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The rates of chemical reactions

This chapter is the first of a sequence that explores the rates of chemical reactions. The chapter begins with a discussion of the definition of reaction rate and outlines the techniques for its measurement. The results of such measurements show that reaction rates depend on the concentration of reactants (and products) in characteristic ways that can be expressed in terms of differential equations known as rate laws. The solutions of these equations are used to predict the concentrations of species at any time after the start of the reaction. The form of the rate law also provides insight into the series of elementary steps by which a reaction takes place. The key task in this connection is the construction of a rate law from a proposed mechanism and its comparison with experiment. Simple elementary steps have simple rate laws, and these rate laws can be combined together by invoking one or more approximations. These approximations include the concept of the rate-determining stage of a reaction, the steady-state concentration of a reaction intermediate, and the existence of a pre-equilibrium. We go on to consider examples of reaction mechanisms, focusing on polymerization reactions and photochemistry, in which reactions are initiated by light.

This chapter introduces the principles of **chemical kinetics**, the study of reaction rates, by showing how the rates of reactions may be measured and interpreted. The remaining chapters of this part of the text then develop this material in more detail and apply it to more complicated or more specialized cases. The rate of a chemical reaction might depend on variables under our control, such as the pressure, the temperature, and the presence of a catalyst, and we may be able to optimize the rate by the appropriate choice of conditions. The study of reaction rates also leads to an understanding of the **mechanisms** of reactions, their analysis into a sequence of elementary steps.

Empirical chemical kinetics

The first steps in the kinetic analysis of reactions are to establish the stoichiometry of the reaction and identify any side reactions. The basic data of chemical kinetics are then the concentrations of the reactants and products at different times after a reaction has been initiated. The rates of most chemical reactions are sensitive to the temperature, so in conventional experiments the temperature of the reaction mixture must be held constant throughout the course of the reaction. This requirement puts severe demands on the design of an experiment. Gas-phase reactions, for instance, are often carried out in a vessel held in contact with a substantial block of metal. Liquid-phase reactions, including flow reactions, must be carried out in an efficient thermostat. Special efforts have to be made to study reactions at low temperatures, as in the study of the kinds of reactions that take place in interstellar clouds. Thus, supersonic expansion of the reaction gas can be used to attain temperatures as low as 10 K. For work in the liquid phase and the solid phase, very low temperatures are often reached by flowing cold liquid or cold gas around the reaction vessel. Alternatively, the entire reaction vessel is immersed in a thermally insulated container filled with a cryogenic liquid, such as liquid helium (for work at around 4 K) or liquid nitrogen (for work at around 77 K). Non-isothermal conditions are sometimes employed. For instance, the shelf-life of an expensive pharmaceutical may be explored by slowly raising the temperature of a single sample.

Experimental techniques

Key points **(a) The rates of chemical reactions are measured by using techniques that monitor the concentrations of species present in the reaction mixture. (b) Examples of experimental techniques include real-time and quenching procedures, flow and stopped-flow techniques, and flash photolysis.**

The method used to monitor concentrations depends on the species involved and the rapidity with which their concentrations change. Many reactions reach equilibrium over periods of minutes or hours, and several techniques may then be used to follow the changing concentrations.

(a) Monitoring the progress of a reaction

A reaction in which at least one component is a gas might result in an overall change in pressure in a system of constant volume, so its progress may be followed by recording the variation of pressure with time.

Example *Monitoring the variation in pressure*

Predict how the total pressure varies during the gas-phase decomposition $2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$ in a constant-volume container.

Method The total pressure (at constant volume and temperature and assuming perfect gas behaviour) is proportional to the number of gas-phase molecules. Therefore, because each mole of N_2O_5 gives rise to $\frac{5}{2}$ mol of gas molecules, we can expect the pressure to rise to $\frac{5}{2}$ times its initial value. To confirm this conclusion, express the progress of the reaction in terms of the fraction, α, of N_2O_5 molecules that have reacted.

Answer Let the initial pressure be p_0 and the initial amount of N_2O_5 molecules present be n. When a fraction α of the N_2O_5 molecules has decomposed, the amounts of the components in the reaction mixture are:

	N_2O_5	NO_2	O_2	Total
Amount:	$n(1-\alpha)$	$2\alpha n$	$\frac{1}{2}\alpha n$	$n(1+\frac{3}{2}\alpha)$

When $\alpha = 0$ the pressure is p_0, so at any stage the total pressure is

$$p = (1+\tfrac{3}{2}\alpha)p_0$$

When the reaction is complete, the pressure will have risen to $\frac{5}{2}$ times its initial value.

Self-test 21.1 Repeat the calculation for $2\,NOBr(g) \rightarrow 2\,NO(g) + Br_2(g)$.

$[p = (1+\frac{1}{2}\alpha)p_0]$

The rates of reactions

Key points **(a) The instantaneous rate of a reaction is the slope of the tangent to the graph of concentration against time (expressed as a positive quantity). (b) A rate law is an expression for the reaction rate in terms of the concentrations of the species that occur in the overall chemical reaction. (c) For a rate law of the form $v = k_r[A]^a[B]^b \ldots$, the rate constant is k_r, the order with respect to A is a, and the overall order is $a + b + \cdots$. (d) The isolation method and the method of initial rates are often used in the determination of rate laws.**

Reaction rates depend on the composition and the temperature of the reaction mixture. The next few sections look at these observations in more detail.

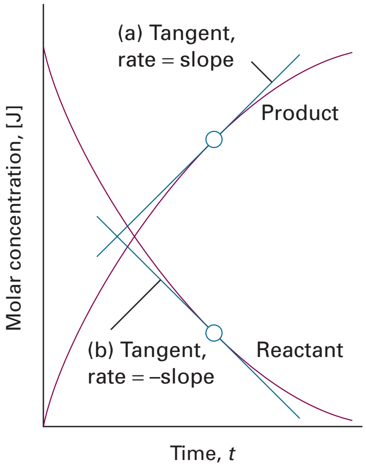

Fig. 21.4 The definition of (instantaneous) rate as the slope of the tangent drawn to the curve showing the variation of concentration with time. For negative slopes, the sign is changed when reporting the rate, so all reaction rates are positive.

(a) The definition of rate

Consider a reaction of the form $A + 2\,B \rightarrow 3\,C + D$, in which at some instant the molar concentration of a participant J is [J] and the volume of the system is constant. The instantaneous **rate of consumption** of one of the reactants at a given time is $-d[R]/dt$, where R is A or B. This rate is a positive quantity (Fig. 21.4). The **rate of formation** of one of the products (C or D, which we denote P) is $d[P]/dt$ (note the difference in sign). This rate is also positive.

It follows from the stoichiometry for the reaction $A + 2\,B \rightarrow 3\,C + D$ that

$$\frac{d[D]}{dt} = \tfrac{1}{3}\frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\tfrac{1}{2}\frac{d[B]}{dt}$$

so the rate of the reaction is related to the rates of change of concentration of products and reactants in several ways. The undesirability of having different rates to describe the same reaction is avoided by using the extent of reaction, ξ (xi, the quantity introduced in Section 6.1a):

$$\xi = \frac{n_J - n_{J,0}}{\nu_J} \qquad [21.1]$$

Definition of the extent of reaction

where ν_J is the stoichiometric number of species J, and defining the unique **rate of reaction**, v, as the rate of change of the extent of reaction:

$$v = \frac{1}{V}\frac{d\xi}{dt} \qquad [21.2]$$

Definition of the rate of reaction

where V is the volume of the system. It follows that

$$v = \frac{1}{\nu_J} \times \frac{1}{V}\frac{dn_J}{dt} \qquad (21.3a)$$

(Remember that ν_J is negative for reactants and positive for products.) For a homogeneous reaction in a constant-volume system the volume V can be taken inside the differential and we use $[J] = n_J/V$ to write

$$v = \frac{1}{\nu_J}\frac{d[J]}{dt} \qquad (21.3b)$$

For a heterogeneous reaction, we use the (constant) surface area, A, occupied by the species in place of V and use $\sigma_J = n_J/A$ to write

$$v = \frac{1}{\nu_J}\frac{d\sigma_J}{dt} \qquad (21.3c)$$

In each case there is now a single rate for the entire reaction (for the chemical equation as written). With molar concentrations in moles per cubic decimetre and time in seconds, reaction rates of homogeneous reactions are reported in moles per cubic decimetre per second ($\text{mol dm}^{-3}\,\text{s}^{-1}$) or related units. For gas-phase reactions, such as those taking place in the atmosphere, concentrations are often expressed in molecules per cubic centimetre (molecules cm^{-3}) and rates in molecules per cubic centimetre per second ($\text{molecules cm}^{-3}\,\text{s}^{-1}$). For heterogeneous reactions, rates are expressed in moles per square metre per second ($\text{mol m}^{-2}\,\text{s}^{-1}$) or related units.

• A brief illustration

If the rate of formation of NO in the reaction $2\,\text{NOBr(g)} \rightarrow 2\,\text{NO(g)} + \text{Br}_2\text{(g)}$ is reported as $0.16\ \text{mmol dm}^{-3}\,\text{s}^{-1}$, we use $\nu_{\text{NO}} = +2$ to report that $v = 0.080\ \text{mmol dm}^{-3}\,\text{s}^{-1}$. Because $\nu_{\text{NOBr}} = -2$ it follows that $\text{d[NOBr]}/\text{d}t = -0.16\ \text{mmol dm}^{-3}\,\text{s}^{-1}$. The rate of consumption of NOBr is therefore $0.16\ \text{mmol dm}^{-3}\,\text{s}^{-1}$, or $9.6 \times 10^{16}\ \text{molecules cm}^{-3}\,\text{s}^{-1}$. •

Self-test 21.2 The rate of change of molar concentration of CH_3 radicals in the reaction $2\,\text{CH}_3\text{(g)} \rightarrow \text{CH}_3\text{CH}_3\text{(g)}$ was reported as $\text{d[CH}_3\text{]}/\text{d}t = -1.2\ \text{mol dm}^{-3}\,\text{s}^{-1}$ under particular conditions. What is (a) the rate of reaction and (b) the rate of formation of CH_3CH_3? [(a) $0.60\ \text{mol dm}^{-3}\,\text{s}^{-1}$, (b) $0.60\ \text{mol dm}^{-3}\,\text{s}^{-1}$]

(b) Rate laws and rate constants

The rate of reaction is often found to be proportional to the concentrations of the reactants raised to a power. For example, the rate of a reaction may be proportional to the molar concentrations of two reactants A and B, so we write

$$v = k_\text{r}[\text{A}][\text{B}] \tag{21.4}$$

with each concentration raised to the first power. The coefficient k_r is called the **rate constant** for the reaction. The rate constant is independent of the concentrations but depends on the temperature. An experimentally determined equation of this kind is called the **rate law** of the reaction. More formally, a rate law is an equation that expresses the rate of reaction as a function of the concentrations of all the species present in the overall chemical equation for the reaction at some time:

$$v = f([\text{A}],[\text{B}],\ldots) \qquad [21.5\text{a}]$$

Definition of the rate law in terms of the concentration

For homogeneous gas-phase reactions, it is often more convenient to express the rate law in terms of partial pressures. In this case, we write

$$v = f(p_\text{A},p_\text{B},\ldots) \qquad [21.5\text{b}]$$

Definition of the rate law in terms of the pressure

The units of k_r are always such as to convert the product of concentrations into a rate expressed as a change in concentration divided by time. For example, if the rate law is the one shown in eqn 21.4, with concentrations expressed in mol dm^{-3}, then the units of k_r will be $\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ because

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

In gas-phase studies, including studies of the processes taking place in the atmosphere, concentrations are commonly expressed in molecules cm^{-3}, so the rate constant for the reaction above would be expressed in $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. We can use the approach just developed to determine the units of the rate constant from rate laws of any form. For example, the rate constant for a reaction with rate law of the form $k_r[\mathrm{A}]$ is commonly expressed in $\mathrm{s^{-1}}$.

- **A brief illustration**

The rate constant for the reaction $\mathrm{O(g) + O_3(g) \rightarrow 2\,O_2(g)}$ is $8.0 \times 10^{-15}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 298 K. To express this rate constant in $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$, we make use of

$$1\ \mathrm{cm} = 10^{-2}\ \mathrm{m} = 10^{-2} \times 10\ \mathrm{dm} = 10^{-1}\ \mathrm{dm}$$

$$1\ \mathrm{mol} = 6.022 \times 10^{23}\ \text{molecules, so } 1\ \text{molecule} = \frac{1\ \mathrm{mol}}{6.022 \times 10^{23}}$$

It follows that

$$\begin{aligned} k_r &= 8.0 \times 10^{-15}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \\ &= 8.0 \times 10^{-15}\ (10^{-1}\ \mathrm{dm})^3 \left(\frac{1\ \mathrm{mol}}{6.022 \times 10^{23}}\right)^{-1} \mathrm{s^{-1}} \\ &= 8.0 \times 10^{-15} \times 10^{-3} \times 6.022 \times 10^{23}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \\ &= 4.8 \times 10^{6}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \end{aligned}$$ ●

Self-test 21.3 A reaction has a rate law of the form $k_r[\mathrm{A}]^2[\mathrm{B}]$. What are the units of the rate constant if the reaction rate is measured in $\mathrm{mol\ dm^{-3}\ s^{-1}}$?

[$\mathrm{dm^6\ mol^{-2}\ s^{-1}}$]

The rate law of a reaction is determined experimentally, and cannot in general be inferred from the stoichiometry of the balanced chemical equation for the reaction. The reaction of hydrogen and bromine, for example, has a very simple stoichiometry, $\mathrm{H_2(g) + Br_2(g) \rightarrow 2\,HBr(g)}$, but its rate law is complicated:

$$v = \frac{k_a[\mathrm{H_2}][\mathrm{Br_2}]^{3/2}}{[\mathrm{Br_2}] + k_b[\mathrm{HBr}]} \tag{21.6}$$

In certain cases the rate law does reflect the stoichiometry of the reaction, but that is either a coincidence or reflects a feature of the underlying reaction mechanism.

A practical application of a rate law is that, once we know the law and the value of the rate constant, we can predict the rate of reaction from the composition of the mixture. Moreover, as we shall see later, by knowing the rate law, we can go on to predict the composition of the reaction mixture at a later stage of the reaction. A rate law is also a guide to the mechanism of the reaction, for any proposed mechanism must be consistent with the observed rate law.

(c) Reaction order

Many reactions are found to have rate laws of the form

$$v = k_r[\mathrm{A}]^a[\mathrm{B}]^b \cdots \tag{21.7}$$

The power to which the concentration of a species (a product or a reactant) is raised in a rate law of this kind is the **order** of the reaction with respect to that species. A reaction with the rate law in eqn 21.4 is **first-order** in A and first-order in B. The **overall order** of a reaction with a rate law like that in eqn 21.7 is the sum of the individual orders, $a + b + \cdots$. The rate law in eqn 21.4 is therefore second-order overall.

A reaction need not have an integral order, and many gas-phase reactions do not. For example, a reaction having the rate law

$$v = k[\mathrm{A}]^{1/2}[\mathrm{B}] \tag{21.8}$$

is half-order in A, first-order in B, and three-halves-order overall. Some reactions obey a **zero-order rate law**, and therefore have a rate that is independent of the concentration of the reactant (so long as some is present). Thus, the catalytic decomposition of phosphine (PH_3) on hot tungsten at high pressures has the rate law

$$v = k_{\mathrm{r}} \tag{21.9}$$

The PH_3 decomposes at a constant rate until it has almost entirely disappeared. Zero-order reactions typically occur when there is a bottle-neck of some kind in the mechanism, as in heterogeneous reactions when the surface is saturated regardless of how much reactant remains. Zero-order reactions are also found for a number of enzyme reactions when there is a large excess of reactant relative to the enzyme, and the amount of enzyme present governs the rate, not the amount of reactant.

When a rate law is not of the form in eqn 21.7, the reaction does not have an overall order and may not even have definite orders with respect to each participant. Thus, although eqn 21.6 shows that the reaction of hydrogen and bromine is first-order in H_2, the reaction has an indefinite order with respect to both Br_2 and HBr and has no overall order.

These remarks point to three important questions:

- How do we identify the rate law and obtain the rate constant from the experimental data? We concentrate on this aspect in this chapter.
- How do we construct reaction mechanisms that are consistent with the rate law? We shall develop the techniques of doing so in Sections 21.8–10 and in Chapter 23.
- How do we account for the values of the rate constants and their temperature dependence? We shall see a little of what is involved in this chapter, but leave the details until Chapter 22.

(d) The determination of the rate law

The determination of a rate law is simplified by the **isolation method** in which the concentrations of all the reactants except one are in large excess. If B is in large excess, for example, then to a good approximation its concentration is constant throughout the reaction. Although the true rate law might be $v = k_{\mathrm{r}}[\mathrm{A}][\mathrm{B}]$, we can approximate [B] by $[\mathrm{B}]_0$, its initial value, and write

$$v = k_{\mathrm{r}}'[\mathrm{A}] \qquad k_{\mathrm{r}}' = k_{\mathrm{r}}[\mathrm{B}]_0 \tag{21.10}$$

which has the form of a first-order rate law. Because the true rate law has been forced into first-order form by assuming that the concentration of B is constant, eqn 21.10 is called a **pseudofirst-order rate law**. The dependence of the rate on the concentration of each of the reactants may be found by isolating them in turn (by having all the other substances present in large excess), and so constructing a picture of the overall rate law.

In the **method of initial rates**, which is often used in conjunction with the isolation method, the rate is measured at the beginning of the reaction for several different initial concentrations of reactants. We shall suppose that the rate law for a reaction with A isolated is $v = k_{\mathrm{r}}'[\mathrm{A}]^a$; then its initial rate, v_0, is given by the initial values of the concentration of A, and we write $v_0 = k_{\mathrm{r}}'[\mathrm{A}]_0^a$. Taking (common) logarithms gives:

$$\log v_0 = \log k_{\mathrm{r}}' + a \log[\mathrm{A}]_0 \tag{21.11}$$

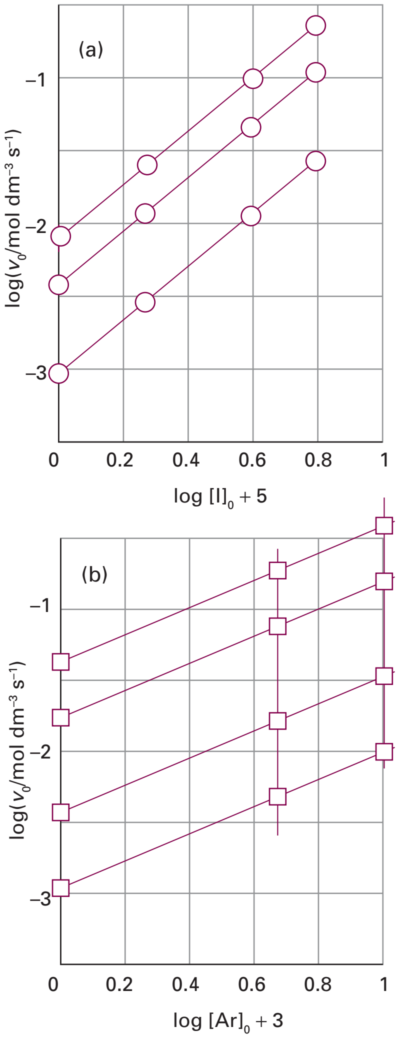

Fig. 21.5 The plot of log v_0 against (a) log$[\text{I}]_0$ for a given $[\text{Ar}]_0$, and (b) log$[\text{Ar}]_0$ for a given $[\text{I}]_0$.

A note on good practice The units of k_r come automatically from the calculation, and are always such as to convert the product of concentrations to a rate in concentration/time (for example, mol dm^{-3} s^{-1}).

For a series of initial concentrations, a plot of the logarithms of the initial rates against the logarithms of the initial concentrations of A should be a straight line with slope *a*.

Example 21.2 *Using the method of initial rates*

The recombination of iodine atoms in the gas phase in the presence of argon was investigated and the order of the reaction was determined by the method of initial rates. The initial rates of reaction of $2\,\text{I(g)} + \text{Ar(g)} \rightarrow \text{I}_2\text{(g)} + \text{Ar(g)}$ were as follows:

$[\text{I}]_0/(10^{-5}\ \text{mol dm}^{-3})$		1.0	2.0	4.0	6.0
$v_0/(\text{mol dm}^{-3}\ \text{s}^{-1})$	(a)	8.70×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}
	(b)	4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
	(c)	8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}

The Ar concentrations are (a) 1.0 mmol dm^{-3}, (b) 5.0 mmol dm^{-3}, and (c) 10.0 mmol dm^{-3}. Determine the orders of reaction with respect to the I and Ar atom concentrations and the rate constant.

Method Plot the logarithm of the initial rate, log v_0, against log$[\text{I}]_0$ for a given concentration of Ar, and, separately, against log$[\text{Ar}]_0$ for a given concentration of I. The slopes of the two lines are the orders of reaction with respect to I and Ar, respectively. The intercepts with the vertical axis give log k_r' and, by using eqn 21.10, k_r.

Answer The plots are shown in Fig. 21.5. The slopes are 2 and 1, respectively, so the (initial) rate law is $v_0 = k_r[\text{I}]_0^2[\text{Ar}]_0$. This rate law signifies that the reaction is second-order in [I], first-order in [Ar], and third-order overall. The intercept corresponds to $k_r = 9 \times 10^9$ mol^{-2} dm^6 s^{-1}.

Self-test 21.4 The initial rate of a reaction depended on concentration of a substance J as follows:

$[\text{J}]_0/(\text{mmol dm}^{-3})$	5.0	8.2	17	30
$v_0/(10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1})$	3.6	9.6	41	130

Determine the order of the reaction with respect to J and calculate the rate constant.
[2, 1.4×10^{-2} dm^3 mol^{-1} s^{-1}]

The method of initial rates might not reveal the full rate law, for once the products have been generated they might participate in the reaction and affect its rate. For example, products participate in the synthesis of HBr, because eqn 21.6 shows that the full rate law depends on the concentration of HBr. To avoid this difficulty, the rate law should be fitted to the data throughout the reaction. The fitting may be done, in simple cases at least, by using a proposed rate law to predict the concentration of any component at any time, and comparing it with the data. A law should also be tested by observing whether the addition of products or, for gas-phase reactions, a change in the surface-to-volume ratio in the reaction chamber affects the rate.

Integrated rate laws

Key points **An integrated rate law is an expression for the concentration of a reactant or product as a function of time. The half-life $t_{1/2}$ of a reaction is the time it takes for the concentration of a species to fall to half its initial value. The time constant τ is the time required for the concentration of a reactant to fall to 1/e of its initial value.**

Because rate laws are differential equations, we must integrate them if we want to find the concentrations as a function of time. Even the most complex rate laws may be integrated numerically. However, in a number of simple cases analytical solutions, known as **integrated rate laws**, are easily obtained, and prove to be very useful. We examine a few of these simple cases here.

(a) First-order reactions

As shown in the following *Justification*, the integrated form of the first-order rate law

$$\frac{d[A]}{dt} = -k_r[A] \qquad (21.12a)$$

is

$$\ln\left(\frac{[A]}{[A]_0}\right) = -k_r t \qquad [A] = [A]_0 e^{-k_r t} \qquad (21.12b)$$

Integrated first-order rate law

where $[A]_0$ is the initial concentration of A (at $t = 0$).

Justification 21.1 *First-order integrated rate law*

First, we rearrange eqn 21.12a into

$$\frac{d[A]}{[A]} = -k_r dt$$

This expression can be integrated directly because k_r is a constant independent of t. Initially (at $t = 0$) the concentration of A is $[A]_0$, and at a later time t it is [A], so we make these values the limits of the integrals and write

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

Because the integral of $1/x$ is ln x, eqn 21.12b is obtained immediately.

Equation 21.12b shows that, if $\ln([A]/[A]_0)$ is plotted against t, then a first-order reaction will give a straight line of slope $-k_r$. Some rate constants determined in this way are given in Table 21.1. The second expression in eqn 21.12b shows that in a first-order reaction the reactant concentration decreases exponentially with time with a rate determined by k_r (Fig. 21.6).

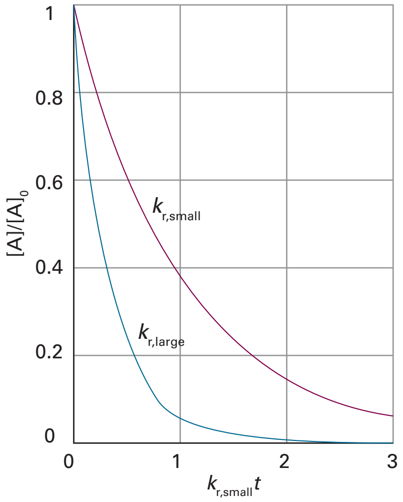

Fig. 21.6 The exponential decay of the reactant in a first-order reaction. The larger the rate constant, the more rapid the decay: here $k_{r,large} = 3k_{r,small}$.

interActivity For a first-order reaction of the form $A \rightarrow nB$ (with n possibly fractional), the concentration of the product varies with time as $[B] = n[B]_0(1 - e^{-k_r t})$. Plot the time dependence of [A] and [B] for the cases $n = 0.5$, 1, and 2.

Table 21.1* Kinetic data for first-order reactions

Reaction	Phase	θ/°C	k_r/s^{-1}	$t_{1/2}$
$2\,N_2O_5 \rightarrow 4\,NO_2 + O_2$	g	25	3.38×10^{-5}	5.70 h
	Br_2(l)	25	4.27×10^{-5}	4.51 h
$C_2H_6 \rightarrow 2\,CH_3$	g	700	5.36×10^{-4}	21.6 min

* More values are given in the *Data section*.

Fig. 21.7 The determination of the rate constant of a first-order reaction: a straight line is obtained when $\ln[A]/[A]_0$ (or, as here, $\ln p/p_0$) is plotted against t; the slope gives k_r.

A note on good practice Because the horizontal and vertical axes of graphs are labelled with pure numbers, the slope of a graph is always dimensionless. For a graph of the form $y = b + mx$ we can write $y = b + (m \text{ units})(x/\text{units})$, where 'units' are the units of x, and identify the (dimensionless) slope with 'm units'. Then $m = \text{slope/units}$. In the present case, because the graph shown here is a plot of $\ln(p/p_0)$ against t/s (with 'units' = s) and k_r is the negative value of the slope of $\ln(p/p_0)$ against t itself, $k_r = -\text{slope/s}$.

Example 21.3 *Analysing a first-order reaction*

The variation in the partial pressure of azomethane with time was followed at 600 K, with the results given below. Confirm that the decomposition

$$CH_3N_2CH_3(g) \rightarrow CH_3CH_3(g) + N_2(g)$$

is first-order in azomethane, and find the rate constant at 600 K.

t/s	0	1000	2000	3000	4000
p/Pa	10.9	7.63	5.32	3.71	2.59

Method As indicated in the text, to confirm that a reaction is first-order, plot $\ln([A]/[A]_0)$ against time and expect a straight line. Because the partial pressure of a gas is proportional to its concentration (provided it can be treated as a perfect gas), an equivalent procedure is to plot $\ln(p/p_0)$ against t. If a straight line is obtained, its slope can be identified with k_r.

Answer We draw up the following table:

t/s	0	1000	2000	3000	4000
$\ln(p/p_0)$	0	−0.357	−0.717	−1.078	−1.437

Figure 21.7 shows the plot of $\ln(p/p_0)$ against t. The plot is straight, confirming a first-order reaction, and its slope is -3.6×10^{-4}. Therefore, $k_r = 3.6 \times 10^{-4}\ \text{s}^{-1}$.

Self-test 21.5 In a particular experiment, it was found that the concentration of N_2O_5 in liquid bromine varied with time as follows:

t/s	0	200	400	600	1000
$[N_2O_5]/(\text{mol dm}^{-3})$	0.110	0.073	0.048	0.032	0.014

Confirm that the reaction is first-order in N_2O_5 and determine the rate constant.

$[k_r = 2.1 \times 10^{-3}\ \text{s}^{-1}]$

(b) Half-lives and time constants

A useful indication of the rate of a first-order chemical reaction is the **half-life**, $t_{1/2}$, of a substance, the time taken for the concentration of a reactant to fall to half its initial value. The time for [A] to decrease from $[A]_0$ to $\tfrac{1}{2}[A]_0$ in a first-order reaction is given by eqn 21.12b as

$$k_r t_{1/2} = -\ln\left(\frac{\tfrac{1}{2}[A]_0}{[A]_0}\right) = -\ln \tfrac{1}{2} = \ln 2$$

Hence

$$t_{1/2} = \frac{\ln 2}{k_r} \qquad \boxed{\text{Half-life of a first-order reaction}} \qquad (21.13)$$

(Note that ln 2 = 0.693.) The main point to note about this result is that, for a first-order reaction, the half-life of a reactant is independent of its initial concentration. Therefore, if the concentration of A at some *arbitrary* stage of the reaction is [A], then it will have fallen to $\tfrac{1}{2}[A]$ after a further interval of $(\ln 2)/k_r$. Some half-lives are given in Table 21.1.

Another indication of the rate of a first-order reaction is the **time constant**, τ (tau), the time required for the concentration of a reactant to fall to 1/e of its initial value. From eqn 21.12b it follows that

$$k_r\tau = -\ln\left(\frac{[A]_0/e}{[A]_0}\right) = -\ln\frac{1}{e} = 1$$

That is, the time constant of a first-order reaction is the reciprocal of the rate constant:

$$\tau = \frac{1}{k_r} \qquad (21.14)$$

Time constant of a first-order reaction

(c) Second-order reactions

We show in the following *Justification* that the integrated form of the second-order rate law

$$\frac{d[A]}{dt} = -k_r[A]^2 \qquad (21.15a)$$

is either of the following two forms:

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k_r t \qquad (21.15b)$$

Integrated second-order rate law

$$[A] = \frac{[A]_0}{1 + k_r t[A]_0} \qquad (21.15c)$$

Alternative form of the integrated rate law

where $[A]_0$ is the initial concentration of A (at $t = 0$).

Justification 21.2 *Second-order integrated rate law*

To integrate eqn 21.15a we rearrange it into

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

The concentration of A is $[A_0]$ at $t = 0$ and $[A]$ at a general time t later. Therefore,

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

Because the integral of $1/x^2$ is $-1/x$, we obtain eqn 21.15b by substitution of the limits

$$\left.\frac{1}{[A]}\right|_{[A]_0}^{[A]} = \frac{1}{[A]} - \frac{1}{[A]_0} = k_r t$$

We can then rearrange this expression into eqn 21.15c.

Equation 21.15b shows that to test for a second-order reaction we should plot $1/[A]$ against t and expect a straight line. The slope of the graph is k_r. Some rate constants determined in this way are given in Table 21.2. The rearranged form, eqn 21.15c, lets us predict the concentration of A at any time after the start of the reaction. It shows that the concentration of A approaches zero more slowly than in a first-order reaction with the same initial rate (Fig. 21.8).

It follows from eqn 21.15b by substituting $t = t_{1/2}$ and $[A] = \frac{1}{2}[A]_0$ that the half-life of a species A that is consumed in a second-order reaction is

$$t_{1/2} = \frac{1}{k_r[A]_0} \qquad (21.16)$$

Half-life of a second-order reaction

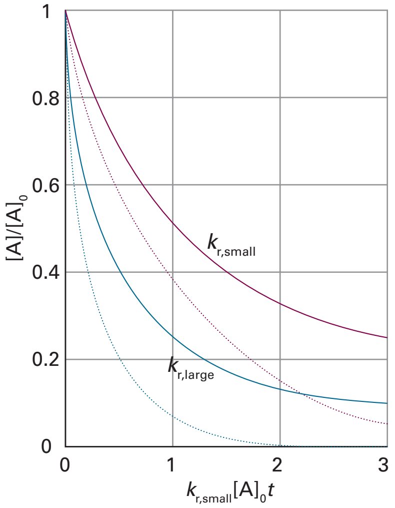

Fig. 21.8 The variation with time of the concentration of a reactant in a second-order reaction. The grey lines are the corresponding decays in a first-order reaction with the same initial rate. For this illustration, $k_{r,large} = 3k_{r,small}$.

interActivity For a second-order reaction of the form $A \rightarrow nB$ (with n possibly fractional), the concentration of the product varies with time as $[B] = nk_r t[A]_0^2/(1 + k_r t[A]_0)$. Plot the time dependence of [A] and [B] for the cases $n = 0.5$, 1, and 2.

Table 21.2* Kinetic data for second-order reactions

Reaction	Phase	$\theta/°\mathrm{C}$	$k_r/(\mathrm{dm^3\ mol^{-1}\ s^{-1}})$
$2\,\mathrm{NOBr} \rightarrow 2\,\mathrm{NO} + \mathrm{Br_2}$	g	10	0.80
$2\,\mathrm{I} \rightarrow \mathrm{I_2}$	g	23	7×10^9
$\mathrm{CH_3Cl} + \mathrm{CH_3O^-}$	$\mathrm{CH_3OH(l)}$	20	2.29×10^{-6}

* More values are given in the *Data section*.

Therefore, unlike a first-order reaction, the half-life of a substance in a second-order reaction varies with the initial concentration. A practical consequence of this dependence is that species that decay by second-order reactions (which includes some environmentally harmful substances) may persist in low concentrations for long periods because their half-lives are long when their concentrations are low. In general, for an *n*th-order reaction (with $n > 1$) of the form A → products, the half-life is related to the rate constant and the initial concentration of A by

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k_r[\mathrm{A}]_0^{n-1}} \tag{21.17}$$

Half-life of an *n*th-order reaction

(See Problem 21.22.)

Another type of second-order reaction is one that is first-order in each of two reactants A and B:

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_r[\mathrm{A}][\mathrm{B}] \tag{21.18}$$

Such a rate law cannot be integrated until we know how the concentration of B is related to that of A. For example, if the reaction is $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{P}$, where P denotes products, and the initial concentrations are $[\mathrm{A}]_0$ and $[\mathrm{B}]_0$, then it is shown in the following *Justification* that, at a time *t* after the start of the reaction, the concentrations satisfy the relation

$$\ln\left(\frac{[\mathrm{B}]/[\mathrm{B}]_0}{[\mathrm{A}]/[\mathrm{A}]_0}\right) = ([\mathrm{B}]_0 - [\mathrm{A}]_0)k_r t \tag{21.19}$$

Integrated rate law of a second-order reaction of the type $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{P}$

Therefore, a plot of the expression on the left against *t* should be a straight line from which k_r can be obtained.

Justification 21.3 *Overall second-order rate law*

It follows from the reaction stoichiometry that, when the concentration of A has fallen to $[\mathrm{A}]_0 - x$, the concentration of B will have fallen to $[\mathrm{B}]_0 - x$ (because each A that disappears entails the disappearance of one B). It follows that

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_r([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x)$$

Because $[\mathrm{A}] = [\mathrm{A}]_0 - x$, it follows that $\mathrm{d}[\mathrm{A}]/\mathrm{d}t = -\mathrm{d}x/\mathrm{d}t$ and the rate law may be written as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_r([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x)$$

The initial condition is that $x=0$ when $t=0$; so the integration required is

$$\int_0^x \frac{\mathrm{d}x}{([\mathrm{A}]_0-x)([\mathrm{B}]_0-x)}=k_{\mathrm{r}}\int_0^t \mathrm{d}t$$

The integral on the right is simply $k_{\mathrm{r}}t$. The integral on the left is evaluated by using the method of partial fractions in which we write

$$\frac{1}{(a-x)(b-x)}=\frac{1}{b-a}\left(\frac{1}{a-x}-\frac{1}{b-x}\right)$$

It follows that

$$\int \frac{\mathrm{d}x}{(a-x)(b-x)}=\frac{1}{b-a}\left[\int\frac{\mathrm{d}x}{a-x}-\int\frac{\mathrm{d}x}{b-x}\right]=\frac{1}{b-a}\left[\ln\frac{1}{a-x}-\ln\frac{1}{b-x}\right]+\text{constant}$$

and therefore that

$$\int_0^x \frac{\mathrm{d}x}{([\mathrm{A}]_0-x)([\mathrm{B}]_0-x)}=\frac{1}{[\mathrm{B}]_0-[\mathrm{A}]_0}\left\{\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]_0-x}\right)-\ln\left(\frac{[\mathrm{B}]_0}{[\mathrm{B}]_0-x}\right)\right\}$$

This expression can be simplified and rearranged into eqn 21.19 by combining the two logarithms by using $\ln y-\ln z=\ln(y/z)$ and noting that $[\mathrm{A}]=[\mathrm{A}]_0-x$ and $[\mathrm{B}]=[\mathrm{B}]_0-x$. Similar calculations may be carried out to find the integrated rate laws for other orders, and some are listed in Table 21.3.

Table 21.3 Integrated rate laws

Order	Reaction	Rate law*	$t_{1/2}$
0	$\mathrm{A}\rightarrow\mathrm{P}$	$v=k_{\mathrm{r}}$ $k_{\mathrm{r}}t=x$ for $0\le x\le[\mathrm{A}]_0$	$[\mathrm{A}]_0/2k_{\mathrm{r}}$
1	$\mathrm{A}\rightarrow\mathrm{P}$	$v=k_{\mathrm{r}}[\mathrm{A}]$ $k_{\mathrm{r}}t=\ln\dfrac{[\mathrm{A}]_0}{[\mathrm{A}]_0-x}$	$(\ln 2)/k_{\mathrm{r}}$
2	$\mathrm{A}\rightarrow\mathrm{P}$	$v=k_{\mathrm{r}}[\mathrm{A}]^2$ $k_{\mathrm{r}}t=\dfrac{x}{[\mathrm{A}]_0([\mathrm{A}]_0-x)}$	$1/k_{\mathrm{r}}[\mathrm{A}]_0$
	$\mathrm{A}+\mathrm{B}\rightarrow\mathrm{P}$	$v=k_{\mathrm{r}}[\mathrm{A}][\mathrm{B}]$ $k_{\mathrm{r}}t=\dfrac{1}{[\mathrm{B}]_0-[\mathrm{A}]_0}\ln\dfrac{[\mathrm{A}]_0([\mathrm{B}]_0-x)}{([\mathrm{A}]_0-x)[\mathrm{B}]_0}$	
	$\mathrm{A}+2\,\mathrm{B}\rightarrow\mathrm{P}$	$v=k_{\mathrm{r}}[\mathrm{A}][\mathrm{B}]$ $k_{\mathrm{r}}t=\dfrac{1}{[\mathrm{B}]_0-2[\mathrm{A}]_0}\ln\dfrac{[\mathrm{A}]_0([\mathrm{B}]_0-2x)}{([\mathrm{A}]_0-x)[\mathrm{B}]_0}$	
	$\mathrm{A}\rightarrow\mathrm{P}$ with autocatalysis	$v=k_{\mathrm{r}}[\mathrm{A}][\mathrm{P}]$ $k_{\mathrm{r}}t=\dfrac{1}{[\mathrm{A}]_0+[\mathrm{P}]_0}\ln\dfrac{[\mathrm{A}]_0([\mathrm{P}]_0+x)}{([\mathrm{A}]_0-x)[\mathrm{P}]_0}$	
3	$\mathrm{A}+2\,\mathrm{B}\rightarrow\mathrm{P}$	$v=k_{\mathrm{r}}[\mathrm{A}][\mathrm{B}]^2$ $k_{\mathrm{r}}t=\dfrac{2x}{(2[\mathrm{A}]_0-[\mathrm{B}]_0)([\mathrm{B}]_0-2x)[\mathrm{B}]_0}$ $+\dfrac{1}{(2[\mathrm{A}]_0-[\mathrm{B}]_0)^2}\ln\dfrac{[\mathrm{A}]_0([\mathrm{B}]_0-2x)}{([\mathrm{A}]_0-x)[\mathrm{B}]_0}$	
$n\ge 2$	$\mathrm{A}\rightarrow\mathrm{P}$	$v=k_{\mathrm{r}}[\mathrm{A}]^n$ $k_{\mathrm{r}}t=\dfrac{1}{n-1}\left\{\dfrac{1}{([\mathrm{A}]_0-x)^{n-1}}-\dfrac{1}{[\mathrm{A}]_0^{n-1}}\right\}$	$\dfrac{2^{n-1}-1}{(n-1)k_{\mathrm{r}}[\mathrm{A}]_0^{n-1}}$

* $x=[\mathrm{P}]$ and $v=\mathrm{d}x/\mathrm{d}t$.