1 Time, concentration, and temperature

1.1 Introduction

The study of chemical kinetics is a fundamental part of chemistry. Chemistry is the study of reactions, therefore determinations of the rate at which these reactions occur (kinetics) are of central importance. The results of kinetic studies (i.e., rates of reactions and rate coefficients) give information which can be applied in different ways.

1. Many important phenomena, such as combustion or stratospheric ozone depletion, involve many reaction steps. Determination of the rate of each step is necessary if we are to understand these processes fully. The practical advantages of such knowledge would be significant, e.g., developing more efficient combustion processes or reducing ozone depletion.

2. Recent developments in experimental techniques (see Chapter 2) have allowed detailed studies of elementary reaction rates. The variation of such rates with temperature or pressure can give microscopic insights into the molecular mechanisms of these reactions. Chemical kinetics therefore provides a wealth of information which is of both practical and fundamental interest. These are just two of the reasons why the field is so interesting and the subject of so much recent study.

The bread and butter of chemical kinetics is the measurement of the rates of chemical reactions. The subject started, as a quantitative field of study, in 1850 when Wilhelmy showed that the rate of hydrolysis of sucrose to form glucose and fructose:

\[ \text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6 \]  

depends on the first power of the sucrose concentration. He was able to follow the conversion by observing, with a polarimeter, the change in rotation of the plane of polarization of light as it passed through the reaction solution, sucrose being dextrorotatory. The hydrolysis, under the conditions he employed, takes the best part of a working day and, not having a thermostatted bath, he had to note the variation in temperature throughout the day and make small corrections to the observed rate.

Rate measurements were restricted to comparatively slow reactions, although not so slow as reaction (1), until the middle of this century, when a variety of experimental techniques were developed which enabled reactions of increasingly labile species to be studied on ever decreasing timescales. More recently, kineticists have been able to take advantage of advances in fast electronics, lasers, and sensitive detection techniques, while microcomputer controlled experiments have greatly facilitated accurate data acquisition.

Figure 1.1 shows the decrease in concentration with time of methyl radicals, resulting from the combination reaction:

\[ \text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6 \]
which is of importance in flame, combustion and pyrolysis chemistry. The methyl radicals were produced by photolyzing propane with a pulsed laser and their concentration measured by observing the absorption spectrum of CH₃ as a function of time. Analysis of the data demonstrates that, in this case, the rate of reaction depends on the square of the methyl radical concentration. The timescale of this reaction (several milliseconds) is short, but modestly so—it is now possible to study reactions on timescales of less than 10⁻¹⁹ s.

In this chapter we shall discuss the more phenomenological side of reaction kinetics, i.e. the way in which reaction rates depend on concentration and temperature, and how rate coefficients are defined and measured. Finally, we shall examine how rate coefficients for forward and reverse reactions are related via the equilibrium constant for the reaction and the general relationship between kinetic and thermodynamic parameters such as enthalpy and entropy. In later chapters we shall discuss the theoretical interpretation of rate coefficients, but it is as well to remember that, at least for the present, reaction kinetics is firmly based on experimental measurement.

1.2 Reaction order

The rate of reaction (2) may be defined as \(-\frac{d[CH₃]}{dt}\), i.e. as the rate of decrease of the methyl radical concentration with time, where the square brackets denote concentration and \(t\) is time. Experiments show that the rate is proportional to the square of the methyl radical concentration, or

\[-d[CH₃]/dt = k₂[CH₃]²\]  
(E 1)

where the constant of proportionality, \(k₂\), is the rate coefficient. This latter term is also known as the rate constant, but as we shall see this so-called constant varies with temperature and sometimes pressure, and hence we shall use the former term. In Wilhelmy's experiment the rate was directly proportional to the sucrose concentration so:

\[-d[CH₃H₂O₁₁]/dt = k₃[CH₃H₂O₁₁]\]  
(E 2)

These equations can be generalized, so that, for a reaction \(A + B \rightarrow \text{Products}\), we may write a rate law in the form:

\[-d[a]/dt = kₐb^b\]  
(E 3)

where \(a\) and \(b\) are the concentrations of the reactants A and B. The exponents, \(a\) and \(b\), which are determined experimentally, are termed the orders of the reaction with respect to A and B. The overall order of the reaction is equal to the sum of \(a\) and \(b\). For example, for reaction (3)

\[H₂ + I₂ \rightarrow 2HI\]  
(R 3)

it is found that the reaction is first order in hydrogen and in iodine and hence second order overall. It must be stressed at this stage that the order of a reaction is not necessarily related to the stoichiometry of the chemical reaction. It is possible for a species which is not consumed in the reaction to occur in the rate law (see Box 1.2) and conversely a reaction may display zeroth-order kinetics in one of the reactants (i.e. it may have a rate which is independent of the concentration of that reactant). A familiar example is the iodination of propanone, which is first order in propanone and hydrogen ions, but zeroth in iodine.

\[I₂ + H⁺ + CH₃COCH₃ \rightarrow CH₃COCH₂H + HI + H⁺\]  
(R 4)

\[-d[I₂]/dt = k₄[H⁺][CH₃COCH₃].\]  
(E 4)

Neither is it necessary for the order of a reaction to be integral. For example, the \(H₂ + Br₂\) reaction is first order in hydrogen but of order one-half in \(Br₂\). Experimental observations of this type provide important clues to the mechanisms of such reactions.

1.3 Molecularity

We ought, at this stage, to distinguish between elementary and multi-step reactions. Hydrogen atoms react with bromine molecules

\[H + Br₂ \rightarrow HBr + Br\]  
(R 5)

by forming a collision complex \(H-Br-Br\); the two reactants collide and stay together for a very short period of time, before rearranging to form the products. The molecularity of the reaction is determined by the number of species involved in forming the collision complex. For reaction (5) this is two and hence the reaction is termed \textit{bimolecular}. As we shall see in Chapter 5, the thermal dissociation of azomethane,

\[CH₃N₂CH₃ \rightarrow 2CH₃ + N₂\]  
(R 6)

entails the acquisition by a reactant molecule of sufficient thermal energy to enable it to fall apart. The process of molecular rearrangement starts to occur in a single molecule and the reaction is termed \textit{unimolecular}.

The distinction between order and molecularity is important. The order of a reaction is based directly on experimental observations of the dependence of the reaction rate on concentration. It is an empirical quantity and in itself says nothing about the mechanism of the reaction, although it may give some clues. The molecularity is deduced from experimental determinations of reaction order, but
depends on the proposal of a consistent mechanism. Thus, experiments show that the CH$_3$ + HCH$_2$ reaction is second order in methyl radicals. Provided the experiments have been conducted accurately, this assertion is incontrovertible. When the reaction is overall second order, we might infer that it involves the coming together of two reactant molecules. This remains an inference, and may be questioned. For example, the decomposition of dinitrogen pentoxide is first order in N$_2$O$_5$; from this we might presume that the reaction is unimolecular and proceeds via a mechanism similar to that described for the decomposition of azomethane. However, we would be wrong! Additional experiments have shown that the reaction involves several steps which combine to give a rate that depends linearly on [N$_2$O$_5$].

A great many important reactions have multi-step mechanisms. We have already alluded to the ionization of propene, in which the enol is formed in a slow step involving the protonation of the ketone to form the enol,

\[
\text{H}^+ + \text{CH}_3\text{C} = \text{CH}_2 \rightarrow \text{H}^+ \text{C} = \text{C} = \text{O} + \text{CH}_3 \text{H} \tag{R 7}
\]

followed by rapid attack by I$_2$ on the enol;

\[
\text{H}^+ \text{C} = \text{C} = \text{O} + I_2 \rightarrow \text{CH}_3\text{C} = \text{C} = \text{O} + \text{CH}_3 \text{H} \tag{R 8}
\]

The overall rate of the reaction is governed by the slow step, which explains why the rate equation contains the first power of the propanone and H$^+$ concentrations, but is independent of [I$_2$]. In Chapter 8 we shall discuss multi-step reactions examining the idea of a rate-determining step, such as the first step discussed above and also spend some time on the important class of chain reactions (Chapter 9). The latter contain several repeating steps, an example being the H$_2$ + Br$_2$ reaction. All of these complex reactions are made up of component elementary reactions (such as (R 5)), which may be ascribed both an order and a molecularity. The overall complex reaction has an experimentally determinable order but strictly speaking no molecularity. Sometimes it is assigned a molecularity corresponding to that of its rate-determining step as with the famous SN$_1$ reaction.

It should be apparent by now that the rate equation of a reaction may be totally unrelated to its stoichiometric equation. An example is the ionization of propene discussed above. The H$_2$ + Br$_2$ reaction looks particularly simple on the basis of its stoichiometry,

\[
\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr} \tag{R 9}
\]

but its order is non-integral (rate $\propto$$[\text{H}_2][\text{Br}_2]^2$) which tells us that appearances can be deceptive. Non-integral orders are a sure sign that a reaction has a multi-step mechanism, but as we have noted in the case of N$_2$O$_5$, an integral order is no guarantee that a reaction is elementary.

Many multi-step reactions involve the reaction of labile species such as atoms, radicals or energetically excited species. The advent of laser based experiments has allowed the isolation and study of many of these elementary reactions. Once the component elementary reactions have been determined the overall reaction can be simulated using a computer model (Chapter 8) and the results compared with experiments. Such studies have taken much of the guess work out of elucidating complex mechanisms and, because the elementary steps involve only a small number of species (generally 1–5), the experimental results often give great insight as to exactly how the molecules interact on a molecular level.

1.4 Determination of reaction orders and rate coefficients

In Chapter 2 we shall discuss experimental methods for studying the rates of chemical reactions. It will be helpful, however, if we first examine how the order and rate coefficient can be determined from the data such experiments provide. The data are normally in the form of something that is related to concentration of reactants or products (for example, conductivity) versus time. Several alternative methods may be used to analyze the data and we shall first discuss them individually before making comparisons between them.

1.4.1 Integral method

For a first-order reaction, such as the thermal decomposition of azomethane, the rate law can be written in the following way:

\[
A \rightarrow \text{Products}
\]

\[
-\frac{da}{dt} = -k \tag{E 5}
\]

integrating, we find (see question 1.3):

\[
\ln(a/a_0) = kt \tag{E 6}
\]

where $a_0$ is the concentration of A at time $t = 0$. Similar equations may be derived for reactions of other orders and some of these are shown in Table 1.1. These equations are valid for like reactants (e.g., A + A), or for stoichiometrically equivalent reactants (e.g., A + B) with equal initial concentrations. When the initial molar concentrations are not the same, or when the reactants are not stoichiometrically equivalent (e.g., A + 2B), more complex expressions are required, and two of the more common ones are shown in Table 1.2.

When we measure the reactant concentration as a function of time, the data should fit an expression of the type shown in the third column of Table 1.1, provided the order is integral. If we think the reaction may be first order, we plot ln(a) vs. t, and expect to get a straight line of gradient $-k$. If we think it is second order we plot $(1/a)$ against time and so on.
Table 1.1 Differential and integral forms of rate equations

<table>
<thead>
<tr>
<th>Order</th>
<th>da/dt</th>
<th>$kt$</th>
<th>Units of $k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$-k$</td>
<td>$(a_0 - a)$</td>
<td>mol dm$^{-3}$ s$^{-1}$</td>
</tr>
<tr>
<td>1</td>
<td>$-ka$</td>
<td>$ln(a_0/a)$</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>2</td>
<td>$-ka^2$</td>
<td>$(1/a) - (1/a_0)$</td>
<td>dm$^3$ mol$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>3</td>
<td>$-ka^3$</td>
<td>$(1/2a^2) - (1/3a_0^2)$</td>
<td>dm$^6$ mol$^{-2}$ s$^{-1}$</td>
</tr>
</tbody>
</table>

Table 1.2 Integrated rate laws for more complex situations

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Order</th>
<th>da/dt</th>
<th>$kt$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A + B → P 2</td>
<td>$-kab$</td>
<td>$\frac{1}{(b_0 - b)}ln\left(\frac{b_0}{b}</td>
<td></td>
</tr>
</tbody>
</table><p>ight)$ | |
| A + 2B → P 3 | $-kab^2$ | $\frac{b_0^2 - b^2}{ab_0^2(b_0^2 + b^2)} + \left(\frac{1}{2b_0^2} - \frac{1}{2b_0^2}ight)^2 ln\left(\frac{b_0^2}{b^2}ight)$ | |</p>

Box 1.1 Dimensions and units of the rate coefficient

The dimensions of the rate coefficient will depend on the order or molecularity of the reaction. The rate of the reaction always has units of concentration time$^{-1}$. Apart from first-order reactions they will always be a function of concentration and time (first-order rate coefficients have the dimensions time$^{-1}$). The dimensions can always be determined from a dimensional analysis of the rate equation. For example for a third-order reaction:

$$-\frac{da}{dt} \propto a^3$$

Dimensions: concentration time$^{-3} \propto$ concentration$^3$

To turn the above relationship into an equation the dimensions on both sides of the equation must be equal and therefore the dimensions of $k$ for a third-order reaction are: concentration$^2$ time$^{-3}$. Therefore:

$$-\frac{da}{dt} = ka^3$$

Dimensions: concentration$^{-1}$ time$^{-1}$ concentration$^2$ time$^{-3}$ concentration$^3$ time$^{-1}$ concentration$^{-3}$

The units of $k$ will depend on the units of concentration and time (usually seconds or minutes). In this book we shall usually use mol dm$^{-3}$ and seconds respectively for these quantities giving units of dm$^3$ mol$^{-1}$ s$^{-1}$ for our third-order rate coefficient, but often you will come across different units for concentration in the literature. Gas phase kinetics often use units of molecule cm$^{-3}$ s$^{-1}$ for concentration and the units of cm, mm, or mbar; which strictly speaking are units of pressure (remember pressure and concentration are directly linked for gases), can also be encountered. Appendix 1 contains conversion factors for a number of common units.

Example 1.1

In the decomposition of azomethane (R 6) at a pressure of 2.18 $\times$ 10$^5$ Pa and a temperature of 578 K, the following time dependent azomethane concentrations were recorded:

<table>
<thead>
<tr>
<th>t/minutes</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
<th>150</th>
<th>180</th>
</tr>
</thead>
<tbody>
<tr>
<td>[azomethane]/10$^9$ mol dm$^{-3}$</td>
<td>8.70</td>
<td>6.52</td>
<td>4.89</td>
<td>3.67</td>
<td>2.75</td>
<td>2.06</td>
<td>1.55</td>
</tr>
</tbody>
</table>

Show that the reaction is first order in azomethane and determine the rate coefficient at this temperature.

We use the integrated expression given in Table 1.1 and plot ln[azomethane] vs. time.

<table>
<thead>
<tr>
<th>t/minutes</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
<th>150</th>
<th>180</th>
</tr>
</thead>
<tbody>
<tr>
<td>ln [azomethane]/10$^9$ mol dm$^{-3}$</td>
<td>2.16</td>
<td>1.90</td>
<td>1.55</td>
<td>1.29</td>
<td>1.07</td>
<td>0.64</td>
<td>0.46</td>
</tr>
</tbody>
</table>

The plot, shown in Fig. 1.2, is a good straight line confirming the first-order kinetics. The slope ($= -9.6 \times 10^{-3}$ min$^{-1}$) is equal to $-k$, so that the rate coefficient is: $k_2 = 1.58 \times 10^{-4}$ s$^{-1}$. We may show that zeroth- or second-order kinetics do not apply by plotting $[A]$ and $1/[A]$ vs. time, where $[A] = [azomethane]$. These plots are shown in Figs 1.3 and 1.4 and clearly demonstrate substantial curvature.

Fig. 1.2 Plot of ln[azomethane] vs. time. The straight line indicates that the reaction is first order with respect to azomethane and the gradient of the line is $-k$.

Fig. 1.3 Plot of [azomethane] vs. time. Significant curvature is observed showing that, as expected, the reaction is not zeroth order with respect to azomethane. These half-lives for the reaction are shown. For a first order decay $t_h$ should be independent of initial concentration on the decay curve.
1.4.2 Isolation Method

When more than one reactant is involved the integrated rate equation becomes more complex. A common way of simplifying the situation is to arrange for all the reagents except one, say $A$, to be present in such great excess that their concentrations can be regarded as effectively constant during the course of the reaction. In practice this generally means that their initial concentrations should be at least 10 times (and hence would have fallen by 10 per cent to $k_0$ for a 1:1 stoichiometric reaction by the end of the reaction) and preferably 100 times or greater, although this may be difficult for technical reasons, such as solubility.

Under these conditions the order with respect to $A$ may be determined by applying the integral equations of Table 1.1. For example:

$$A + B \rightarrow \text{Products}$$

$$-\frac{d[A]}{dt} = k' \beta \theta^\beta = k' \theta$$

(E 7)

$$k' = k_0 \beta$$

(E 8)

and $k_0$ is the concentration of $B$ which is assumed to remain constant, $\beta$, the order with respect to $B$ may then be found by varying $k_0$, since a plot of $k'$ against $\log k_0$ should give a straight line of gradient $\beta$.

Example 1.2.

The flash photolysis (see Chapter 2) of iodine vapour in a large excess of argon produces iodine atoms, which then recombine according to the reaction:

$$1 + I + Ar \rightarrow I_2 + Ar.$$  

(R 10)

The role played by $Ar$ is discussed briefly in Box 1.2 and more fully in Chapter 6. For the present we examine simply its effect on the rate equation. The rate of reaction may be determined by measuring $[I_2]$ as a function of time at several different argon pressures. In each case the iodine concentration before the flash was $1 \times 10^{-5}$ mol dm$^{-3}$.

$$t/10^{-3}\text{ s} \quad 2 \quad 4 \quad 6 \quad 8 \quad 10$$

$[I_2]/10^{-8}$ mol dm$^{-3}$

| $I_2$/10$^{-8}$ mol dm$^{-3}$ | 8.46 | 8.70 | 8.90 | 9.05 | 9.15 | $[Ar] = 2.0 \times 10^{-3}$ mol dm$^{-3}$
|-----------------------------|------|------|------|------|------|-------------------|
| $I_2$/10$^{-8}$ mol dm$^{-3}$ | 8.53 | 8.96 | 9.19 | 9.34 | 9.44 | $[Ar] = 4.0 \times 10^{-3}$ mol dm$^{-3}$
|-----------------------------|------|------|------|------|------|-------------------|
| $I_2$/10$^{-8}$ mol dm$^{-3}$ | 8.77 | 9.19 | 9.39 | 9.52 | 9.60 | $[Ar] = 6.0 \times 10^{-3}$ mol dm$^{-3}$

Note that the timescale for this reaction is in milliseconds, flash photolysis allows for the study of reactions at these and at much shorter timescales. The concentration of argon atoms is very much greater than that of iodine and, in any case, $Ar$ is not consumed in the reaction so that we are justified in using the isolation method, since $[Ar]$ is not disturbed by reaction.

From the stoichiometry of the reaction, $[I_2] = 2([I_2]_0 - [I_2])$, where $[I_2]_0$ is the molecular iodine concentration before the flash and also, since all the iodine atoms must eventually recombine, the molecular iodine concentration at long times after the flash. Since $[Ar]$ is constant, we evaluate $[I]$ and use the integral expressions shown in Table 1.1. for the second-order case. Figure 1.5 shows second-order plots, whose linearity demonstrates that the reaction is second order in $I$.

$$-\frac{d[I]}{dt} = k'[I]^2.$$ 

(E 9)

The slope of the plots give $k'$, which clearly depend on $[Ar]$, as expected from the relationship $k' = k_{10} [Ar]^{\beta}$.

$[Ar]/10^{-3}$ mol dm$^{-3}$

| $[Ar]$/$10^{-3}$ mol dm$^{-3}$ | 2.0 | 4.0 | 6.0 | $k' = 10^2$ dm$^3$ mol$^{-1}$ s$^{-1}$
|-----------------------------|------|------|------|-------------------|
| $k'/[Ar]$/$10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$ | 3.5 | 6.9 | 10.4 | $k'/[Ar]/10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$ | 1.75 | 1.73 | 1.73

Figure 1.6 shows a plot of $\log k'$ vs. $\log [Ar]$. Its unit slope demonstrates that $\alpha = 1$, i.e. that the order with respect to argon is one, and that overall the reaction is third order. The table confirms this conclusion, since $k'/[Ar]$ is constant, and also gives us a mean value for the third-order rate coefficient $k_{10}$.

14 Determination of reaction orders and rate coefficients

Fig. 1.4 Plot of $[I]$ (mol dm$^{-3}$) vs. time. Once again the graph is curved, showing that second order kinetics do not apply.

Fig. 1.5 Second-order plots for reaction (10) for varying initial argon pressure. The straight lines confer second-order kinetics with respect to iodine.

Fig. 1.6 Plot of $\log k'$ vs. $\log [Ar]$. The straight line graph with unit slope shows that the reaction is first order with respect to argon.
There are two general points arising from this example, which warrant further comment. Firstly, the isolation method is not limited to use in conjunction with the integral method. It can also be used with the half-life and differential methods which are discussed below. Secondly, some ambiguity can arise in the definition of rate coefficients for elementary reactions which are second order in one of the reactants. Thus we may write:

\[ -\frac{d[N]}{dt} = k_{(2)}[N]^2[\text{Ar}] \]  

and

\[ \frac{d[I_2]}{dt} = k_{(2)}[I]^2[\text{Ar}] \]  

Since, by stoichiometry, \(-\frac{d[I]}{dt} = 2 \frac{d[I_2]}{dt}\) (two iodine atoms are removed for every iodine molecule produced), it follows that \(k_{(2)} = 2k_{(1)}\). It is therefore necessary when quoting the rate coefficient for iodine atom recombination to state clearly whether one is referring to \(k_{(1)}\) or \(k_{(2)}\). Kineticists generally (but not always!) use the convention associated with \(k_{(2)}\), so that

\[ -\frac{d[I]}{dt} = 2k_{(2)}[I]^2[\text{Ar}] \]  

and this is the form that we shall adopt throughout the rest of this book. To be consistent, therefore, we should revise our rate coefficient in Example 1.2 to 6.7 \times 10^6 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}.

**Box 1.2 Pressure dependent reactions.**

Energy is released when chemical bonds are formed. When the two iodine atoms combine to form an iodine molecule, energy equal to the bond dissociation energy of \(I_2\), is released into the iodine molecule. The energy, corresponding to all the reaction exothermicity, is contained within the \(I-I\) bond, which will rupture, reforming the reactant iodine atoms. However, if some of the reaction exothermicity can be removed from a newly formed iodine molecule it will no longer have enough energy to dissociate. The molecule is stabilized. Collisions with the argon bath gas are one way in which energy can be removed and the molecule stabilized. During the collision some of the rotational and vibrational energy of the iodine molecule is transferred to translational excitation of the argon atom.

Therefore once the molecule is formed, two processes can occur: reassociation or stabilization.

\[ I + I \rightarrow I_2 \rightarrow I + I \]  

where \(I_2\) represents the nascent \(I_2\) molecule and \(M\) the ‘third body’; argon.

The rate of stabilization is dependent on the collision frequency with the argon bath gas, which is in turn related to the pressure of argon. As the pressure rises, stabilization becomes increasingly competitive with reassociation (the rate of which is pressure independent) and hence the rate of formation of \(I_2\) increases with the pressure of bath gas.

**1.4.3 Half-life method**

The half-life of a reaction \(\tau_L\) is the time taken for 50 per cent of the reactant \(\theta\) to be consumed and hence \(\tau_L\) may be found by substituting \(x = \frac{a_0}{2}\) in column three of Table 1.1 and equating this to \(k_{(2)}\). For a first-order reaction:

\[ \ln \left( \frac{a_0}{2} \right) = -\frac{k\tau_L}{a_0} \]  

therefore,

\[ \tau_L = \ln 2/k \]  

The resulting expressions for integral orders and for a general order \(x\) are shown in Table 1.3. Note that the half-life is always inversely proportional to \(k\) and its dependence on \(a_0\) is determined by the order of the reaction. These relationships may therefore by used to determine both the order of a reaction and its rate coefficient. There are two possible methods.

1. We can follow a reaction over several half-lives and examine the dependence of the sequence of half-lives on the concentration at the start of that half-life period.

2. Several experiments can be performed, each with a different initial concentration and the first half-life for each experiment determined.

These two methods are demonstrated in Examples 1.3 and 1.4.

**Table 1.3 Half-life expressions**

<table>
<thead>
<tr>
<th>Reaction Order</th>
<th>(\tau_L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(a_0/(2k))</td>
</tr>
<tr>
<td>1</td>
<td>((\ln 2)/k)</td>
</tr>
<tr>
<td>2</td>
<td>(1/(2ka_0))</td>
</tr>
<tr>
<td>3</td>
<td>(3/(2ka_0^2))</td>
</tr>
<tr>
<td>(x)</td>
<td>(2^{-x-1} - 1) (a_0^{-1}k_{(2)}^{-1})</td>
</tr>
</tbody>
</table>

**Example 1.3**

We apply the first method to the decomposition of azomethane (R8). Figure 1.3 (which we used to demonstrate that the reaction is not zeroth order in azomethane) shows a plot of [azomethane] vs. \(t\) and three half-lives are indicated. The following data can be obtained on three half-lives of the reaction:

<table>
<thead>
<tr>
<th>Initial concentration/ (10^{-3} \text{mol dm}^{-3})</th>
<th>8.70</th>
<th>6.00</th>
<th>4.35</th>
</tr>
</thead>
<tbody>
<tr>
<td>Half-life/minutes</td>
<td>72</td>
<td>70</td>
<td>72</td>
</tr>
</tbody>
</table>

The half-lives are clearly independent of the concentration at the start of the relevant time period, as is required for a first-order reaction (Table 1.3). The mean half-life may be used to calculate \(k_{(2)}\).
\[ k_0 = \ln 2 / t_1 = \ln 2 / (71 \times 60) \]
\[ k_0 = 1.63 \times 10^{-4} \text{ s}^{-1} \]

In good agreement with the value obtained using the integral method.

Example 1.4

We showed in Fig. 1.1 the decay of methyl radicals as determined in a flash photolysis experiment. In this example, we determine the order and rate coefficient for the reaction from the measurement of half-lives.

\[
\begin{array}{cccc}
[\text{CH}_3\text{O}] & \text{mol dm}^{-3} & 2.0 & 5.0 & 10.0 & 20.0 \\
\tau_1 & \text{10}^{3} \text{s} & 80 & 35 & 16 & 7.5 \\
10^{10} \text{dm}^3 \text{mol}^{-1} / (2\text{[CH}_3\text{O]}\tau_1 & 3.1 & 2.9 & 3.1 & 3.3 \\
\end{array}
\]

Table 1.3 demonstrates that, except for a first-order reaction, \( \tau_1 \) is proportional to \( a_0^{1/2-1} \) so that a plot of \( \tau_1 \) vs. \( \log a_0 \) has a slope of \(-1/2\). Figure 1.7 shows the half-lives plotted in this way and the slope has a value of \(-0.95\) or approximately \(-1\). Hence the reaction order, \( x \), is 2. The rate coefficient may now be determined from the relevant expression in Table 1.3. We must remember though our convention since two radicals are removed in each elementary reaction. Thus,

\[ k_2 = 1 / (2[\text{CH}_3\text{O}]\tau_1) \]

The values of \( k_2 \) calculated for each datum point are shown in the above table; they agree reasonably well and give a mean rate coefficient of \( k_2 = 3.1 \times 10^{-10} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1} \).

Finally we note that the general relationship shown in Table 1.3 between \( \tau_1 \) and the order, \( x \), applies even if \( a \) is non-integral.

1.4.4 The differential method

Taking logs of the generalised rate law at time \( t = 0 \),

\[ \frac{\mathrm{d}a_0}{\mathrm{d}t} = k_0 a_0^x \ldots \quad (E \, 15) \]

gives:

\[ \log(\frac{\mathrm{d}a_0}{\mathrm{d}t}) = \log k + x \log a_0 + \beta \log b_0 + \ldots \quad (E \, 16) \]

By varying the values of \( a_0 \) (holding \( b_0 \) etc. constant) and measuring the initial rates, we can find the order, \( x \), with respect to A and by a similar method, this time varying \( b_0 \) only, \( \beta \) can be obtained.

So called initial rate methods can be useful in elucidating the mechanism of complex reactions, where the rate of reaction may be dependent on the concentration of the products (e.g. in the \( \text{H}_3\text{B} / \text{Br}_3 \) system described in Chapter 9 it is found that increasing concentrations of the product, \( \text{HBr} \), slows down the rate of reaction and alters the order with respect to bromine). At the start of the reaction the concentration of products will be extremely small and the effects of reactions involving the products will be negligible.

Alternatively, for a reaction rate given by

\[ -\frac{\mathrm{d}a}{\mathrm{d}t} = k a^x \quad (E \, 17) \]

\[ \log(\frac{\mathrm{d}a}{\mathrm{d}t}) = \log k + x \log a \quad (E \, 18) \]

Tangents to the concentration vs. time plot at various points along the graph give \( -\log(\frac{\mathrm{d}a}{\mathrm{d}t}) \). If these are plotted against the corresponding values of \( \log a \) then \( k \) and \( a \) can be calculated from the intercept and gradient respectively. This procedure is illustrated schematically in Fig. 1.8.

![Fig. 1.7 Plot of log k vs. log (initial methyl concentration). The gradient of the graph \((-0.95) = -(x-1)\) confirms the expected order of two with respect to methyl radical concentration.](attachment:image1.png)

![Fig. 1.8 (a) Estimates of the rate of reaction can be obtained by drawing tangents to the concentration vs. time graph. (b) A plot of the rates vs. the corresponding value of \( \log a \) gives a straight line plot with gradient \( x \). Note that the intercept with the \( y \) axis corresponds to \( \log k \) (see 1(E 18)).](attachment:image2.png)
Example 1.5
The initial rates of reaction between two organic bromides, X and Y, and hydroxide ions, were measured as a function of initial concentrations:

\[ [X]_0 \text{ mol dm}^{-3} = 2 \times 10^{-1} \quad 2 \times 10^{-1} \]
\[ [OH^-]_0 \text{ mol dm}^{-3} = 10^{-2} \quad 10^{-2} \]
\[ \text{Initial rate} / \text{dm}^3 \text{ mol}^{-3} \text{ s}^{-1} = 2.1 \times 10^{-5} \quad 4.2 \times 10^{-5} \quad 8.1 \times 10^{-6} \]
\[ [Y]_0 \text{ mol dm}^{-3} = 2 \times 10^{-3} \quad 4 \times 10^{-3} \quad 2 \times 10^{-3} \]
\[ [OH^-]_0 \text{ mol dm}^{-3} = 10^{-3} \quad 10^{-3} \quad 2 \times 10^{-3} \]
\[ \text{Initial rate} / \text{dm}^3 \text{ mol}^{-3} \text{ s}^{-1} = 1.5 \times 10^{-2} \quad 2.8 \times 10^{-2} \quad 1.4 \times 10^{-2} \]

For the first set of experimental data we shall calculate the orders with respect to the organic halide X and OH\(^{-}\). The reaction can be written as:

\[ X + OH^- \rightarrow \text{products} \]

therefore the generalized rate equation is:

\[ -d[X]/dt = R = k[X]^a[OH^-]^b \]

(E 19)

and the initial rate will be given by:

\[ -d[X]/dt = R_0 = k[X]_0^a[OH^-]_0^b \]

(E 20)

taking logs:

\[ \log(R_0) = \log k + a \log [X]_0 + b \log[OH^-]_0 \]

(E 21)

The results of the first two experiments allow us to formulate two simultaneous equations to solve for \(a\) and \(b\):

\[ \log(2.1 \times 10^{-5}) = \log k + a \log(0.2) + b \log(0.01) \]

\[ \log(4.2 \times 10^{-5}) = \log k + a \log(0.2) + b \log(0.01) \]

Subtracting these two equations gives:

\[ \log(4.2 \times 10^{-5}/2.1 \times 10^{-5}) = a \log(0.2/0.1) \]

and hence \(a = 1\). A similar analysis for the second and third experiments gives:

\[ \log(8.1 \times 10^{-6}/2.1 \times 10^{-6}) = b \log(0.02/0.01), \quad b = 0.95 \]

Within the expected errors for such an experiment we would predict that the order with respect to \([OH^-]\) was also one. Calculate the orders with respect to the organic halide \(Y\) and \(OH^-\) for the second set of data. (Orders with respect to \(Y\) and \(OH^-\) are 1 and 0).

1.5 A comparison of the techniques

In many cases use of the isolation method means that many reactions can be studied under pseudo-first order conditions, greatly easing the analysis. Two important points should be noted about first order kinetics:

1. With the integral method we do not need to know the absolute concentration of \(A\), but rather its relative value (or some quantity directly proportional to it). For many kinetic determinations, especially those occurring on short timescales, it is much more convenient to measure some property (conductivity, light absorption or fluorescence) that is proportional to concentration. Because we only require relative values we do not need to calibrate the apparatus to the absolute concentration, thus simplifying the experiment.

2. Once again, using the half-life technique we do not require absolute concentrations, as the half-life is independent of initial concentration for a first-order reaction. We shall return to, and illustrate these points in Chapter 2.

Generally we are interested in the magnitude of the rate coefficient and this is best extracted from an integrated plot. It is always worthwhile calculating 4 over a number of half-lives to check that there are no secondary reactions systematically affecting the data.

If, on the other hand, we are interested in the order of the reaction, this can be obtained in one plot using the differential method. However, a few notes of caution about the differential method:

1. The rate coefficient can only be found by extrapolation to an intercept, increasing the error in \(k\).

2. Determining tangents by eye from a concentration vs. time plot is generally subject to considerable uncertainty.

3. Merely following the initial rates can be an oversimplification if the rate of reaction is affected by the formation of products. While the rate coefficient and order obtained will be correct at times close to \(t = 0\), they may not be valid over the whole course of the reaction. A good example is the reaction of hydrogen and bromine to give hydrogen bromide (p. 223), a chain reaction.

\[ H_2 + Br_2 \rightarrow 2HBr \]  

(R 9)

\[ d[Br]/dt \propto [H_2][Br_2]^2 \]  

(E 22)

However, owing to the complex interaction of reactants and products the overall expression is (E 23):

\[ d[HBr]/dt \propto [H_2][Br_2]^2/[Br_2 + C[HBr]] \]  

(E 23)

where \(C\) is a constant and the term in [HBr] becomes more significant as reaction proceeds. Note the non integer order, typical of a chain mechanism (Chapter 9).

1.6 Dependence on temperature

Thus far, we have discussed the rates of chemical reactions and their dependence on concentration only. It is also found experimentally that the rate and, hence the rate coefficient, both depend on the temperature \((T)\) and that this dependence is often very strong. For the present we shall content ourselves with a phenomenological discussion.

It is found experimentally that the vast majority of reactions have rate coefficients that follow the relationship:

\[ k = A \exp(-E_{exp}/RT) \]  

(E 24)

where \(A\) is called the pre-exponential or \(A\) factor and \(E_{exp}\) is the activation energy. We have added the subscript \(exp\) to indicate that the latter is experimentally determined and defined. We see from this relationship that, provided
$E_{\text{exp}}$ is positive (which is generally the case), the rate coefficient increases with temperature, and that a straight line relationship can be obtained, and hence $A$ and $E_{\text{exp}}$ determined, by plotting in $k$ vs. $1/T$:

$$\ln k = \ln A - E_{\text{exp}}/RT.$$  \hspace{1cm} (E.25)

Table 1.4 gives activation energies for a few representative reactions and demonstrates the wide range of temperature dependencies.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Activation Energy/KJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$</td>
<td>183.0</td>
</tr>
<tr>
<td>$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$</td>
<td>157.0</td>
</tr>
<tr>
<td>$\text{CaCl}_2 + \text{H}_2\text{O} \rightarrow \text{CaCl}_2\text{OH} + \text{HCl}$</td>
<td>180.0</td>
</tr>
<tr>
<td>$\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$</td>
<td>19.5</td>
</tr>
<tr>
<td>$\text{Cl}_2 + \text{D}_2 \rightarrow \text{ClD} + \text{D}_2$</td>
<td>2.1</td>
</tr>
<tr>
<td>$\text{CH} + \text{CH}_4 \rightarrow \text{CH}_2\text{H}_4 + \text{H}$</td>
<td>-1.7</td>
</tr>
</tbody>
</table>

### Example 1.6

In Example 1.1 we determined the rate coefficient for aromatome decomposition at 576 K. Similar determinations over a range of temperatures allow us to calculate $A$ and $E_{\text{exp}}$:

- $T/K$: 523, 541, 560, 576, 593
- $k/s^{-1}$: $1.8 \times 10^{-6}$, $1.6 \times 10^{-9}$, $6.0 \times 10^{-5}$, $1.6 \times 10^{-4}$, $9.5 \times 10^{-4}$

We plot in $k$ vs. $1/T$ (Figure 1.9):

$$\ln (k/10^6 s^{-1}) = 0.59, 2.71, 4.09, 5.08, 6.86$$

We plot in $k$ vs. $1/T$ (Figure 1.9):

$$1/1000 K/T = 1.912, 1.848, 1.786, 1.736, 1.686$$

A linear least squares fit to the data gives a value of $2.6 \times 10^6 K^{-1}$ for $E_{\text{exp}}/R$ and hence an activation energy of $220$ KJ mol$^{-1}$, and returns a value of $2.0 \times 10^{-4} s^{-1}$ for $A$. If we have drawn the graph by eye, then instead of making the long extrapolation to $1/T = 0$, it is best to take a value from the line and use the calculated value $E_{\text{exp}}$ and eqn (24) to calculate $A$. E.g. at $1000 K/1.75 = 1.75$, in $k = -8.67$ (remember we have plotted $In(k/10^6 s^{-1})$, hence:

$$\ln A = -8.67 + 1.75 \times 26.0 = 36.83$$

$$A = 1.0 \times 10^5 s^{-1}.$$  

The temperature-dependent form of the rate coefficient, eqn (E.24) is called the Arrhenius equation after Svante Arrhenius, who published a paper in 1889 demonstrating that a wide range of reactions have temperature dependencies that conform to this equation. It arises because the reactants have to overcome an energy barrier (Fig. 1.10) when their valence electrons are rearranged as the products are formed. In Chapter 3 we shall examine, in some detail, theories of chemical kinetics which attempt to rationalize the Arrhenius equation. Arrhenius's paper followed one by van't Hoff, in which an equation compatible with (E.24) was proposed on the basis of the relationships between the equilibrium constants and the rate constants for the forward and reverse reactions. An interesting account of these developments may be found in articles by Logan and Laidler.

It is important to emphasize that the Arrhenius equation is an experimental observation that is only followed approximately over a finite temperature range. In the paragraph above we introduced some ideas as to what physical property at least one of the parameters might represent and we shall investigate the relationship between experimental observations of $A(T)$ (the rate coefficient as a function of temperature) and theories of bimolecular reactions in Chapter 3.

---

1.7 Thermodynamics and its relationship to kinetics

Equilibrium is dynamic with reaction proceeding in both forward and reverse directions, but with equal rates so that the equilibrium concentrations are maintained. Thus, for the isomerization equilibrium between cis and trans 3-phenylpropenonitrile:

$$\text{cis-C}_6\text{H}_5\text{CH}=\text{CHCN} \rightleftharpoons \text{trans-C}_6\text{H}_5\text{CH}=\text{CHCN}$$  \hspace{1cm} (R.11)

we have at equilibrium...
\[ \rho_f = \frac{k_i \langle \text{cis-C}_6\text{H}_5\text{CH}=\text{CHCN} \rangle_{\text{eq}}}{k_i \langle \text{trans-C}_6\text{H}_5\text{CH}=\text{CHCN} \rangle_{\text{eq}}} = 1 \]  
\[ \text{E 26} \]

where \( \rho_f \) and \( \rho_i \) are the rates of the forward and reverse reactions and the subscripts \( f \) and \( i \) refer to equilibrium. Therefore

\[ \frac{k_i}{k_f} = K_{11} \]  
\[ \text{E 28} \]

where \( K_{11} \) is the equilibrium constant.

Returning to reactive systems far from equilibrium, it sometimes turns out that a reaction rate is easier to measure in one direction than another. For example, the recombination of methyl radicals to form ethane (R 2)

\[ \text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6 \]  
\[ \text{R 2} \]

has been studied by flash photolysis over a wide range of temperatures and pressures. The reverse decomposition reaction is important in a variety of high temperature processes, such as combustion and there is considerable interest in the value of \( k_2 \). The decomposition rate has been measured, but it is difficult to make such measurements over a wide range of temperatures. We discussed above the relationship between the rate coefficients and the equilibrium constant at equilibrium; the rate coefficients are constant (at a given \( T \) and \( P \)) and do not change as equilibrium is approached. Therefore it is possible to use the measured value of \( k_2 \) and the equilibrium constant \( K_2 \) to calculate the value of the dissociation rate coefficient \( k_2 \).

\[ k_2 = k_f/k_i \]  
\[ \text{E 29} \]

However, we need to know \( K_2 \). Firstly we recall that rate coefficients generally have concentration units, so that \( K \) in equation (29) is \( K_2 \). Converting to \( K_2 \) (\( K_2 = K_f/k_i \langle \text{RT} \rangle^{-1} \)) and invoking the relationship between \( K_2 \) and \( \Delta G^\circ \) (\( \Delta G^\circ = -RT \ln K_2 \)) and \( \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \),

\[ \Delta H^\circ = \Delta H^\circ_f \exp(-\Delta S^\circ_f/RT) \exp(\Delta S^\circ_i/RT) \]  
\[ \text{E 31} \]

where \( \Delta H^\circ_f \) and \( \Delta S^\circ_f \) are the standard enthalpy and entropy of reaction at temperature \( T \):

\[ \Delta H^\circ_f = \Delta H^\circ_f (\text{C}_2\text{H}_6) - 2\Delta H^\circ_f (\text{CH}_3) \]  
\[ \text{E 32} \]

\[ \Delta S^\circ_f = \Delta S^\circ_f (\text{C}_2\text{H}_6) - 2\Delta S^\circ_f (\text{CH}_3) \]  
\[ \text{E 33} \]

where \( \Delta H^\circ_f \) and \( \Delta S^\circ_f \) are the molar standard enthalpy of formation and the molar third law entropy of the respective species at temperature \( T \). These quantities are well known for stable compounds such as ethane, but what about radicals, for which we cannot use standard experimental thermochemical techniques?\text{CH}_3 is spectroscopically well characterized, so that its geometry and vibrational frequencies are known and the techniques of statistical mechanics may be used to calculate \( S^\circ (\text{CH}_3) \). For \( \Delta H^\circ_f (\text{CH}_3) \), we simply turn the problem on its head and measure forward and backward rate coefficients, choosing a system where both measurements are feasible. The approach is illustrated in the following example for determining the heat of formation of the t-butyl (methyl-2-propyl) radical.

**Example 1.7**

At 288 K the forward and reverse rate coefficients for reaction (12)

\[ \text{Br} + \text{i-C}_6\text{H}_{13} \rightarrow \text{HBr} + \text{t-C}_6\text{H}_{13} \]  
\[ \text{R 12} \]

\[ \Delta H^\circ_f (\text{kJmol}^{-1}) = 112 - 134.2 - 36.4 \text{ ??} \]

\[ S^\circ (\text{kJmol}^{-1} \text{K}^{-1}) = 175 \text{ 295.3 198.7 313} \]

were determined to be \( k_1 = 1.02 \times 10^{6} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} \) and \( k_2 = 1.67 \times 10^{4} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} \). The equilibrium constant is therefore equal to \( 1.02 \times 10^{6} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} \cdot 1.67 \times 10^{4} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} = 8.10 \times 10^{4} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} \). In \( K_2 = 9.70 \) and hence \( \Delta G^\circ = 24.0 \text{ kJmol}^{-1} \) using \( \Delta G^\circ = \Delta H^\circ - RT \ln K_2 \), \( \Delta S^\circ_f = +41.4 \text{ Jmol}^{-1} \text{K}^{-1} \). Using the relationship \( \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \) the reaction enthalpy \( \Delta H^\circ_f \) was +36.3 \text{ kJmol}^{-1} \). Using the measured values for the enthalpy of formation of the other three components, a value for \( \Delta H^\circ_f (\text{t-C}_6\text{H}_{13}) \) of +50.4 \text{ kJmol}^{-1} \) was calculated.

**1.8 Parallel and consecutive reactions**

We conclude this introductory chapter with a brief look at how elementary reactions can couple together. We shall return to the subject in much greater detail in Chapter 8.

**1.8.1 Parallel reactions**

In some circumstances a reactant may be removed by two or more reactions. We are interested in knowing what is the overall rate of removal of the reactant and what fraction of it is removed by the various different channels. A relevant example involves chlorine atoms generated by the ultraviolet (UV) photolysis of chlorofluorocarbons (CFCs) in the stratosphere. Chlorine can react with ozone or methane, the former reaction being part of a catalytic cycle removing ozone, the latter forming a relatively harmless 'reservoir' species holding the chlorine in an unreactive form.

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]  
\[ \text{R 13} \]

\[ \text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3 \]  
\[ \text{R 14} \]

As both of these are elementary reactions we can immediately write down the rate equations for each reaction:

\[ -d[C]/dt = k_{31} [C][O_3] \]  
\[ \text{E 34} \]

\[ -d[C]/dt = k_{45} [Cl][CH_4] \]  
\[ \text{E 35} \]
24 - Time, concentration, and temperature

Chlorine atoms will be lost by both processes and hence the overall rate of loss will be the sum of the two individual rates:

$$-\frac{d[Cl]}{dt} = k_{15}[Cl][O_3] + k_{14}[Cl][CH_4].$$

(E 36)

The concentrations of ozone and methane will be much higher than that of the chlorine atoms and hence we can make a pseudo-first-order approximation

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

(E 37)

where $k' = k_{14}[O_3] + k_{14}[CH_4]$. The fraction of chlorine atoms reacting with either ozone or methane will depend on the ratio of the pseudo-first-order rate coefficients for the particular reaction to the overall rate of loss:

$$f(ClO) = \frac{k_{14}[O_3]}{k'}$$

(E 38)

where $f(ClO)$ is the fraction of ClO formed.

1.8.2 Consecutive reactions

An elementary reaction may form part of a chain of reactions, the product of the first reaction going on to form a second product e.g. for two consecutive first order reactions we have:

$$A \rightarrow B \rightarrow C.$$  

(R 15,16)

The overall reaction involves the conversion of A to C via the intermediate B. The concentration profiles of the three species will depend on the relative values of the rate coefficients $k_{15}$ and $k_{14}$. The differential equations controlling the concentrations of A, B and C can be solved and Fig. 1.11 shows two possible extremes. In the first case, where $k_{14}$ is much smaller than $k_{15}$, we get substantial conversion of A into B before much C is formed. The growth of C approximately matches the decay of B, the rate-determining step of the reaction is the reaction of B to C. In the second case, B is a very reactive intermediate, as $k_{14}$ is very large. The concentration of B never builds up to any substantial level; as soon as a B molecule is formed it rapidly reacts to form C. The growth of C now approximately matches the decay of A. After a short initiation period we note that the concentration of B remains approximately constant and this value is known as the steady-state concentration. During this period of constant [B], written as $[B]_{ss}$, the rate of formation of B must equal its rate of decay. We shall make use of the so-called steady-state approximation in Chapters 5 and 6 and discuss in more detail its derivation and applicability in Chapter 8.

1.9 Questions

1.1 Write a concise definition of order and molecularity.

1.2 When concentrations of reactants are measured in mol dm$^{-3}$, what are appropriate units for (i) the rate, (ii) the rate coefficient, for

(a) a reaction of zero order;

(b) a reaction of order 1.5.

1.3 Derive equation $\ln k_0(a) = k_0$ from the rate law for a first order reaction.

The following data give the pseudo-first-order rate coefficient for (R 17) under conditions where [CH] $\ll$ [O$_3$]:

$$\text{CH} + \text{O}_2 \rightarrow \text{Products}$$

(R 12)

$$[\text{O}_3] = 10^{-7} \text{ mol dm}^{-3}$$

$$k'[a] = 19.6 \text{ sec}^{-1}$$

$$19.6 \times \frac{1}{29850} = 4.5 \times \frac{1}{45700} = 59 \times \frac{1}{64700} = 80 \times \frac{1}{80700}$$

Determine the bimolecular rate coefficient.

CH radicals are known to play important roles in combustion. For example the reaction of CH with $N_2$ is thought to lead to the formation of nitrogen oxides in car exhausts. These compounds play an important role in urban smog formation.

1.4 The thermal decomposition of dimethyl ether has been studied by measuring the increase in pressure with time.

$$\text{(CH$_3$)$_2$O} \rightarrow \text{CH}_4 + \text{H}_2 + \text{CO}$$

(R 18)

The data in the table were obtained at 777 K with an initial pressure of ether equal to 312 mmHg (torr).

| Time/sec | 390 | 777 | 1155 | 2000 | 3000 | 3155 |
| Pressure increase/mmHg | 96 | 179 | 250 | 353 | 467 |

Show that the reaction is first order and find the rate coefficient.

1.5 Methane is an important trace constituent of our lower atmosphere (the Troposphere). It is a significant greenhouse gas absorbing infrared radiation from the Earth's surface leading to potential global warming. The main mechanism for methane removal is reaction with the hydroxyl radical:

$$\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3.$$  

(R 19)

The temperature of the troposphere declines with altitude. Calculate the relative change in the rate coefficient for reaction (19) at the Earth's surface ($T = 295$ K) and at the top of the troposphere ($T = 220$ K). Reaction (19) has an activation energy of 19.5 kJ mol$^{-1}$.

1.6 The rate of a certain reaction doubles on increasing the temperature from 290 K to 300 K. Evaluate the activation energy.

1.7 Experiments have established that the rate coefficient for the reaction

- Fig. 1.11 Concentrations of A, B, and C during the conversion of A to C via the consecutive reactions, (R 15) and (R 16), (a) $k_{15} > k_{14}$, (b) $k_{15} \ll k_{14}$.
H + H₂O₂ \rightarrow \text{OH} + \text{H}_2\text{O} \quad (\text{R 20})

is given by the expression \( k_\text{20} = 1.0 \times 10^{10} \exp(-1800/T) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \). If \( \Delta H^\circ \) and \( \Delta S^\circ \) for the reaction are −285 kJ mol\(^{-1}\) and 24.5 J K\(^{-1}\) mol\(^{-1}\) respectively, obtain an Arrhenius expression for the rate coefficient of the reverse reaction.

References
