential factor; **same units as k**)

E_a is the activation energy (**J mol^{-1}**)

R is the molar gas constant (**$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$**)

T is the temperature (**K**).

Note that the presence of the molar gas constant does not mean the equation only applies to gases. It applies equally well to reactions in solution. Figure 9.23 shows how the value of k increases exponentially with temperature.

Taking logarithms of both sides gives an alternative form of the Arrhenius equation

$$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (9.24b)$$

The form of the Arrhenius equation is explained in terms of the energies of colliding molecules on p.429.



The rate constant, k , and hence the reaction rate, increase with temperature and decrease with increasing E_a .



If $y = e^x$, then $x = \ln y$
For $k = Ae^{-\frac{E_a}{RT}}$, this means that
 $-\frac{E_a}{RT} = \ln \frac{k}{A} = \ln k - \ln A$, and
 $\ln k = \ln A - \frac{E_a}{RT}$

The properties of exponential functions, e^x , are described in Maths Toolkit MT3 (p.1310) and MT4 (p.1312).



Towards the end of the nineteenth century, the Swedish chemist, Svante Arrhenius, examined kinetic data from many reactions and noticed that a plot of the logarithm of the rate constant, $\ln k$, against $1/T$ is a straight line. This led to the relationship in Equations 9.24(a and b), which became known as the **Arrhenius equation**.

$$y = mx + c$$

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



Cooking involves chemical reactions and the rate of cooking depends critically on temperature.

i When you use an Arrhenius plot of $\ln k$ against $1/T$ to find a value of A , remember that the intercept must be with the y -axis where $\frac{1}{T} = 0$.

i Be careful to be accurate when using the terms **rate** and **rate constant**. When all concentrations are 1 mol dm^{-3} , the two quantities have the same numerical value—but the units are different. For other concentrations, they have different numerical values. k is constant for a given temperature, whereas the rate usually varies throughout the reaction.

i As a rough rule of thumb (taking into account a range of activation energies), the rates of reaction for many organic reactions in solution increase by a factor of 2 to 4 when the temperature is raised from 25°C to 35°C .

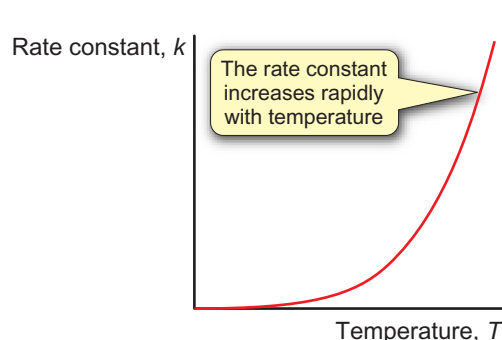


Figure 9.23 The rate constant, k , of a reaction increases exponentially with temperature, T .

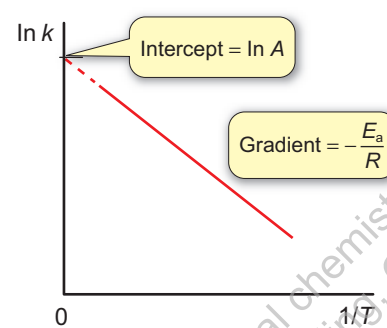


Figure 9.24 An Arrhenius plot of $\ln k$ against $1/T$. The activation energy can be found from the gradient and a value of A from the intercept at $1/T = 0$.

Equation 9.24b is useful because it is the equation of a straight line ($y = mx + c$). A plot of $\ln k$ against $\frac{1}{T}$ (Figure 9.24) is a straight line with gradient $-\frac{E_a}{R}$ and intercept $\ln A$ (see Worked example 9.8).

The value of the activation energy, E_a , determines how sensitive the reaction is to changes of temperature. A high value of E_a corresponds to a reaction that is very sensitive to changes of temperature, whereas a low value of E_a corresponds to a reaction that is less sensitive to changes of temperature.

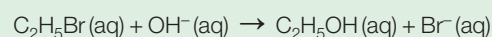
An often quoted rule of thumb is that the rate of a reaction increases by a factor of two for a 10K rise in temperature. This applies in only limited circumstances and should be treated with caution. For some reactions of organic compounds in solution, where the activation energy is about $+50 \text{ kJ mol}^{-1}$, the rate of the reaction does double when the temperature is raised from 25°C to 35°C . It is not a general rule, though, and does not apply to other temperature ranges nor to reactions with different activation energies.

Reactions in the gas phase have a wide range of sensitivities to temperature. Some, with low activation energies, are only weakly sensitive to temperature. Radical recombination reactions in the gas phase, such as the reaction of two methyl radicals to give ethane, have zero activation energy (see Table 9.4, p.427) and their rate constants are independent of temperature. The reverse reaction, the reaction of ethane to form two methyl radicals, has a high activation energy (about $+365 \text{ kJ mol}^{-1}$) and the rate constant increases by a factor of 100 when the temperature is raised from 25°C to 35°C , although much higher temperatures are required for the reaction to have a measurable rate.



Worked example 9.8 Finding an activation energy

The rate constant for the hydrolysis of bromoethane in alkaline solution was measured at different temperatures.



Use the results in the following table to find a value for the activation energy of the reaction.

Temperature/ $^\circ\text{C}$	25	28	31	34	37	40	43	46
$k/10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	8.5	13	19	25	37	51	70	96



→ Strategy

Use the Arrhenius equation in the form of Equation 9.24b

$$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (9.24b)$$

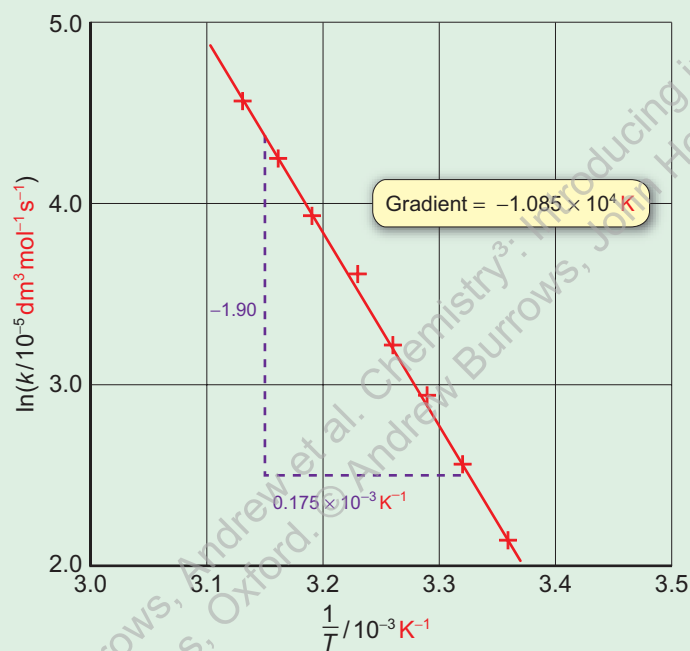
Plot a graph of $\ln k$ against $1/T$ (T must be in K).

The gradient of the line = $-\frac{E_a}{R}$.

Solution

Tabulate the data you need to plot the graph of $\ln k$ against $1/T$. Take care to include the correct units.

Temperature/°C	25	28	31	34	37	40	43	46
Temperature/K	298	301	304	307	310	313	316	319
$(1/T)/10^{-3} \text{ K}^{-1}$	3.36	3.32	3.29	3.26	3.23	3.19	3.16	3.13
$k/10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	8.5	13	19	25	37	51	70	96
$\ln(k/10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	2.14	2.56	2.94	3.22	3.61	3.93	4.25	4.56



The graph is a straight line.

$$\text{Gradient} = -1.085 \times 10^4 \text{ K} = -\frac{E_a}{R}$$

$$\text{So, } E_a = -(R \times \text{gradient}) = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times -1.085 \times 10^4 \text{ K}) = 9.02 \times 10^4 \text{ J mol}^{-1}$$

$$\text{Activation energy } E_a = +90 \text{ kJ mol}^{-1}$$

Question

The decomposition of a drug in humans was found to be a first order process. The activation energy for the decomposition is $+95 \text{ kJ mol}^{-1}$ and $A = 5 \times 10^{10} \text{ s}^{-1}$.

- What is the rate constant for the decomposition at blood temperature, 310 K ?
- How long will it take the concentration of the drug in the blood to fall to half its initial value?

Σ See the Maths notes in Worked example 9.4 (p.395) and Worked example 9.6 (p.410) about plotting logarithm values.

Σ See Maths note on p.381 about finding the gradient of a straight line.

If you know the value of the rate constant, k_1 , at a particular temperature, T_1 , you can use the Arrhenius equation to calculate the value of the rate constant, k_2 , at any other temperature, T_2 .

Using Equation 9.24b (p.421)

$$\ln k_1 = \ln A - \frac{E_a}{R} \left(\frac{1}{T_1} \right)$$

You can write a corresponding equation for T_2

$$\ln k_2 = \ln A - \frac{E_a}{R} \left(\frac{1}{T_2} \right)$$

Subtracting the first equation from the second gives

$$\ln k_2 - \ln k_1 = \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (9.25)$$

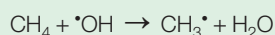
➞ A similar approach is used in the treatments of the van 't Hoff equation in Section 15.5 (p.714) and the Clausius–Clapeyron equation in Section 17.2 (p.775).

Equation 9.25 allows you to find the ratio of two rate constants at different temperatures, as illustrated in Worked example 9.9.



Worked example 9.9 Comparing rate constants at different temperatures

The main mechanism for removing methane from the atmosphere is the reaction with hydroxyl radicals



The activation energy for the reaction is $+14.1 \text{ kJ mol}^{-1}$. Calculate the ratio of the rate constants for the reaction at the Earth's surface (at 295 K) and at the top of the troposphere (at 220 K).

Strategy

Use Equation 9.25 to find a value for the ratio k_2/k_1 , where k_2 is the rate constant at the Earth's surface and k_1 is the rate constant at the top of the troposphere. When using the Arrhenius equation, temperatures should always be in K and activation energies in J mol^{-1} .

Solution

$$T_2 = 295 \text{ K} \text{ and } T_1 = 220 \text{ K.}$$

Substituting these values into Equation 9.25

$$\begin{aligned} \ln \frac{k_2}{k_1} &= \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{+14.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{220 \text{ K}} - \frac{1}{295 \text{ K}} \right) \\ &= \frac{+14.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} (1.156 \times 10^{-3} \text{ K}^{-1}) = 1.96 \\ \frac{k_2}{k_1} &= 7.1 \end{aligned}$$

The rate constant for the removal of methane is 7 times greater at the surface of the Earth than at the top of the troposphere. (For the same reactant concentrations, the reaction occurs 7 times faster at the Earth's surface than at the top of the troposphere.)

Question

Sucrose is hydrolysed in the digestive system to form glucose and fructose. The activation energy for the reaction is $+108 \text{ kJ mol}^{-1}$. At 298 K , the rate constant is $1.85 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Calculate the rate constant for the reaction at body temperature, 37°C (310 K).

Energy profiles

The temperature dependence of a reaction can be interpreted through an **energy profile** of the reaction. This is a plot of potential energy, E_{pe} , as the reaction takes place. Figure 9.25 shows the energy profile for the elementary reaction



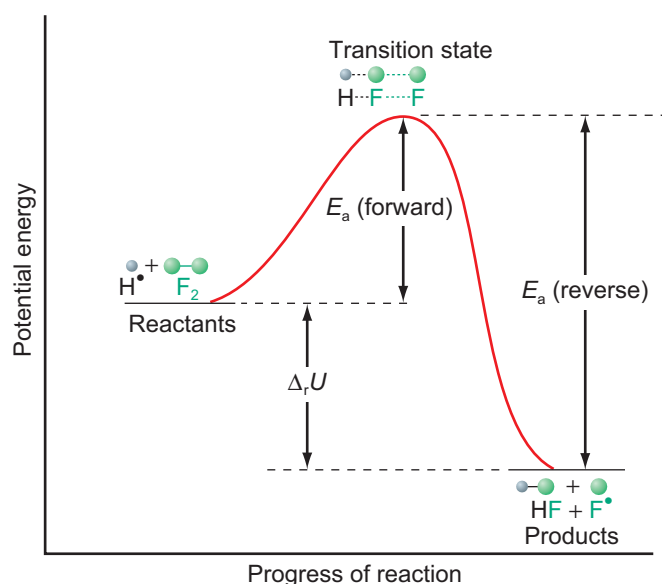


Figure 9.25 Energy profile for the elementary reaction $\text{H}^\bullet + \text{F}_2 \rightarrow \text{HF} + \text{F}^\bullet$ (not drawn to scale).

The *x*-axis follows the **progress of the reaction** from reactants to products. (It is sometimes called the reaction coordinate or extent of reaction.) The reaction is exothermic, so the products are at lower potential energy than the reactants. But, for the reaction to proceed, an energy barrier has first to be overcome because of the need to rearrange the electrons in the system.

The highest point on the energy profile is called the **transition state**. The difference in energy between the reactants and the transition state is the **activation energy**, E_a . In Figure 9.25, the activation energy for the forward reaction is labelled E_a (forward). The activation energy for the reverse reaction, E_a (reverse), is larger than E_a (forward) because the reverse reaction is endothermic. $\Delta_r U$ is the energy change for the reaction.

The activation energy for the forward reaction is $+10 \text{ kJ mol}^{-1}$, which is much less than the energy needed to break the bond in F_2 ($+158 \text{ kJ mol}^{-1}$). This is because, in the transition state, the F–F bond is not fully broken and the H–F bond is already partly formed.

Distribution of energies

The energies of reactant molecules are spread over a wide range and the distribution of energies among the molecules depends on the temperature.

In a gas, the distribution of molecular speeds (*s*) is described by the Maxwell–Boltzmann distribution. The shape of the distribution of kinetic energies of molecules is very similar, since E_{KE} is proportional to s^2 . Figure 9.26(a) plots the number of collisions with a particular kinetic energy at a temperature T_1 (blue curve) and at a higher temperature T_2 (red curve). As the temperature increases, more molecules move at higher speeds and have higher kinetic energies. As a result, more collisions occur with higher kinetic energies. There is still a spread of energies at T_2 , but a greater fraction of collisions have higher energies.

Consider now an elementary reaction, $\text{A} + \text{B} \rightarrow \text{products}$, taking place in the gas phase. The activation energy, E_a , for the reaction is shown by the dotted line in Figure 9.26(b). The dotted line shows the minimum kinetic energy along the line of approach needed in a collision for reaction to occur. The shaded area under the curve to the right of E_a gives the number of collisions with enough energy to react. This area is greater at the higher temperature.

The enthalpy profiles described in Section 1.6 show how the *enthalpy* of the system changes as the reaction takes place.

i The energy change of reaction $\Delta_r U$ is the change in internal energy (see Section 13.5, p.634). The value of $\Delta_r U$ is usually very close to the value of the enthalpy change of reaction, $\Delta_r H$.

i The Maxwell–Boltzmann distribution of molecular speeds in a gas is described in Section 8.5 (p.359). Figure 8.12(b) shows the distribution of speeds at different temperatures.

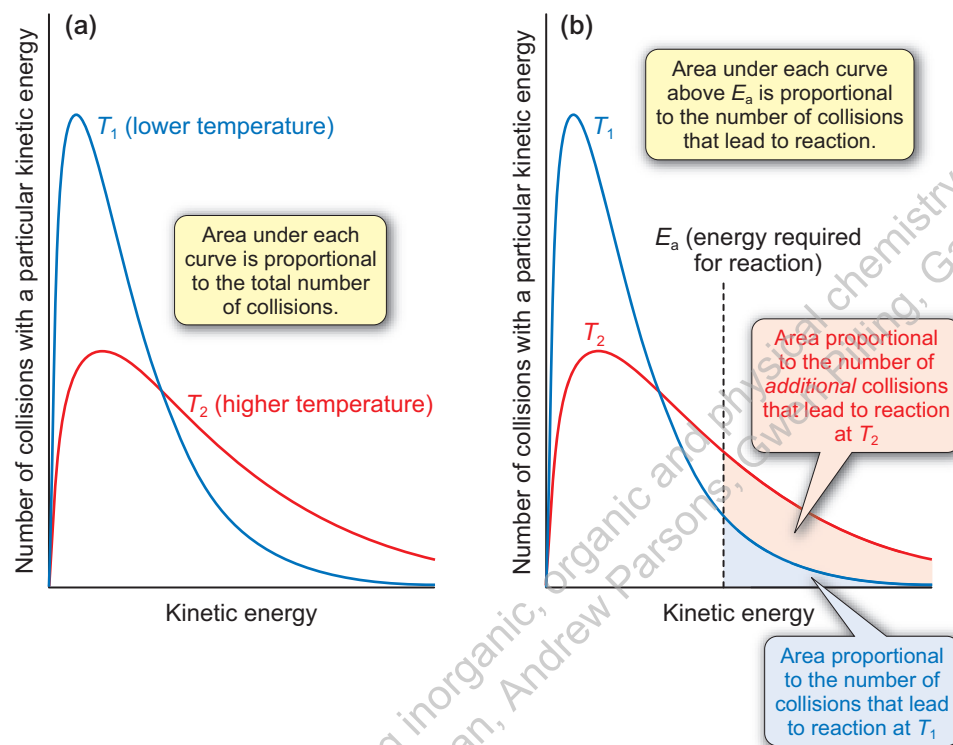


Figure 9.26 (a) Number of collisions with a particular kinetic energy at temperature, T_1 , and at a higher temperature, T_2 . (b) The number of collisions with enough energy to react is greater at the higher temperature.

Look again at the form of the Arrhenius equation (Equation 9.24a, p.421). The rate constant increases with temperature because, at a higher temperature, more colliding molecules have sufficient energy to overcome the energy barrier. The term $e^{-\frac{E_a}{RT}}$ gives the fraction of collisions that have the required energy. As T increases, E_a/RT becomes smaller and approaches zero (so that $e^{-\frac{E_a}{RT}}$ approaches 1). If $e^{-\frac{E_a}{RT}} = 1$, all the collisions would have enough energy to react and $k = A$.

Fraction of collisions with the minimum energy for reaction

$$k = A e^{-\frac{E_a}{RT}}$$

(9.24a)

Rate constant if all the collisions had enough energy to overcome the energy barrier

Table 9.4 shows values of A factors and activation energies for some first and second order elementary reactions. Note the radical recombination reaction of two methyl radicals, which has zero activation energy. There is no energy barrier to reaction, so the rate of the reaction is independent of temperature.

Table 9.4 A factors and activation energies for some first and second order elementary reactions

Elementary reaction	A	E_a / kJ mol ⁻¹
First order (gas phase)	/ s⁻¹	
CH ₃ NC → CH ₃ CN	5.0×10^{13}	+160
cyclopropane → propene	1.6×10^{15}	+272
C ₆ H ₅ CH ₂ CH ₃ → C ₆ H ₅ CH ₂ • + CH ₃ •	7.1×10^{15}	+314
C ₂ H ₆ → 2 CH ₃ •	2.0×10^{17}	+365
Second order (gas phase)	/ dm³ mol⁻¹ s⁻¹	
CH ₃ • + CH ₃ • → C ₂ H ₆	3.6×10^{10}	0
Cl• + O ₃ → ClO• + O ₂	1.7×10^{10}	+2
H• + F ₂ → HF + F•	9×10^9	+10
HF + F• → H• + F ₂	1.3×10^{10}	+422
Second order (aqueous solution)	/ dm³ mol⁻¹ s⁻¹	
C ₂ H ₅ Br + OH ⁻ → C ₂ H ₅ OH + Br ⁻	4.3×10^{11}	+90

Activation energy for a complex reaction

The discussion of the effect of temperature so far refers only to elementary reactions, but the rates of complex reactions also depend on temperature. If the kinetics of the reactions is governed by a rate-determining step (such as in the S_N1 hydrolysis of a halogenoalkane; see p.413), the Arrhenius equation applies to the rate constant for that step.

For many complex reactions, however, the rate constants of several reactions contribute to the overall rate constant. Very often, the temperature dependence of the overall rate constant does follow the Arrhenius equation and a plot of $\ln k$ against $1/T$ gives a straight line with gradient $-E_a/R$. E_a in this case is called an **effective activation energy** and its interpretation depends on the reaction being studied.



Summary

- The way the rate constant varies with temperature is described by the Arrhenius equation

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

- A plot of $\ln k$ against $1/T$ is a straight line with a gradient $-E_a/R$.
- The activation energy, E_a , is the energy barrier reactants must overcome in order to form products.
- The rate constant of a reaction increases with temperature because a greater fraction of reactant molecules has enough energy to pass over the energy barrier.
- An energy profile shows how the potential energy of the system changes as the reaction progresses.



For practice questions on these topics, see questions 1, 15, and 16 at the end of this chapter (p.439 and p.441).

 The use of models to describe the behaviour of chemical systems at a molecular level is discussed in Section 8.4 (p.354), when the kinetic model of gases is introduced.

 To obtain a theoretical estimate of the rate constant, the calculated A factor is combined with a value for E_a calculated using quantum mechanics.

 The idea of the molecularity of an elementary reaction is introduced in Section 9.6 (p.413), where the S_N1 (unimolecular) and S_N2 (bimolecular) mechanisms for the hydrolysis of halogenoalkanes are discussed.

 The kinetics of the methyl isocyanide isomerization are discussed in Section 9.6 (p.414).

9.8 Theories of reactions

Theories of elementary reactions provide a framework for understanding how reactions take place. A reaction theory is based on a **model** of how the reaction occurs at a molecular level. The model is then described in mathematical terms so that predictions can be made about the reaction. One way to assess the value of a theory—and in turn the quality of the model on which it is based—is to compare the theoretical estimate of a rate constant with the experimental value. These predicted rate constants are often used in situations where experimental measurements are difficult to make, or they may be used to help design an experiment. There are two commonly used theories of reaction.

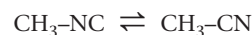
- **Collision theory** is based on a simple model in which the reactant molecules behave like hard spheres. Collisions between the spheres may result in reaction. A calculated collision frequency is used to estimate the A factor in the Arrhenius equation for the reaction.
- **Transition state theory** is a more sophisticated and detailed theory that assumes the reactants form a transition state—a short-lived complex at the maximum on the energy profile. The A factor is then calculated, based on an assumed structure for the transition state.

In this chapter, the theories are used to estimate the A factor for a reaction, which can then be compared with the value of A obtained experimentally from an Arrhenius plot as described in Section 9.7 (p.421). Before looking at these theories in detail, you need to understand what is meant by the molecularity of an elementary reaction.

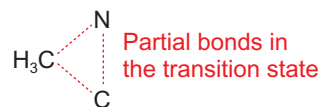
Molecularity

The **molecularity** of an elementary reaction (see Section 9.6, p.413) can now be more accurately defined as the number of reactant molecules involved in the transition state.

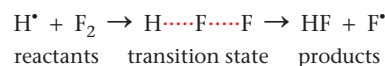
In a **unimolecular** reaction, the transition state involves just one molecule of the reactant. A bond in the reactant molecule may break to form two product molecules, or the reactant molecule may rearrange during the reaction to form the product, as in the isomerization of methyl isocyanide



The transition state involves one molecule of CH_3NC in a high-energy state in which the $\text{CH}_3\text{-N}$ bond is partly broken and the new $\text{CH}_3\text{-C}$ bond is partly formed. For this to happen, the NC group partly rotates



In a **bimolecular** reaction, the transition state involves two reactant molecules. In some cases, the two molecules come together to form a single larger molecule. In other cases, as the two molecules come together, bonds break and new bonds form to give two new product molecules. For example, in the reaction between $\text{H}^\bullet$ and F_2 (Equation 9.26, p.424 and Figure 9.25, p.425), the transition state involves one atom of $\text{H}^\bullet$ and one molecule of F_2 in a high-energy state in which the H-F bond is partly formed and the F-F bond partly broken.



It is important not to confuse *molecularity* with the *order* of a reaction. A bimolecular reaction is second order, but the origins of the terms are different. Reaction orders are experimentally determined from the observed kinetics of the reaction. The molecularity is

a theoretical interpretation of the kinetics to explain the way in which the reaction occurs. Molecularities apply only to the elementary steps of a complex reaction, whereas the overall order of the reaction may take a quite different value.

Collision theory

In the model for collision theory, for a reaction to occur two molecules must collide with a certain minimum kinetic energy along their line of approach. The energy profiles used in the collision theory represent the potential energy of the two molecules as they approach and then collide and react to form the products. These energy profiles are discussed in Section 9.7 (for example, see Figure 9.25, p.425, for the $\text{H}^\bullet + \text{F}_2$ reaction). For a reaction to occur, colliding molecules must have sufficient energy to overcome the energy barrier, E_a .

Consider a simple bimolecular reaction in the gas phase between two reactants A and B. Collision theory uses the kinetic theory of gases developed in Section 8.4 (p.354) to find an expression for the A factor in the Arrhenius equation, which is related to the number of collisions between A and B molecules per second. This expression for the A factor shown below

$$\sigma \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} N_A$$

depends on the collision cross-section, σ , which is related to the size of the molecules and their average relative speed. (k_B is the Boltzmann constant. μ is called the reduced mass and is equal to $\frac{m_A m_B}{m_A + m_B}$, where m_A and m_B are the masses of the reactant molecules. N_A is the Avogadro constant.)

But not all the collisions result in reaction, so to obtain an expression for the rate constant, k , the expression above is multiplied by the fraction of the collisions, $e^{-\frac{E_a}{RT}}$, that have enough energy to surmount the energy barrier, E_a , and react. So,

$$k = \sigma \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} N_A e^{-\frac{E_a}{RT}}$$

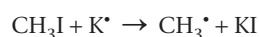
For most reactions, this gives a value of the rate constant that is too large, sometimes by several orders of magnitude. This is explained by assuming that not all collisions with enough energy to overcome the energy barrier actually go on to form products. Better agreement is obtained if a probability factor, P , is introduced, where the value of P is less than one

$$k = P \sigma \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} N_A e^{-\frac{E_a}{RT}} = A e^{-\frac{E_a}{RT}}$$

Comparing this expression with the Arrhenius equation, you can see that

$$A = P \sigma \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} N_A \quad (9.27)$$

P is sometimes interpreted as a **steric factor**—the reactants need to collide in a specific orientation to react. Figure 9.27 shows the gas phase reaction



Reaction can only take place if the potassium atom ($\text{K}^\bullet$) approaches in the direction of the iodine atom in the CH_3I molecule. This reduces the effective cross-section from that expected using a hard sphere model for collisions.

It is difficult, though, to predict P to give reliable estimates for rate constants. Collision theory is widely applied to simple reactions, such as those between atoms and diatomic molecules, but not to more complicated reactions. Transition theory, discussed below, provides a more detailed theoretical treatment.

Speeds of molecules, collision cross-section, and the collision frequency, Z , (for collisions between molecules in a pure gas), are introduced in Section 8.5 (p.358). The Boltzmann constant k_B is the gas constant R divided by the Avogadro constant and is discussed in Section 10.3 (p.458), when discussing the population of energy levels in spectroscopy.

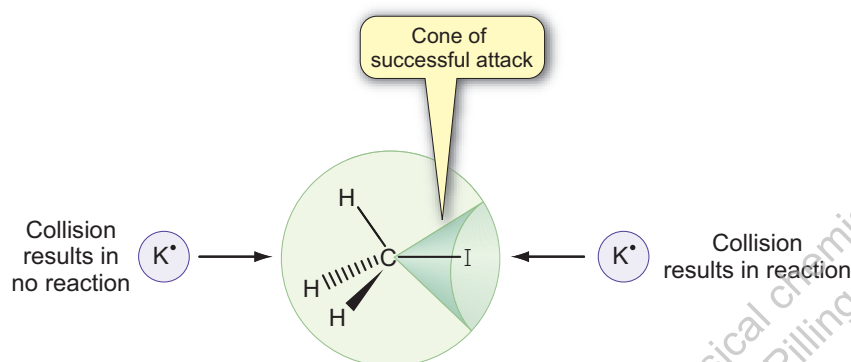


Figure 9.27 In the gas phase reaction between a K atom and a molecule of CH_3I , only those collisions in which K approaches CH_3I along a direction that lies inside the cone lead to reaction—even though the energy of collisions in other orientations may exceed the activation energy.

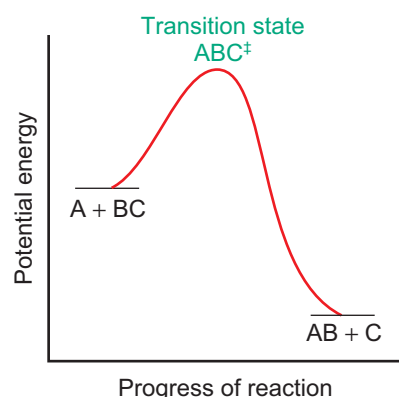


Figure 9.28 Energy profile for the reaction $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$.

i The symbol $\ddagger$ is used as a superscript to denote the transition state and also the quantities (such as $\Delta^\ddagger G$ and $K^\ddagger$) involved in the formation and reaction of the transition state.

The Planck constant, h , is introduced in Section 3.2 (p.120). It appears in Equation 9.28 because the expression is derived by considering the energy levels associated with $\text{ABC}^\ddagger$.

For a reaction, the equilibrium constant, K , is related to the standard Gibbs energy change of reaction, $\Delta_r G^\ominus$, by the equation

$$\Delta_r G^\ominus = -RT \ln K \quad (\text{see Section 15.3, p.703})$$

and hence to the standard enthalpy change, $\Delta_r H^\ominus$, and standard entropy change, $\Delta_r S^\ominus$

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus \quad (\text{see Section 14.5, p.673})$$

Transition state theory

In the model for the transition state theory, the reaction pathway from reactants to products passes through a transition state at the highest point of the energy profile. This is illustrated in Figure 9.28 for a bimolecular reaction with a rate constant k



Transition state theory assumes that a pre-equilibrium (see Section 9.6, p.417) is established between the reactants and the transition state, $\text{ABC}^\ddagger$, which then goes on to form the products



where $K^\ddagger$ is the **equilibrium constant** for the reversible initial step to form the transition state and $k^\ddagger$ is the **rate constant** for the formation of products from the transition state.

To obtain an expression for the rate constant, k , for the overall reaction, the theory uses the ideas developed on p.416 for a series of elementary steps involving a pre-equilibrium, together with an estimate of the rate constant, $k^\ddagger$. The resulting equation is

$$k = \frac{k_B T}{h} K^\ddagger \quad (9.28)$$

where k_B is the Boltzmann constant (see p.429) and h is the Planck constant.

This is an important expression because it links k with thermodynamic functions for the formation of the transition state. $K^\ddagger$ is the equilibrium constant for the formation of the transition state and is related to the corresponding Gibbs energy change by the equation

$$\Delta^\ddagger G = -RT \ln K^\ddagger$$

where $\Delta^\ddagger G$ is the Gibbs energy change for the formation of the transition state from the reactants and is called the **Gibbs energy of activation**.

Rearranging the equation to give an expression for $K^\ddagger$

$$\ln K^\ddagger = -\frac{\Delta^\ddagger G}{RT} \quad \text{and} \quad K^\ddagger = e^{-\frac{\Delta^\ddagger G}{RT}} \quad (\text{If } \ln y = x, \text{ then } y = e^x)$$

Equation 9.28 can now be rewritten as

$$k = \frac{k_B T}{h} e^{-\frac{\Delta^\ddagger G}{RT}}$$

This expression can be further extended, since $\Delta^\ddagger G = \Delta^\ddagger H - T\Delta^\ddagger S$, where $\Delta^\ddagger H$ is the **enthalpy of activation** and $\Delta^\ddagger S$ is the **entropy of activation**. Using the mathematical relationship,

$e^{a+b} = e^a \times e^b$, you can obtain an expression for the overall rate constant in terms of $\Delta^\ddagger H$ and $\Delta^\ddagger S$. Comparing this with the Arrhenius equation

$$k = \frac{k_B T}{h} e^{\frac{\Delta^\ddagger S}{R}} e^{-\frac{\Delta^\ddagger H}{RT}} = A e^{-\frac{E_a}{RT}}$$

you can see that the term in blue corresponds to the A factor in the Arrhenius equation and $\Delta^\ddagger H$ corresponds to E_a .

$$A = \frac{k_B T}{h} e^{\frac{\Delta^\ddagger S}{R}} \quad (9.29)$$

Equation 9.29 shows the importance of entropy changes during the formation of the transition state, since these affect the value of the rate constant and hence the rate of the reaction.

The next section describes the use of $\Delta^\ddagger G$ in plotting Gibbs energy profiles for reactions.

Gibbs energy profiles for reactions

An alternative way to follow the progress of a reaction is to plot Gibbs energy, G , as the reaction takes place (rather than the potential energy as in Section 9.7). This is called a **Gibbs energy profile**. Transition state theory links the Gibbs energy of activation, $\Delta^\ddagger G$, directly to the rate constant, k , for the reaction—the greater the value of $\Delta^\ddagger G$, the smaller the value of the rate constant and the slower the reaction. As shown in the previous section, the value of $\Delta^\ddagger G$ contains a contribution both from the enthalpy of activation, $\Delta^\ddagger H$, and the entropy of activation, $\Delta^\ddagger S$. Calculated values of $\Delta^\ddagger S$, using Equation 9.29 and experimental A factors, provide information about the structures of transition states.

Figure 9.29 shows the Gibbs energy profile for a concerted single step reaction, such as the alkaline hydrolysis of bromomethane, which proceeds by an S_N2 mechanism (see Section 9.6, p.413). There is a single maximum corresponding to the transition state for the reaction. The Gibbs energy change for the reaction, $\Delta_r G$, corresponds to the difference in Gibbs energy between the reactants and products.

For a complex reaction involving two steps, such as the alkaline hydrolysis of 2-bromo-2-methylpropane, which proceeds by an S_N1 mechanism (see Section 9.6, p.413), the Gibbs energy profile shows two maxima corresponding to the transition states for the two steps, and a minimum corresponding to the formation of the intermediate. In the example in Figure 9.30 (p.432), $k_1 \ll k_2$, so that $\Delta^\ddagger G_1$, the Gibbs energy of activation for the formation of the transition state in step 1 is much larger than $\Delta^\ddagger G_2$, the Gibbs energy of activation for the formation of the transition state in step 2.

i An **intermediate** in a reaction can be detected spectroscopically, but cannot usually be isolated. It occurs at a minimum in the Gibbs energy

profile. A **transition state** occurs at a maximum in the Gibbs energy profile. It is very difficult to detect and cannot be isolated.

Take care not to confuse the Gibbs energy of activation, $\Delta^\ddagger G$, with the Gibbs energy change for the overall reaction, $\Delta_r G$. The Gibbs energy change for a reaction is related to the spontaneity of the reaction. For a reaction to be spontaneous, the value of $\Delta_r G$ must be negative. Not all spontaneous reactions take place in practice, however. In cases where the Gibbs energy of activation is very large, the rate constant may be too small for significant reaction to occur under normal conditions.



This screencast discusses transition state theory and the importance of Gibbs energy profiles.

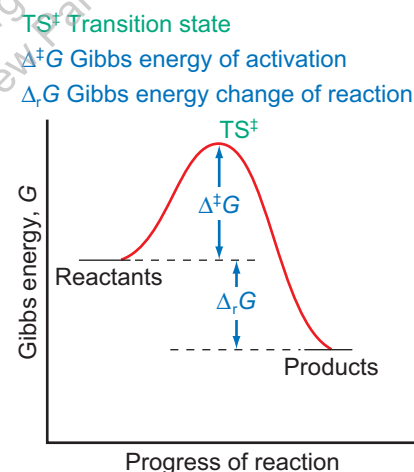


Figure 9.29 Gibbs energy profile for a single step reaction, such as the alkaline hydrolysis of bromomethane.

➞ The mechanism of S_N2 reactions is discussed in Section 20.3. Figure 20.10 (p.924) shows a Gibbs energy profile for an S_N2 reaction.

➞ The mechanism of S_N1 reactions is discussed in Section 20.3. Figure 20.15 (p.928) shows a Gibbs energy profile for an S_N1 reaction.

i The Gibbs energy change of reaction, $\Delta_r G$, is related to the enthalpy change for the reaction, $\Delta_r H$, and the entropy change, $\Delta_r S$, by the equation:

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

For a spontaneous reaction, $\Delta_r G < 0$. This is explained in Section 14.5 (p.673).

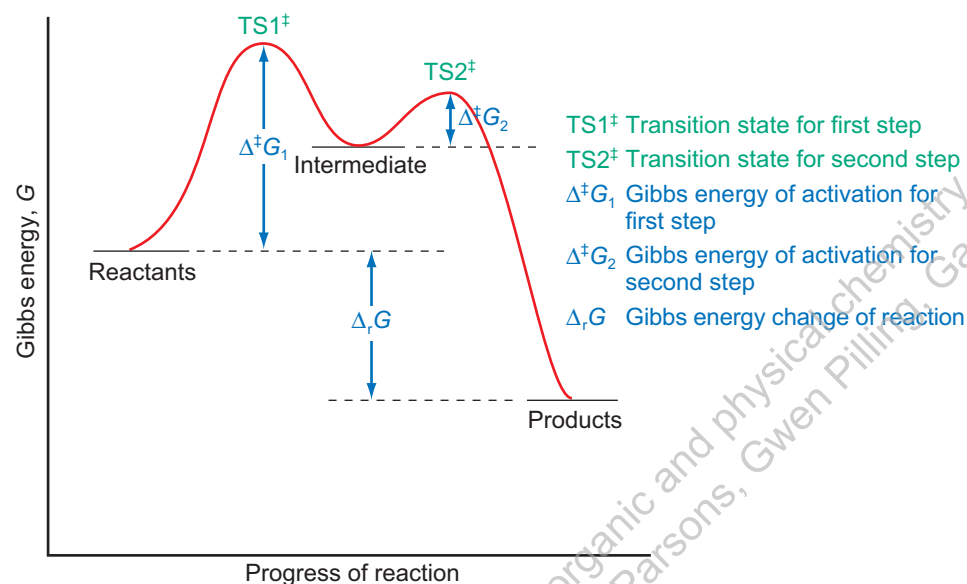


Figure 9.30 Gibbs energy profile for a two-step reaction, such as the alkaline hydrolysis of 2-bromo-2-methylpropane.

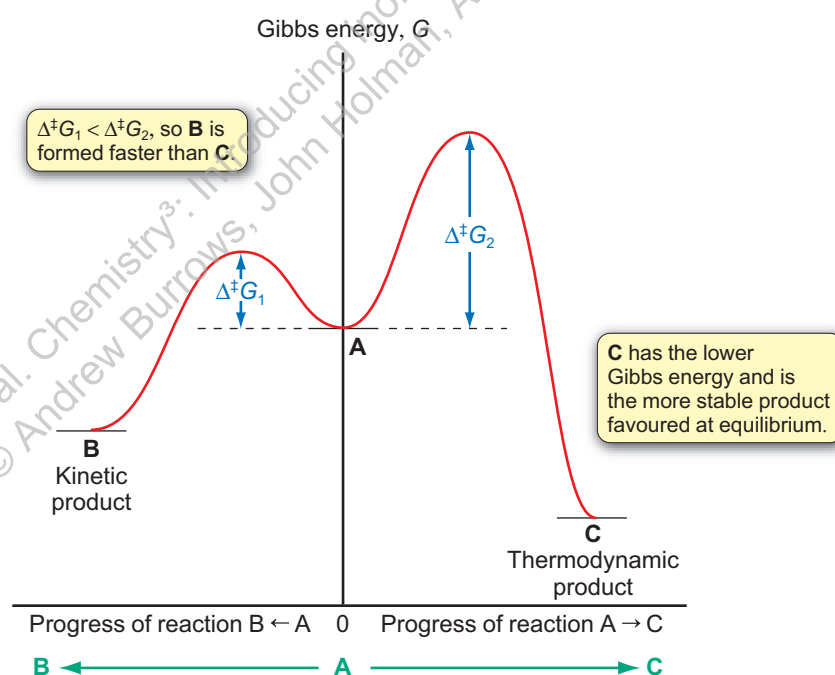


Figure 9.31 Kinetic and thermodynamic products.

Competing reactions

When two reactions take place independently in parallel, each reaction has its own Gibbs energy profile. For example, Figure 9.31 shows the Gibbs energy profiles for the parallel reactions



The reaction $A \rightarrow B$ has the lower $\Delta^\ddagger G$, but the product C has the lower Gibbs energy and is favoured at equilibrium. The reaction $A \rightarrow B$ will occur more rapidly than $A \rightarrow C$, so product

The kinetics of parallel reactions are discussed in Section 9.6 (p.414).

B will form initially. B is known as the **kinetic product**. For longer reaction times, since both reactions are reversible, the system comes to equilibrium to form C as the major product. C is known as the **thermodynamic product**. This process takes longer because the rate constant for $A \rightarrow C$ is smaller than that for $A \rightarrow B$.

Gibbs energy profiles are used extensively in organic chemistry and biochemistry to illustrate the mechanism of reactions. They can be particularly useful when considering competing reactions, as they can help chemists choose the best reaction conditions to maximize a desired reaction and minimize unwanted reactions.

For examples of the use of Gibbs energy profiles in organic chemistry, see Sections 19.1 (p.861) and 20.3 (p.924).



Summary

- The molecularity of a reaction is the number of reactant molecules involved in forming the transition state.
- Collision theory is most useful for bimolecular reactions in the gas phase. It relates the A factor in the Arrhenius equation to the frequency of collisions taking place with the correct orientation for reaction.
- Transition state theory shows that the rate constant, k , depends on the Gibbs energy of activation, $\Delta^\ddagger G$. The A factor is related to $\Delta^\ddagger S$ and the activation energy, E_a , to $\Delta^\ddagger H$.
- Gibbs energy profiles are used extensively in organic chemistry and biochemistry to illustrate the mechanisms of reactions.



For practice questions on these topics, see questions 4, 20, and 23 at the end of this chapter (pp.440–442).

9.9 Catalysis

A **catalyst** is a substance that increases the rate of a chemical reaction without being consumed in the reaction. It does not appear in the overall equation for the reaction. Some substances slow down chemical reactions and these are often called negative catalysts or inhibitors.

The catalyst does not affect the *amount* of product formed—only the *rate* at which it is formed. Only a small amount of catalyst is usually needed. It is not changed chemically in the reaction and can be recovered at the end of the reaction. Sometimes a catalyst may be changed *physically*. For example, the surface of a solid catalyst may crumble or become roughened. This suggests that the catalyst is taking part in the reaction but is being regenerated.

Figure 9.32 shows Gibbs energy profiles for an uncatalysed reaction and for the same reaction in the presence of a catalyst. The catalyst acts by providing an alternative pathway for the reaction in which the rate-determining step has a lower Gibbs energy of activation than that of the uncatalysed reaction. At a given temperature, the rate constant is greater for the catalysed reaction, so the reaction is faster. Note that in Figure 9.32 the uncatalysed reaction proceeds through a single transition state, whereas the mechanism for the catalysed reaction involves the formation of an intermediate. Table 9.5 compares the effective activation energies for some catalysed and uncatalysed reactions.

There are two types of catalytic reaction.

- In **heterogeneous catalysis**, the catalyst is in a different physical state from that of the reactants. Many industrial processes involve this type of catalysis, in which a mixture of gases or liquids is passed over a solid catalyst, such as a *d*-block metal or one of its compounds. An advantage of heterogeneous catalysis is that the product (and any unreacted starting materials) are easily separated from the catalyst.



A **catalyst** increases the rate of a chemical reaction without being consumed in the reaction.



For a complex reaction made up of a number of elementary reactions, E_a for the overall reaction is called the effective activation energy; see Section 9.7 (p.427).

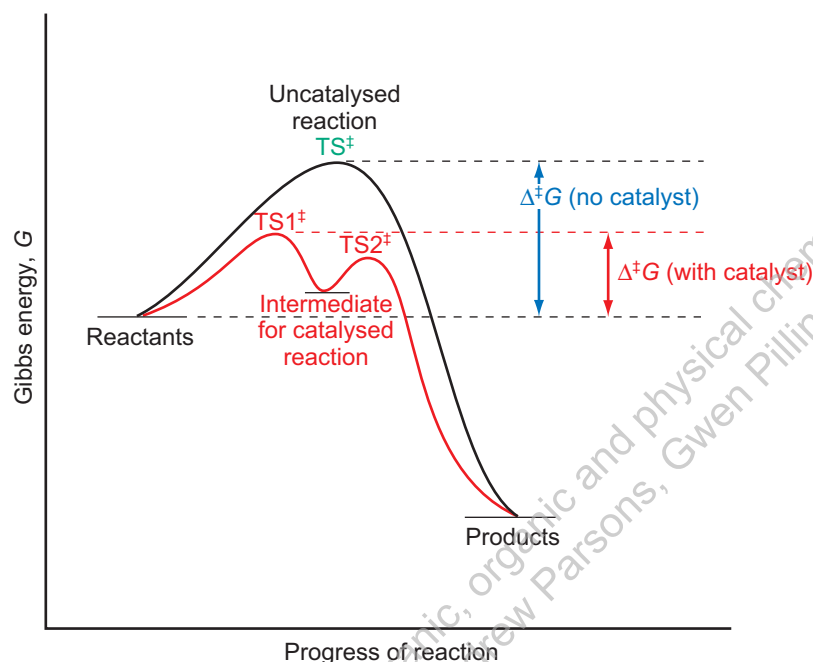


Figure 9.32 Gibbs energy profiles for a catalysed and an uncatalysed reaction.

Table 9.5 Effective activation energies of catalysed and uncatalysed reactions

Reaction	Catalyst	$E_a / \text{kJ mol}^{-1}$
$2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$	none	+350
	tungsten	+162
$2\text{N}_2\text{O}(\text{g}) \rightarrow 2\text{N}_2(\text{g}) + \text{O}_2(\text{g})$	none	+245
	gold	+121
$2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$	none	+184
	gold	+105
$2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{aq}) + \text{O}_2(\text{aq})$	none	+75
	platinum	+49
	catalase (enzyme)	+23

- In **homogeneous catalysis**, the catalyst is in the same physical state as the reactants. Many organic acid–base catalysed reactions involve this type of catalysis. Enzyme reactions in cells take place in aqueous solution and involve homogeneous catalysis.

Enzyme-catalysed reactions

Enzymes catalyse a wide range of reactions in your body. These reactions take place in dilute solution at 37 °C. Without the presence of enzymes, the reactions would take place much too slowly to sustain life. An enzyme is normally a protein molecule, and is specific for a particular reaction.

The enzyme interacts with the reactant, called the **substrate**, at a specific location in the enzyme called the **active site**. The three-dimensional shape of the active site fits the shape

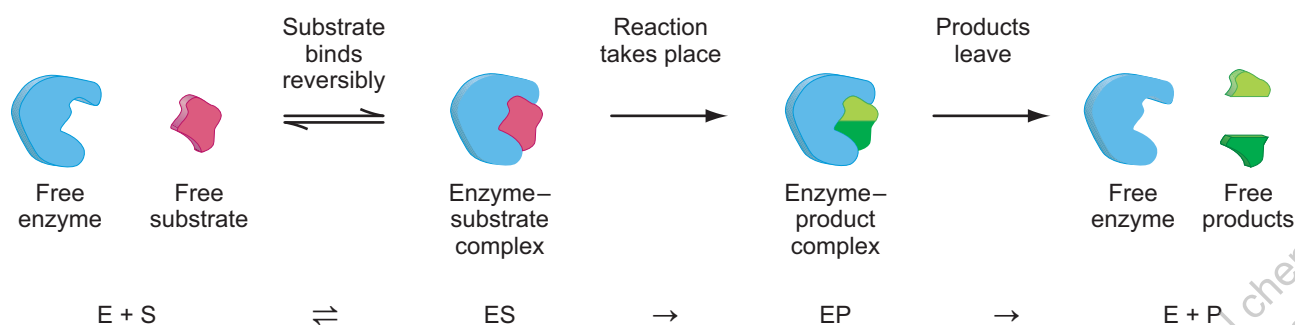


Figure 9.33 The simple 'lock and key' model for enzyme catalysis.

of the substrate. The substrate becomes bound to the active site by non-covalent interactions that depend very specifically on the three-dimensional shapes of the enzyme and substrate. The reaction then takes place in the active site. The products are less strongly bound and fit the active site less well, so they are released from the enzyme, which is then free to react with another molecule of the substrate. The whole process, sometimes called the 'lock and key' model, is summarized in Figure 9.33.

Figure 9.34 shows the Gibbs energy profile for this simple model of enzyme catalysis.

What happens, of course, is more complex. Scientists believe that in many cases, the substrate is not quite a perfect fit and must alter its shape to fit into the active site. This means that both the substrate and the active site are in strained arrangements, which can help the reaction to occur.

Experimental studies of enzyme-catalysed reactions are often carried out by measuring the initial rate of formation of the product in a solution containing a low concentration of the enzyme. A series of experiments is carried out with different initial concentrations of the substrate, $[S]_0$, to find out how the initial rate depends on $[S]$. Another series of experiments in which $[S]_0$ is constant and the initial enzyme concentration, $[E]_0$, is varied gives the dependence of the rate on $[E]$.

Kinetic experiments such as these showed that enzyme-catalysed reactions have the following two characteristics:

- For a given initial enzyme concentration, and low values of $[S]_0$, the rate of product formation is directly proportional to $[S]_0$, so the reaction is **first order with respect to $[S]$** .

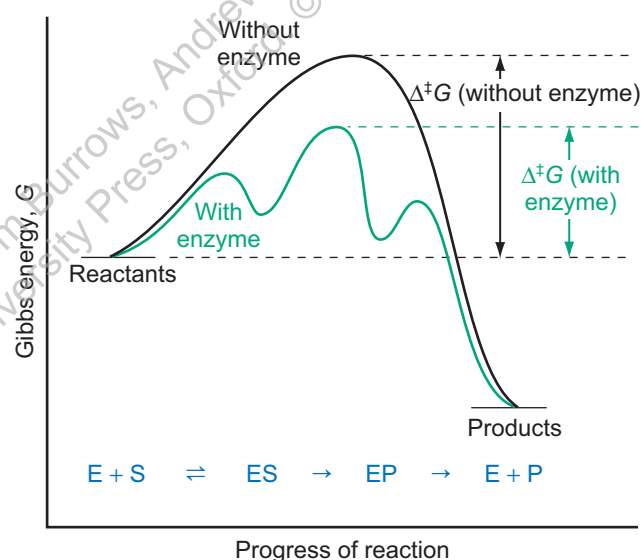
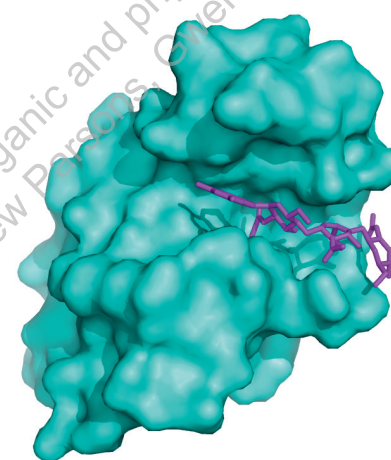


Figure 9.34 Gibbs energy profile for an enzyme-catalysed reaction.



Computer graphics representation of a lysozyme molecule, an important catalytic enzyme that is capable of cleaving sugar structures in biological systems. In this image the protein is shown in green-blue and the substrate in purple. The classical 'lock and key' description of enzyme action is clearly illustrated in this image by the insertion of the substrate into the active site.

i The initial rate method of investigating the kinetics of a reaction is described in Section 9.5 (p.405).



Zero order reactions are discussed in Section 9.5 (Boxes 9.6 and 9.7, p.408).

- For a given initial enzyme concentration, and *high values* of $[S]_0$, the rate of product formation is independent of $[S]_0$, so the reaction is *zero order with respect to* $[S]$.

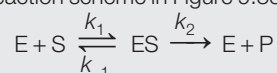
Biochemists Leonor Michaelis and Maud Menten working in Germany studied enzyme reactions at the beginning of the twentieth century and derived an expression to explain their kinetic behaviour for different substrate concentrations. The kinetics of enzyme-catalysed reactions explained in this way are known as **Michaelis–Menten kinetics**. You can see how the Michaelis–Menten equation is derived in Box 9.8.



Box 9.8 The Michaelis–Menten mechanism

A quantitative analysis of the kinetics of enzyme-catalysed reactions uses the steady state approximation and other ideas developed in Section 9.6 (p.412) for complex reactions.

The enzyme–product complex, EP, is short-lived and only reacts to give E + P, so the reaction scheme in Figure 9.33 can be simplified to



Applying the steady state approximation (Equation 9.15, p.416) to the concentration of the enzyme–substrate complex, ES

$$\begin{aligned} \frac{d[ES]}{dt} &= (\text{rate of formation of ES} - \text{rate of consumption of ES}) = 0 \\ &= k_1[E][S] - k_{-1}[ES] - k_2[ES] \\ \frac{d[ES]}{dt} &= k_1[E][S] - (k_{-1} + k_2)[ES] = 0 \end{aligned} \quad (9.30)$$

The concentration of the substrate is usually much larger than that of the enzyme, so that $[S]$ is effectively constant in a particular experiment.

It is not possible to measure $[ES]$ but the total enzyme concentration $[E]_0$ is known. (The free enzyme concentration, $[E]$, in Equation 9.30 is less than $[E]_0$, because some of the enzyme is bound up in the enzyme–substrate complex.) So

$$[E]_0 = [E] + [ES] \quad \text{and} \quad [E] = [E]_0 - [ES]$$

Substituting for $[E]$ in Equation 9.30 gives

$$\frac{d[ES]}{dt} = k_1[E]_0[S] - k_1[ES][S] - (k_{-1} + k_2)[ES] = 0$$

Rearranging this equation

$$[ES] = \frac{k_1[E]_0[S]}{(k_1[S] + k_{-1} + k_2)}$$

The rate of formation of the product, P, is given by

$$\frac{d[P]}{dt} = k_2[ES] = \frac{k_1k_2[E]_0[S]}{k_1[S] + k_{-1} + k_2}$$

Dividing the numerator and the denominator by k_1 gives

$$\text{rate of formation of product} = \frac{k_2[E]_0[S]}{[S] + \left(\frac{k_{-1} + k_2}{k_1}\right)}$$

This can be written as

$$\text{rate of the enzyme-catalysed reaction} = \frac{k_2[E]_0[S]}{[S] + K_M} \quad (9.31)$$

$$\text{where } K_M = \frac{k_{-1} + k_2}{k_1}$$

Equation 9.31 is called the **Michaelis–Menten equation** and K_M the **Michaelis constant**. You can distinguish two extreme situations.

(a) Reactions with low substrate concentrations

When $[S]$ is very small, $K_M \gg [S]$, so that

$$\text{rate of the reaction} = \frac{k_2[E]_0[S]}{K_M}$$

The rate of reaction increases linearly with $[S]$, that is, it is first order with respect to $[S]$.

(b) Reactions with large substrate concentrations

When $[S]$ is large, $[S] \gg K_M$, so that

$$\text{rate of reaction} = k_2[E]_0$$

The rate of reaction is now independent of $[S]$. Under these conditions, all of the enzyme molecules have substrates attached at any moment during the reaction and $[ES] = [E]_0$. The enzyme is said to be **saturated**. If the substrate concentration increases, no more enzyme–substrate complexes can be formed, and the rate of the reaction is independent of the concentration of the substrate. The rate of reaction remains constant at the maximum value, $(\text{rate})_{\text{max}}$, and the reaction is zero order with respect to $[S]$.

Figure 1 illustrates how the rate of an enzyme-catalysed reaction varies with the concentration of the substrate.

Often $k_{-1} \gg k_2$, so that $K_M = k_{-1}/k_1$ and is equal to $1/K_c$, where K_c is the equilibrium constant for the formation of ES from E and S. Under these conditions, the mechanism involves a pre-equilibrium, $E + S \rightleftharpoons ES$ (see Section 9.6, p.417).

Analysing experimental data for enzyme-catalysed reactions

Measurements of the overall rate of an enzyme-catalysed reaction, as a function of the substrate concentration, $[S]$, provides information on the equilibrium constant for formation of the enzyme–substrate complex, ES, and on the rate constant for the reaction of ES to form the product, P.



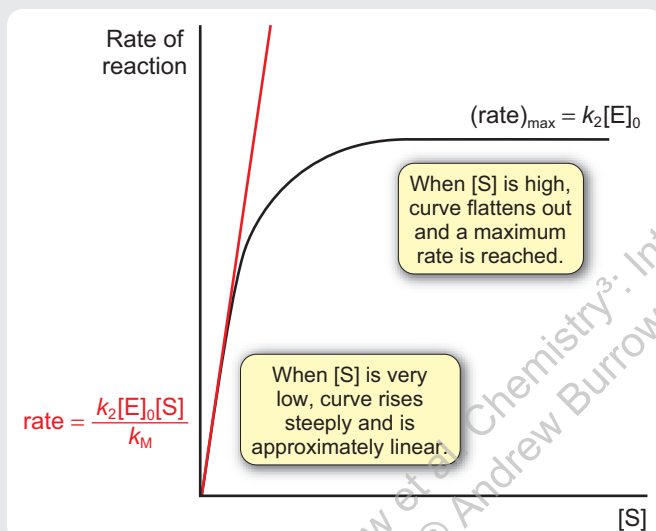
→ It is always a good idea to use a straight line plot to analyse experimental data. This can be done here by taking the reciprocal of the rate from Equation 9.31.

$$\begin{aligned}\frac{1}{\text{rate}} &= \frac{1}{k_2[E]_0} + \frac{K_M}{k_2[E]_0[S]} \\ &= \frac{1}{(\text{rate})_{\max}} + \frac{K_M}{(\text{rate})_{\max}[S]}\end{aligned}\quad (9.32)$$

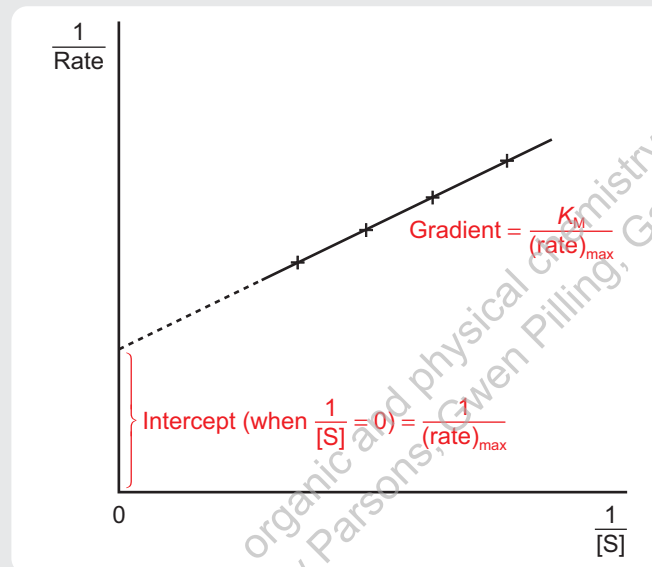
where the maximum rate, $(\text{rate})_{\max} = k_2[E]_0$

A plot of $1/\text{rate}$ against $1/[S]$ gives a straight line. The intercept on the y-axis (where $1/[S] = 0$) is $1/(\text{rate})_{\max}$ and the gradient of the line is $K_M/(\text{rate})_{\max}$. The ratio of the gradient to the intercept is K_M . This is called a **Lineweaver–Burk** plot and is illustrated in Figure 2. A value for k_2 can also be found, since $[E]_0$ is known and

$$k_2 = \frac{(\text{rate})_{\max}}{[E]_0}$$



▲ **Figure 1** The dependence of the rate of an enzyme-catalysed reaction on the concentration of the substrate, $[S]$. (The plot is obtained from a series of experiments with different values of $[S]$.)



▲ **Figure 2** A Lineweaver–Burk plot of $1/(\text{rate})$ against $1/[S]$ allows the Michaelis constant, K_M , and the maximum rate of reaction, $(\text{rate})_{\max}$ to be found.

Question

The following results were obtained for the enzyme-catalysed hydrolysis of ATP at 20°C .

The initial concentration of the enzyme, ATPase, was $1.5 \times 10^{-8} \text{ mol dm}^{-3}$.

$[\text{ATP}]_0 / \mu\text{mol dm}^{-3}$	0.5	1.0	2.0	4.0
Initial rate / $\mu\text{mol dm}^{-3} \text{ s}^{-1}$	0.54	0.82	1.11	1.36

Determine the maximum rate, $(\text{rate})_{\max}$, and the Michaelis constant, K_M , for the reaction.



Summary

- A catalyst increases the rate of a chemical reaction without being consumed in the reaction.
- Catalysts act by providing an alternative pathway for reaction in which the rate-determining step has a lower Gibbs energy of activation than the uncatalysed reaction.
- The Michaelis–Menten equation is used to analyse the kinetics of enzyme-catalysed reactions.



For a practice question on these topics, see question 24 at the end of this chapter (p.443).



Concept review

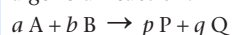
By the end of this chapter, you should be able to do the following.

- Understand what is meant by the rate of a reaction.
- Write a differential for the rate in terms of consumption of a reactant or formation of a product.
- Be aware of the different techniques used to monitor the progress of a reaction.
- Write the rate equation for an elementary reaction from the stoichiometric chemical equation and understand the meaning of the terms order and rate constant.
- Understand that the mechanism of a complex reaction involves a series of elementary reactions and that the rate equation must be determined experimentally.
- Describe and use a range of methods for investigating the kinetics of a reaction, including the isolation technique (when there is more than one reactant), drawing tangents to a plot of concentration against time, measuring initial rates, and using integrated rate equations and half lives.
- Explain how kinetic studies can be used as evidence for organic reaction mechanisms.
- Explain why some reactions show zero order kinetics.
- Explain the kinetics of a series of reactions using the idea of pre-equilibrium and the steady state approximation.
- Explain the effect of temperature on the rate of a reaction.
- Understand what is meant by the molecularity of an elementary reaction.
- Be familiar with the outlines of collision theory and transition state theory and their importance.
- Draw and interpret Gibbs energy profiles for reactions.
- Explain how a catalyst speeds up a reaction and understand the difference between heterogeneous and homogeneous catalysis.
- Understand the Michaelis–Menten mechanism for an enzyme-catalysed reaction, and use a Lineweaver–Burk plot to analyse experimental data.



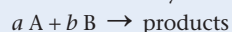
Key equations

Definition of rate of reaction for a general reaction:



$$\text{Rate of reaction} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{p} \frac{d[P]}{dt} = \frac{1}{q} \frac{d[Q]}{dt} \quad (9.4)$$

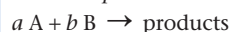
For an *elementary* reaction:



$$\text{Rate of reaction} = k [A]^a [B]^b \quad (9.5)$$

where k is the rate constant, and the stoichiometric coefficients in the chemical equation, a and b , are the orders with respect to A and B, respectively. The overall order is $a + b$.

For a *complex* reaction:



$$\text{Rate of reaction} = k[A]^m[B]^n \quad (9.11)$$

where k is the overall rate constant, and m and n are the orders with respect to A and B, respectively. The overall order is $m + n$.

Reaction mechanisms of complex reactions

For a reversible *elementary* reaction:

$$\frac{k_1}{k_{-1}} = K_c \quad (9.14)$$

The steady state approximation for a reactive intermediate X:

$$\frac{d[X]}{dt} = (\text{rate of formation of X} - \text{rate of consumption of X}) = 0 \quad (9.15)$$

The Arrhenius equation

$$k = A e^{-\frac{E_a}{RT}} \quad (9.24a)$$

$$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (9.24b)$$

$$\ln k_2 - \ln k_1 = \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (9.25)$$

Michaelis–Menten equation

$$\text{Rate of an enzyme-catalysed reaction} = \frac{k_2[E]_0[S]}{[S] + K_M} \quad (9.31)$$

$$\text{where } K_M = \frac{k_{-1} + k_2}{k_1}$$

Table 9.2 A summary of equations for elementary reactions

Type of reaction	Order of reaction	Differential rate equation	Integrated rate equation	Half life, $t_{1/2}$
$A \rightarrow \text{products}$	First order	$-\frac{d[A]}{dt} = k[A]$	$\ln [A]_t = \ln [A]_0 - kt$	$\frac{\ln 2}{k}$
$A + A \rightarrow \text{products}$	Second order	$-\frac{d[A]}{dt} = 2k[A]^2$	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + 2kt$	$\frac{1}{2k[A]_0}$
$A + B \rightarrow \text{products}$ where $[A] \ll [B]$	Pseudo-first order	$-\frac{d[A]}{dt} = k'[A]$ where $k' = k[B]_0$	$\ln [A]_t = \ln [A]_0 - k't$ $= \ln [A]_0 - kt[B]_0$	$\frac{\ln 2}{k'} = \frac{\ln 2}{k[B]_0}$

Table 9.3 Using integrated rate equations to study complex reactions**

	Order		
	0	1	2
Rate equation	Rate = k'	Rate = $k'[A]$	Rate = $k'[A]^2$
Integrated rate equation	$[A]_t = [A]_0 - k't$	$\ln [A]_t = \ln [A]_0 - k't$	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + 2k't^*$
Plot of $[A]$ vs. t	Straight line	Curve	Curve
Plot of $\ln [A]$ vs. t	Curve	Straight line	Curve
Plot of $\frac{1}{[A]}$ vs. t	Curve	Curve	Straight line
Half life, $t_{1/2}$	Not constant	Constant	Not constant

* The multiplication factor before k' depends on the stoichiometry of the reaction.

** The order of a complex reaction may be higher than 2 or have a fractional value.

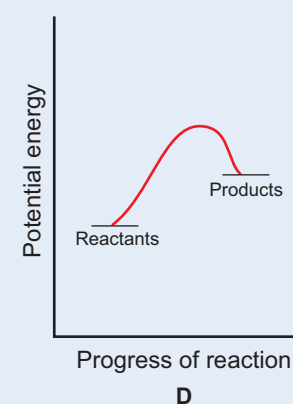
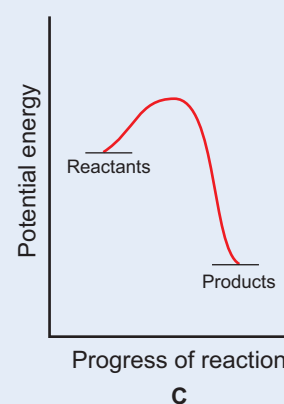
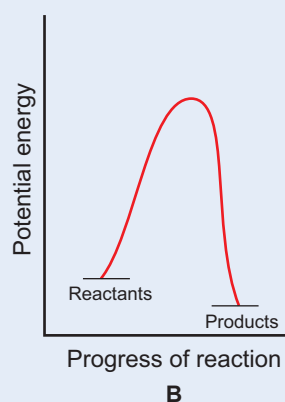
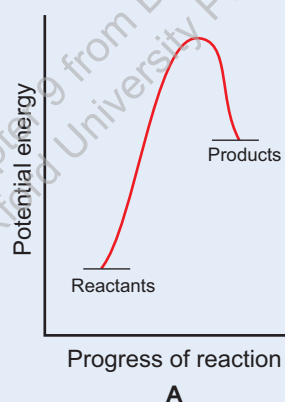


Questions

More challenging questions are indicated by an asterisk *.

Note: Radical dots are not shown on stable radicals such as O_2 , NO, and NO_2 unless relevant to the reaction.

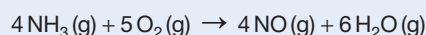
- 1 The energy profiles A–D represent four different reactions. All the diagrams are drawn to the same scale. (Sections 9.1 and 9.7)



Which of the energy profiles A–D represents:

- (a) the most exothermic reaction;
- (b) the most endothermic reaction;
- (c) the reaction with the largest activation energy;
- (d) the reaction with the smallest activation energy?

- 2 The oxidation of ammonia in air is catalysed by platinum metal



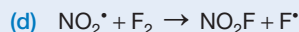
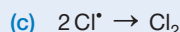
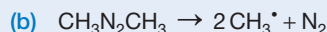
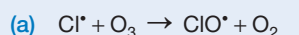
Write an expression for the rate of reaction in terms of differentials for the consumption of the reactants and formation of the products. (Sections 9.2 and 9.4)

- 3 Under certain experimental conditions, the rate of the following reaction is $5.86 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$

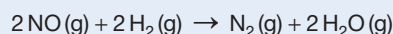


Calculate values for $\frac{d[\text{N}_2\text{O}]}{dt}$, $\frac{d[\text{N}_2]}{dt}$, and $\frac{d[\text{O}_2]}{dt}$ under these conditions. (Sections 9.2 and 9.4)

- 4 Write the rate equation for the following elementary reactions and give the molecularity for each reaction. (Sections 9.4 and 9.8)



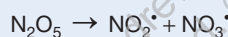
- 5 For the complex reaction of NO and H₂



the rate equation is given by

$$\text{rate of reaction} = k[\text{NO}]^2[\text{H}_2] \quad (\text{Section 9.5})$$

- (a) What are the orders of the reaction with respect to NO and H₂?
- (b) What is the overall order of the reaction?
- (c) What will happen to the rate of reaction if:
- [H₂] is doubled;
 - [H₂] is halved;
 - [NO] is doubled;
 - [NO] is increased by a factor of three?
- 6 The gas phase decomposition of dinitrogen pentoxide (N₂O₅)



was studied in a large stainless steel cell, at 294 K and a pressure of 1 bar. The concentration of N₂O₅ was monitored using infrared spectroscopy. The following results were obtained. (Section 9.4)

<i>t</i> /s	0	10	20	30	40	50
[N ₂ O ₅]/10 ⁻⁹ mol dm ⁻³	34.0	27.0	19.5	15.0	11.5	8.7

<i>t</i> /s	60	70	80	90	100
[N ₂ O ₅]/10 ⁻⁹ mol dm ⁻³	6.6	5.1	3.9	2.9	2.2

Show that the reaction is first order and find a value for the rate constant at 294 K.

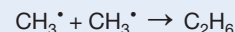
- 7 The data below were obtained for the decomposition of difluorine oxide (F₂O) at 298 K. (Sections 9.4 and 9.5)



<i>t</i> /s	0	60	120	180	240	300	360	420
[F ₂ O]/10 ⁻³ mol dm ⁻³	7.2	5.5	4.6	3.8	3.3	2.9	2.6	2.4

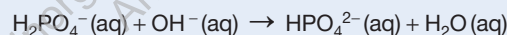
Verify that this is a second order reaction and determine the rate constant at 298 K.

- 8 The reaction of methyl radicals to form ethane was investigated in a laser flash photolysis experiment at 300 K.



The rate constant for this reaction at 300 K is $3.7 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The concentration of methyl radicals, [CH₃•], at time *t* = 0 was $1.70 \times 10^{-8} \text{ mol dm}^{-3}$. Calculate a value for [CH₃•] at *t* = $1.00 \times 10^{-3} \text{ s}$. (Section 9.4)

- 9 The acid-catalysed hydrolysis of sucrose shows first order kinetics. The half life for the reaction at room temperature was found to be 190 min. Calculate the rate constant for the reaction under these conditions. (Section 9.4)
- 10 The reaction between H₂PO₄⁻ and OH⁻ was investigated at 298 K using the initial rate method

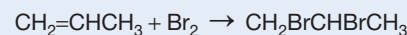


The following results were obtained. (Section 9.5)

	Initial rate / 10 ⁻³ mol dm ⁻³ min ⁻¹	[OH ⁻] ₀ / 10 ⁻³ mol dm ⁻³	[H ₂ PO ₄ ⁻] ₀ / 10 ⁻³ mol dm ⁻³
Experiment 1	2.0	0.40	3.0
Experiment 2	3.7	0.55	3.0
Experiment 3	7.1	0.75	3.0

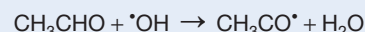
- (a) Plot a log-log graph to determine the order of reaction with respect to OH⁻ (aq).
- (b) What further experiments would you need to do to find the order with respect to H₂PO₄⁻?

- 11 The addition of bromine to propene is an elementary reaction with a rate constant, *k*



Kinetic studies were carried out at 298 K using excess Br₂. For [Br₂]₀ = 0.20 mol dm⁻³, the pseudo-first order rate constant, *k'*, for the reaction was found to be 900 s⁻¹. What is the value of *k* at 298 K? (Section 9.4)

- 12* The elementary reaction between ethanal (CH₃CHO) and •OH radicals



was studied at 298 K, by laser flash photolysis, using laser-induced fluorescence to detect •OH as a function of time. The ethanal concentration was $3.3 \times 10^{-7} \text{ mol dm}^{-3}$ and this concentration was much higher than the concentration of •OH radicals. The following data for the concentration of •OH radicals, relative to their concentration at zero time, were obtained. (Section 9.4)

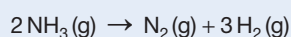
$t/10^{-3} \text{ s}$	0	0.2	0.4	0.6	0.8	1.0	1.2	1.5
$[\text{OH}]/[\text{OH}]_0$	1	0.55	0.31	0.16	0.09	0.05	0.03	0.01

- (a) Write a rate equation for the reaction.
- (b) Show that, under the above conditions, the reaction follows pseudo-first order kinetics.
- (c) Determine the pseudo-first order rate constant, k' .
- 13* The investigation described in Question 12 was repeated a number of times, each time using a different concentration of ethanal, $[\text{CH}_3\text{CHO}]_0$. A value for k' was found in each case. The following results were obtained.

$[\text{ethanal}]_0/10^{-7} \text{ mol dm}^{-3}$	1.2	2.4	4.0	5.1
$k'/10^3 \text{ s}^{-1}$	1.12	2.10	3.65	4.50

Confirm that the reaction is first order with respect to ethanal and determine the second order rate constant for the reaction. (Incorporate the value of k' determined in Question 12 into your analysis.) (Section 9.4)

- 14 The decomposition of ammonia on a platinum surface at 856°C



shows the following dependence of the concentration of ammonia gas on time

t/s	0	200	400	600	800	1000	1200
$[\text{NH}_3]/10^{-3} \text{ mol dm}^{-3}$	2.10	1.85	1.47	1.23	0.86	0.57	0.34

Find the order of the reaction and a value for the rate constant at 856°C . Suggest an explanation for the order you obtain. (Section 9.5)

- 15 Rate constants at a series of temperatures were obtained for the decomposition of azomethane



T/K	523	541	560	576	593
$k/10^{-6} \text{ s}^{-1}$	1.8	15	60	160	950

Use the data in the table to find the activation energy, E_a , for the reaction. (Section 9.7)

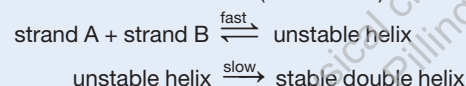
- 16 The A factor for the reaction of methane with hydroxyl radicals is $1.11 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.



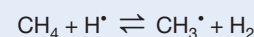
The activation energy for the reaction is $+14.1 \text{ kJ mol}^{-1}$. (Section 9.7)

- (a) Calculate the rate constant for the reaction at 220 K , which corresponds to a region close to the top of the troposphere.
- (b) Compare the value you obtain in (a) with the value for the rate constant at 300 K , when $k = 3.9 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This corresponds to a region nearer the Earth's surface, see Box 9.3 (p.396). Comment on the difference between the values for the rate constant at the two temperatures.

- 17 The mechanism for the formation of a DNA double helix from two strands A and B is as follows (Section 9.6)



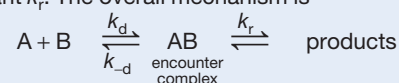
- (a) Experiments show that the overall reaction is first order with respect to strand A and first order with respect to strand B. Write the equation for the overall reaction.
- (b) Write the rate equation for the overall reaction.
- (c) Assuming the processes involved are elementary reactions, derive an expression for the rate constant for the overall reaction in terms of the rate constants for the individual steps.
- 18 The reaction of methane with hydrogen atoms is an elementary process.



The rate constant for the forward reaction at 1000 K is $1.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The equilibrium constant, K_c , at the same temperature is 19.8 . Calculate the rate constant for the reverse reaction at 1000 K . (Section 9.6)

- 19* Molecules move much more slowly in solution than in the gas phase. The progress of a molecule is frequently stopped, and the direction of motion changed, on collision with solvent molecules.

A reaction in solution between two reactants, A and B, can be described by a model involving three processes. In the first, the reactants diffuse towards one another (rate constant, k_d). When they encounter one another they form AB, called an *encounter complex*, and stay together for $\sim 10^{-10} \text{ s}$, trapped in a *solvent cage*. The separation of A and B by leaving the solvent cage is described by a rate constant k_{-d} . Alternatively, the encounter complex can react, to form the products, with a rate constant k_r . The overall mechanism is



The individual steps can be treated as elementary reactions, and the steady state approximation can be applied to AB, since it is so short-lived. (Section 9.6)

- (a) What is the order of each of the three steps in the mechanism and what are the units of the rate constants for each step?
- (b) Show that the rate of forming the products is given by

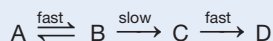
$$\text{rate of reaction} = \frac{k_d k_r}{k_{-d} + k_r} [\text{A}][\text{B}]$$

and write down an expression for the overall rate constant, k .

- (c) Simplify this expression for a case in which:
- reaction to form the products is much faster than diffusion of A and B from the solvent cage;
 - diffusion of A and B from the solvent cage is much faster than reaction to form the products.

In each case, state which is the rate-determining step.

- 20 An exothermic reaction proceeds by the following three-step mechanism



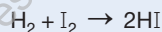
The first step occurs rapidly and a pre-equilibrium is established. The second step is slow and is the rate-determining step. (Section 9.8)

- Draw the shape of the Gibbs energy profile for the reaction.
 - How would the Gibbs energy profile differ if the third step were the rate-determining step of the reaction?
- 21 After intravenous injection of a drug to treat hypertension (high blood pressure), the blood plasma of the patient was analysed for the remaining drug at various times after the injection. (Section 9.5)

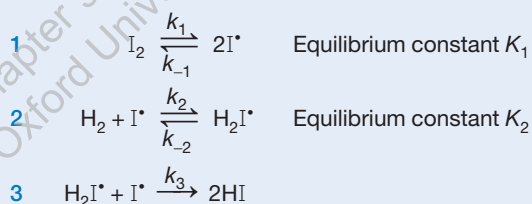
t/min	50	100	150	200	250	300	400	500
[drug]/ $10^{-9} \text{ g cm}^{-3}$	650	445	304	208	142	97	45	21

- Is the removal of the drug in the body a first or a second order process?
- Calculate the rate constant, k , and the half life, $t_{1/2}$, for the process.
- An essential part of drug development is achieving an optimum value of $t_{1/2}$ for effective operation and elimination of the drug from the bloodstream. What would be the possible problems if $t_{1/2}$ were too short or too long?

- 22* The reaction between hydrogen and iodine is a complex reaction.



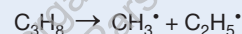
Kinetics experiments show that the reaction is first order with respect to H_2 and first order with respect to I_2 . The following mechanism has been proposed



where each step is an elementary reaction. Reaction 3 is the rate-determining step and both reactions 1 and 2 form pre-equilibria. (Section 9.6)

- Assuming reaction 1 is at equilibrium, obtain an expression for $[\text{I}^*]$ in terms of $[\text{I}_2]$ and the rate constants k_1 and k_{-1} .
- Assuming reaction 2 is at equilibrium, obtain an expression for $[\text{H}_2\text{I}^*]$ in terms of $[\text{H}_2]$, $[\text{I}^*]$, and the rate constants k_2 and k_{-2} .
- Write down the rate equation for reaction 3 and substitute in this the expressions for $[\text{I}^*]$ and $[\text{H}_2\text{I}^*]$ you obtained in (a) and (b).
- Compare the rate equation you have derived from the reaction mechanism with that found experimentally and write an expression for the rate constant, k , for the overall reaction.

- 23* The dissociation of propane in which a C–C bond breaks to form a methyl radical and an ethyl radical is a *unimolecular* reaction.

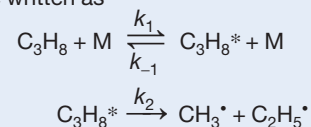


The rate of formation of CH_3^* (and of C_2H_5^*) is given by

$$\frac{d[\text{CH}_3^*]}{dt} = k_{\text{overall}}[\text{C}_3\text{H}_8], \text{ where } k_{\text{overall}} \text{ is the unimolecular rate constant for the reaction. (Sections 9.6 and 9.8)}$$

- Explain what is meant by the term '*unimolecular*'.

The propane molecules obtain sufficient energy to dissociate by colliding with other molecules, M, where M may be an unreactive gas such as nitrogen. The mechanism for this process can be written as



where C_3H_8^* is a propane molecule in a high energy state, which has sufficient energy to dissociate.

- By applying the steady state approximation to C_3H_8^* , derive an expression for $[\text{C}_3\text{H}_8^*]$. Since the rate of formation of CH_3^* is equal to $k_2[\text{C}_3\text{H}_8^*]$, show that

$$k_{\text{overall}} = \frac{k_1 k_2 [\text{M}]}{k_{-1} [\text{M}] + k_2}$$

- Show that:
 - when $[\text{M}]$ is very large, $k_{\text{overall}} \approx \frac{k_1 k_2}{k_{-1}}$
 - when $[\text{M}]$ is very small, $k_{\text{overall}} \approx k_1 [\text{M}]$
- What are the rate-determining stages in the mechanism under each of the conditions in (c)(i) and (c)(ii)? Sketch a graph to show the dependence of k_{overall} on $[\text{M}]$.
- It is always better to find a linear expression to analyse experimental data. Show that

$$\frac{1}{k_{\text{overall}}} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1 [\text{M}]}$$

A plot of $1/k_{\text{overall}}$ (y -axis) against $1/[\text{M}]$ (x -axis) is a straight line. What are the gradient and the intercept on the y -axis at $1/[\text{M}] = 0$?

24 At *low substrate concentrations*, the initial rate of an enzyme-catalysed reaction was found to be directly proportional to the initial substrate concentration, $[S]_0$, and directly proportional to the initial enzyme concentration, $[E]_0$. (Section 9.9)

- (a) Outline the series of experiments that led to these results.
- (b) Write a rate equation for the reaction under these conditions and explain the observed kinetics in terms of the mechanism for the reaction. What is the rate-determining step under these conditions?

At *much higher substrate concentrations*, the initial rate was found to be constant and independent of the initial substrate concentrations. The initial enzyme concentration was the same in each experiment.

- (c) Write a rate equation for the reaction under these conditions and explain the observed kinetics in terms of the mechanism for the reaction. What is the rate-determining step under these conditions?

Chapter 9 from Burrows, Andrew et al. Chemistry³: Introducing inorganic, organic and physical chemistry
2nd Edition. Oxford University Press, Oxford. © Andrew Burrows, John Holman, Andrew Parsons, Gwen Pilling, Gareth Price 2013