

# 9

## Thermodynamics of Chemical Transformations

### 9.1 Transformations of Matter

Transformations of matter take place in many ways, through chemical, nuclear and elementary particle reactions. We shall speak of ‘chemical transformations’ in this broader sense. Though thermodynamics was founded in our daily experience, its reach is vast, ranging from the most simple changes like the melting of ice, to the state of matter during the first few minutes after the ‘big bang’, to the radiation that fills the entire universe today.

Let us begin by looking at the transformation that matter undergoes at various temperatures. Box 9.1 gives an overview of the reactions that take place at various temperatures, ranging from those during the first few minutes after the ‘big bang’ [1] to terrestrial and interstellar temperatures. All these transformations or reactions can be associated with enthalpies of reaction and an equilibrium characterized by the vanishing of the corresponding affinities.

Our present knowledge of the universe is based on the radiation emitted by galaxies that we can detect and on the motion of galaxies due to gravitational forces exerted by matter that is visible and invisible. Astrophysical data on observable gravitational effects indicate that only about 4% of the energy density in the universe is in the form of the protons, neutrons and electrons that make up ordinary matter in all the visible galaxies. Of the rest, 74% is in an unknown form spread diffusely throughout the universe; this is called **dark energy**. The remaining 22% is matter in galaxies that is not visible and is called **dark matter**; its presence is inferred through the gravitational effects it has on visible matter. The universe is also filled with thermal radiation<sup>1</sup> at a temperature of about 2.73 K (usually called **cosmic microwave background**) and particles called neutrinos, which interact only very weakly with protons, neutrons and electrons.

The small amount of matter that is in the form of stars and galaxies is not in thermodynamic equilibrium. The affinities for the reactions that are currently occurring in the stars are not zero. The nuclear reactions in the stars produce all the known elements from hydrogen [2–4]. Hence, the observed properties, such as the abundance of elements in stars and planets, cannot be described using the theory of chemical equilibrium.

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<sup>1</sup>The precise thermodynamic nature of thermal radiation is discussed in Chapter 11.

### Box 9.1 Transformation of matter at various temperatures

**Temperature  $>10^{10}$  K.** This was the temperature during the first few minutes of the universe after the ‘big bang’. At this temperature, the thermal motion of the protons and neutrons is so violent that even the strong nuclear forces cannot bind them as nuclei of elements. Electron–positron pairs appear and disappear spontaneously and are in thermal equilibrium with radiation. (The threshold for electron–positron pair production is about  $6 \times 10^9$  K.)

**Temperature range  $10^9$ – $10^7$  K.** At about  $10^9$  K, nuclei begin to form and nuclear reactions occur in this range. Temperatures as high as  $10^9$  are reached in stars and supernova, where heavier elements are synthesized from H and He. The *binding energy per nucleon* (proton or neutron) is in the range  $(1.0\text{--}1.5) \times 10^{-12}$  J  $\approx (6.0\text{--}9.0) \times 10^6$  eV, which corresponds to  $(6.0\text{--}9.0) \times 10^8$  kJ mol $^{-1}$ .

**Temperature range  $10^6$ – $10^4$  K.** In this range, electrons bind to nuclei to form atoms, but the bonding forces between atoms are not strong enough to form stable molecules. At a temperature of about  $1.5 \times 10^5$  K, hydrogen atoms begin to ionize. The ionization energy of 13.6 eV corresponds to 1310 kJ mol $^{-1}$ . Heavier atoms require larger energies for complete ionization. Complete ionization of carbon, for example, requires 490 eV of energy, which corresponds to 47187 kJ mol $^{-1}$ .<sup>\*</sup> Carbon atoms will be completely dissociated at  $T \approx 5 \times 10^6$  K into electrons and nuclei. In this temperature range, matter exists as free electrons and nuclei, a state of matter called *plasma*.

**Temperature range  $10^4$ – $10^2$  K.** Chemical reactions take place in this range. The chemical bond energies are of the order of  $10^2$  kJ mol $^{-1}$ . The C–H bond energy is about 414 kJ mol $^{-1}$ . At a temperature of about  $5 \times 10^4$  K, chemical bonds will begin to break. The intermolecular forces, such as hydrogen bonds, are of the order 10 kJ mol $^{-1}$ . The enthalpy of vaporization of water, which is essentially the breaking of hydrogen bonds, is about 40 kJ mol $^{-1}$ .

<sup>\*</sup>1 eV =  $1.6 \times 10^{-19}$  J = 96.3 kJ mol $^{-1}$ ;  $T = (\text{Energy in J mol}^{-1})/R = (\text{Energy in J})/k_B$ .

A knowledge of the rates of reactions and the history of the star or planet is necessary to understand the abundance of elements.

When a system reaches thermodynamic equilibrium, however, its history is of no importance. Regardless of the path leading to equilibrium, the state of equilibrium can be described by general laws. In this chapter we shall first look at the nature of chemical reactions and equilibrium; then we study the relation between entropy production and the rates chemical reactions that drive the system to equilibrium.

## 9.2 Chemical Reaction Rates

In studying chemical reactions and their evolution to equilibrium, it is also our purpose to look explicitly at the entropy production while the reactions are in progress. In other words, we would like to obtain explicit expressions for the entropy production  $d_i S/dt$  in terms of the rates of reactions. The introduction of reaction rates takes us beyond the classical thermodynamics of equilibrium states that was formulated by Gibbs and others.

In general, the laws of thermodynamics cannot specify reaction rates. Though affinity is the driving force of chemical reactions, the rates are not determined solely by affinities, but depend on many factors, such as the presence of catalysts which does not change the affinity. However, as we shall see in later chapters, close to the thermodynamic equilibrium – called the ‘linear regime’ – thermodynamic formalism can be used to

show that rates are linearly related to the affinities. The general topic of specifying the rates of chemical reactions has become a subject in itself and goes by the name of ‘chemical kinetics’. Kinetic equations express reaction rates as functions of state variables. Some basic aspects of chemical kinetics will be discussed in this section.

We have already seen that the entropy production due to a chemical reaction may be written in the form (see Equation (4.1.16))

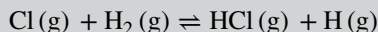
$$\frac{d_i S}{dt} = \frac{A}{T} \frac{d\xi}{dt} \quad (9.2.1)$$

in which  $\xi$  is the extent of reaction introduced in Section 2.5 and  $A$  is the affinity, expressed in terms of the chemical potentials. The time derivative of  $\xi$  is related to the rate of reaction. The precise definition of the rate of reaction is given in Box 9.2. For the following simple reaction<sup>2</sup>:



### Box 9.2 Reaction rate and reaction velocity

The reaction rate is defined as the number of reactive events per second per unit volume. It is usually expressed as  $\text{mol L}^{-1} \text{s}^{-1}$ . Chemical reactions depend on collisions. In most reactions, only a very small fraction of the collisions result in a chemical reaction. For each reacting species, since the number of collisions per unit volume is proportional to its concentration, the rates are proportional to the product of the concentrations. A **reaction rate** refers to conversion of the reactants to the products or vice versa. Thus, for the reaction



the **forward rate**  $R_f = k_f[\text{Cl}][\text{H}_2]$  and the **reverse rate**  $R_r = k_r[\text{HCl}][\text{H}]$ , in which  $k_f$  and  $k_r$  are the rate constants. In a reaction, both forward and reverse reactions take place simultaneously. For thermodynamic considerations, we define the **velocity** of a reaction as the **rate of net conversion** of the reactants to products. Thus:

$$\begin{aligned} \text{Reaction velocity } v &= \text{Forward rate} - \text{Reverse rate} \\ &= k_f[\text{Cl}][\text{H}_2] - k_r[\text{HCl}][\text{H}] \\ &= R_f - R_r \end{aligned}$$

In a homogeneous system, the reaction velocity  $v$  is given in terms of the extent of reaction:

$$v = \frac{d\xi}{V dt} = R_f - R_r$$

in which  $V$  is the volume of the system. In practice, monitoring the progress of a reaction by noting the change in some property (such as spectral absorption or refractive index) of the system generally amounts to monitoring the change in the extent of reaction  $\xi$ .

<sup>2</sup>For a detailed study of this reaction, see *Science*, **273** (1996), 1519.

the affinity  $A$  and the extent of reaction  $\xi$  are defined by

$$A = \mu_{\text{Cl}} + \mu_{\text{H}_2} - \mu_{\text{HCl}} - \mu_{\text{H}} \quad (9.2.3)$$

$$d\xi = \frac{dN_{\text{Cl}}}{-1} = \frac{dN_{\text{H}_2}}{-1} = \frac{dN_{\text{HCl}}}{1} = \frac{dN_{\text{H}}}{1} \quad (9.2.4)$$

As explained in Box 9.2, the forward reaction rate is  $k_f[\text{Cl}][\text{H}_2]$ , in which the square brackets indicate concentrations and  $k_f$  is the forward rate constant, which depends on temperature. Similarly, the reverse reaction rate is  $k_r[\text{HCl}][\text{H}]$ . The time derivative of  $\xi$  is the *net rate of conversion* of reactants Cl and  $\text{H}_2$  to the products HCl and H due to the forward and reverse reactions. Since the reaction rates are generally expressed as functions of concentrations, it is more convenient to define this net rate per unit volume. Accordingly, we define a **reaction velocity**  $v$  as

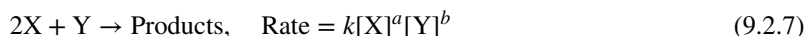
$$v = \frac{d\xi}{V dt} = k_f[\text{Cl}][\text{H}_2] - k_r[\text{HCl}][\text{H}] \quad (9.2.5)$$

Note that this equation follows from Equation (9.2.4) and the definition of the forward and reverse rates. For example, in a homogeneous system, the rate of change of the concentration of Cl is  $d(N_{\text{Cl}}/V) dt = -k_f[\text{Cl}][\text{H}_2] + k_r[\text{HCl}][\text{H}]$ . More generally, if  $R_f$  and  $R_r$  are the forward and reverse reaction rates, we have

$$v = \frac{d\xi}{V dt} = R_f - R_r \quad (9.2.6)$$

The reaction velocity units are  $\text{mol L}^{-1} \text{s}^{-1}$ .

In the above example, the rate of reaction bears a direct relation to the stoichiometry of the reactants, but this is not always true. In general, for a reaction such as

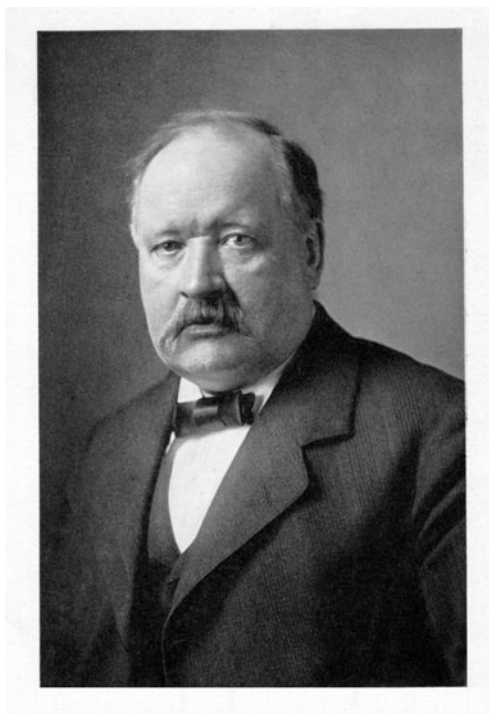


in which  $k$  is a temperature-dependent **rate constant** and the exponents  $a$  and  $b$  are not necessarily integers. The rate is said to be of *order  $a$  in  $[\text{X}]$*  and of *order  $b$  in  $[\text{Y}]$* . The sum of all the orders of the reactants,  $a + b$ , is the **order of the reaction**. Reaction rates can take complex forms because they may be the result of many intermediate steps with widely differing rates that depend on the presence of catalysts. If all the intermediate steps are known, then each step is called an **elementary step**. Rates of elementary steps do bear a simple relation to the stoichiometry: the exponents equal the stoichiometric coefficients. If reaction (9.2.7) were an elementary step, for example, then its rate would be  $k[\text{X}]^2[\text{Y}]$ .

In many cases, the temperature dependence of the rate constant is given by the **Arrhenius equation**:

$$k = k_0 e^{-E_a/RT} \quad (9.2.8)$$

Svante Arrhenius (1859–1927) proposed it in 1889 and showed its validity for a large number of reactions [5,6]. The term  $k_0$  is called the **pre-exponential factor** and  $E_a$  the **activation energy**. For the forward reaction of Equation (9.2.2),  $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$ , we have, for example,  $k_0 = 7.9 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$  and  $E_a = 23 \text{ kJ mol}^{-1}$ . When  $T$  varies over a wide range, the Arrhenius equation was found to be inaccurate in predicting the variation of the rate constant, though it is quite useful for many reactions.



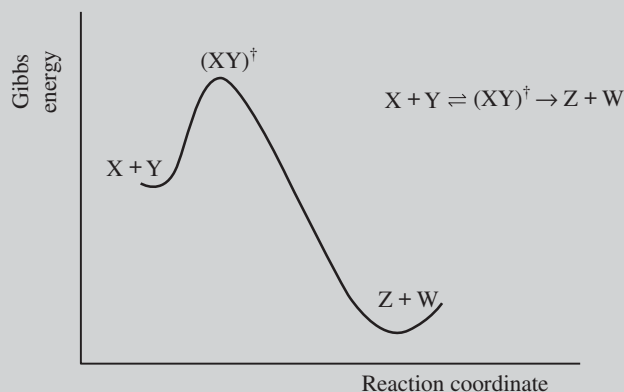
*Svante August Arrhenius (1859–1927).*

A more recent theory that is based on statistical mechanics and quantum theory was developed in the 1930s by Wigner, Pelzer, Eyring, Polyani and Evans. According to this theory, the reaction occurs through a **transition state** (see Box 9.3). We shall discuss transition state theory in some detail later in this chapter. The concept of a transition state leads to the following expression for the rate constant:

$$k = \kappa \left( \frac{k_B T}{h} \right) e^{-(\Delta H^\ddagger - T\Delta S^\ddagger)/RT} = \kappa \left( \frac{k_B T}{h} \right) e^{-\Delta G^\ddagger/RT} \quad (9.2.9)$$

in which  $k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$  is the Boltzmann constant and  $h$  is Planck's constant. The terms  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are the transition-state enthalpy and entropy respectively, as explained briefly in Box 9.3. The term  $\kappa$  is small, of the order of unity, which is characteristic of the reaction. *A catalyst increases the rate of reaction by altering the transition state such that  $(\Delta H^\ddagger - T\Delta S^\ddagger) = \Delta G^\ddagger$  decreases.*

### Box 9.3 Arrhenius equation and transition state theory



According to the Arrhenius equation, the rate constant of a chemical reaction is of the form

$$k = k_0 e^{-E_a/RT}$$

The rate constant  $k$  has this form because, for the reactants to convert to products, the collisions must have sufficient energy to overcome an energy barrier. As shown in the above figure, the transformation from the reactants to the products is schematically represented with a 'reaction coordinate' and the energy of the molecules undergoing the reaction.

According to the transition state theory, the reactants  $X$  and  $Y$  reversibly form a **transition state**  $(XY)^\ddagger$ . The transition state then irreversibly transforms to the products. The difference in the enthalpy and entropy between the free molecules  $X$  and  $Y$  and the transition state are denoted by  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  respectively. The main result of the transition state theory (which is obtained using principles of statistical mechanics and quantum mechanics) is that the rate constant is of the form

$$k = \kappa (k_B T/h) \exp[-(\Delta H^\ddagger - T\Delta S^\ddagger)/RT] = \kappa (k_B T/h) \exp[-\Delta G^\ddagger/RT]$$

in which  $k_B = 1.381 \times 10^{23} \text{ J K}^{-1}$  is the Boltzmann constant and  $h = 6.626 \times 10^{-34} \text{ J s}$  is Planck's constant;  $\kappa$  is a term of the order of unity that is characteristic of the reaction.

*A catalyst increases the rate of reaction by altering the transition state such that  $(\Delta H^\ddagger - T\Delta S^\ddagger) = \Delta G^\ddagger$  decreases.*

#### 9.2.1 Rate Equations Using the Extent of Reactions

Reaction rates are generally determined empirically. The mechanisms of reactions, which detail all the elementary steps, are usually a result of long and detailed study. Once the reaction rate laws are known, the time variation of the concentration can be obtained by integrating the rate equations, which are coupled differential equations. (Box 9.4 lists elementary first- and second-order reactions.) For example, if we have an elementary reaction of the form



then the concentrations are governed by the following differential equations:

$$-\frac{1}{V} \frac{d\xi}{dt} = \frac{d[X]}{dt} = -k_f[X] + k_r[Y]^2 \quad (9.2.11)$$

$$2\frac{1}{V} \frac{d\xi}{dt} = \frac{d[Y]}{dt} = 2k_f[X] - 2k_r[Y]^2 \quad (9.2.12)$$

### Box 9.4 Elementary reactions

To obtain an explicit analytic expression for the concentrations of the reactants and products as a function of time, we must solve differential equations such as (9.2.11) and (9.2.12). Generally, this is possible only in the case of simple reactions. For more complex reactions, one can obtain numerical solutions using a computer. Two elementary reactions for which we can obtain explicit expressions for the concentrations as functions of time are given below.

**First-order reaction.** For a decomposition reaction  $X \rightarrow \text{Products}$ , in which the reverse reaction rate is so small that it can be neglected, we have the differential equation

$$\frac{d[X]}{dt} = -k_f[X]$$

It is easy to see that solution of this equation is

$$[X](t) = [X]_0 e^{-k_f t}$$

in which  $[X]_0$  is the concentration at time  $t = 0$ . This is the well-known exponential decay; in a given amount of time,  $[X]$  decreases by the same fraction. In particular, the time it takes for any initial value of  $[X]$  to decrease by a factor of 1/2 is the **half-life**. It is usually denoted by  $t_{1/2}$ . The half-life can be computed by noting that  $\exp(-k_f t_{1/2}) = 1/2$ , i.e.

$$t_{1/2} = \frac{\ln(2)}{k_f} = \frac{0.6931}{k_f}$$

**Second-order reaction.** For the elementary reaction  $2X \rightarrow \text{Products}$ , if the reverse reaction can be neglected, the rate equation is

$$\frac{d[X]}{dt} = -2k_f[X]^2$$

The solution is obtained by evaluating

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

which gives us

$$\frac{1}{[X]} - \frac{1}{[X]_0} = 2k_f t$$

Given  $[X]_0$  at  $t = 0$  and  $k_f$ , this expression gives us the value  $[X]$  at any time  $t$ .

Without loss of generality, we may assume  $V = 1$  and simplify the notation. These two equations are not independent. *In fact, there is only one independent variable  $\xi$  for every independent reaction.* If  $[X]_0$  and  $[Y]_0$  are the values of the concentrations at  $t = 0$ , then by assigning  $\xi(0) = 0$  and using  $d\xi = -d[X]$  and  $2d\xi = d[Y]$  it is easy to see that  $[X] = [X]_0 - \xi$  and  $[Y] = [Y]_0 + 2\xi$ . Substituting these values into Equation (9.2.1) we obtain

$$\frac{d\xi}{dt} = k_f([X]_0 - \xi) - k_r([Y]_0 + 2\xi)^2 \quad (9.2.13)$$

In this equation, the initial concentrations  $[X]_0$  and  $[Y]_0$  appear explicitly and  $\xi(0) = 0$  for all initial concentrations. The solution  $\xi(t)$  of such an equation can be used to obtain the rate of entropy production, as will be shown explicitly in Section 9.5. Differential equations such as these, and more complicated system of equations, can be solved numerically on a computer, e.g. using software such as *Mathematica* or *Maple* (sample programs are provided in Appendix 9.1). Furthermore, in describing reactions involving solid phases, concentration cannot be used to describe the change in the amount of a solid phase; the extent of reaction  $\xi$ , which represents the change in the total amounts of a reactant or product, is a convenient variable for this purpose.

When many reactions are to be considered simultaneously, we will have one  $\xi$  for each independent reaction, denoted by  $\xi_k$ , and the entire system will be described by a set of coupled differential equations in  $\xi_k$ . Only in a few cases can we find analytical solutions to such equations, but they can be readily solved numerically using *Mathematica*, *Maple* or other software that is designed specifically for solving rate equations.

### 9.2.2 Reaction Rates and Activities

Though reaction rates are generally expressed in terms of concentrations, one could equally well express them in terms of activities. In fact, we shall see in the following sections that the connection between affinities and reaction rates can be made more easily if the reaction rates are expressed in terms of activities. For example, for the elementary reaction



the forward rate  $R_f$  and the reverse rate  $R_r$  may be written as

$$R_f = k_f a_X a_Y \quad \text{and} \quad R_r = k_r a_W^2 \quad (9.2.15)$$

The rate constants  $k_f$  and  $k_r$  in Equation (9.2.15) will have units of  $\text{mol L}^{-1} \text{s}^{-1}$ ; their numerical values and units differ from those of the rate constants when  $R_f$  and  $R_r$  are expressed in terms of concentrations (Exercise 9.11).

Experimentally, we know that reaction rates do depend on the activities; they are not specified by concentrations alone. For example, at fixed values of temperature and concentrations of the reactants, it is well known that the rates of ionic reactions can be altered by changing the ionic strength of the solution (usually known as the ‘salt effect’). This change in the rate is due to a change in the activities. It has become general practice, however, to express the reaction rates in terms of the concentrations and to include the effects of changing activities in the rate constants. Thus, the rate constants are considered functions of the ionic strength when rates are expressed in terms of concentrations. Alternatively, if the rates are expressed in terms of activities, then the rate constant is independent of the ionic strength; a change in rate due to a change in ionic strength would be because activity depends on ionic strength.



### 9.3 Chemical Equilibrium and the Law of Mass Action

In this section we shall study chemical equilibrium in detail. At equilibrium, the pressure and temperature of all components and phases are equal; the affinities and the corresponding reaction velocities vanish. For example, for a reaction such as



at equilibrium we have

$$A = \mu_X + \mu_Y - 2\mu_Z = 0 \quad \text{and} \quad \frac{d\xi}{dt} = 0 \quad (9.3.2)$$

or

$$\mu_X + \mu_Y = 2\mu_Z \quad (9.3.3)$$

The condition that the ‘thermodynamic force’, affinity  $A$ , equals zero implies that the corresponding ‘thermodynamic flow’, i.e. the reaction velocity  $d\xi/dt$ , also equals zero. The condition  $A = 0$  means that at equilibrium the ‘stoichiometric sum’ of the chemical potentials of the reactants and products are equal, as in Equation (9.3.3). This result can be generalized to an arbitrary chemical reaction of the form

$$a_1A_1 + a_2A_2 + a_3A_3 + \cdots + a_nA_n \rightleftharpoons b_1B_1 + b_2B_2 + b_3B_3 + \cdots + b_mB_m \quad (9.3.4)$$

in which the  $a_k$  are the stoichiometric coefficients of the reactants  $A_k$  and the  $b_k$  are the stoichiometric coefficients of the products  $B_k$ . The corresponding condition for chemical equilibrium will then be

$$a_1\mu_{A_1} + a_2\mu_{A_2} + a_3\mu_{A_3} + \cdots + a_n\mu_{A_n} = b_1\mu_{B_1} + b_2\mu_{B_2} + b_3\mu_{B_3} + \cdots + b_m\mu_{B_m} \quad (9.3.5)$$

Such equalities of chemical potentials are valid for all reactions: changes of phase, and chemical, nuclear and elementary particle reactions. Just as a difference in temperature drives the flow of heat until the temperatures difference vanishes, a nonzero affinity drives a chemical reaction until the affinity vanishes.

To understand the physical meaning of the mathematical conditions such as Equation (9.3.3) or (9.3.5), we express the chemical potential in terms of experimentally measurable quantities. We have seen in Section 5.3 (Equation (5.3.5)) that the chemical potential in general can be expressed as

$$\mu_k(p, T) = \mu_k^0(T) + RT \ln a_k \quad (9.3.6)$$

in which  $a_k$  is the activity and  $\mu_k^0(T_0) = \Delta G_f^0[k, T]$  is the standard molar Gibbs energy of formation (Box 5.1), the value of which may be found in data tables. This being a general expression, for gases, liquids and solids we have the following explicit expressions:

- *Ideal gas*:  $a_k = p_k/p_0$ , where  $p_k$  is the partial pressure.
- *Real gases*: expressions for activity can be derived using Equation (6.2.30), as was shown in Section 6.2.
- *Pure solids and liquids*:  $a_k \approx 1$ .
- *Solutions*:  $a_k \approx \gamma_k x_k$ , where  $\gamma_k$  is the activity coefficient and  $x_k$  is the mole fraction.

For ideal solutions,  $\gamma_k = 1$ . For nonideal solutions,  $\gamma_k$  is obtained by various means, depending on the type of solution. The chemical potential can also be written in terms of the concentrations by appropriately redefining  $\mu_k^0$ .

We can now use Equation (9.3.6) to express the condition for equilibrium (9.3.3) in terms of the activities, which are experimentally measurable quantities:

$$\mu_X^0(T) + RT \ln(a_{X,\text{eq}}) + \mu_Y^0(T) + RT \ln(a_{Y,\text{eq}}) = 2[\mu_Z^0(T) + RT \ln(a_{Z,\text{eq}})] \quad (9.3.7)$$

where the equilibrium values of the activities are indicated by the subscript 'eq'.

This equation can be rewritten as

$$\frac{a_{Z,\text{eq}}^2}{a_{X,\text{eq}} a_{Y,\text{eq}}} = \exp \left[ \frac{\mu_X^0(T) + \mu_Y^0(T) - 2\mu_Z^0(T)}{RT} \right] \equiv K(T) \quad (9.3.8)$$

$K(T)$ , as defined above, is called the **equilibrium constant**. It is a function only of temperature. That the equilibrium constant as defined above is a function of  $T$  only is an important thermodynamic result. It is called the **law of mass action**.  $\mu_k^0(T) = \Delta G_f^0[k, T]$  is the standard molar Gibbs energies of formation of compound  $k$  at a temperature  $T$ . The 'Standard Thermodynamic Properties' table at the end of the book lists this quantity at  $T = 298.15$  K. It is convenient and conventional to define the **Gibbs energy of reaction**  $\Delta G_r$  as

$$\begin{aligned} \Delta G_r^0(T) &= -[\mu_X^0(T) + \mu_Y^0(T) - 2\mu_Z^0(T)] \\ &= 2\Delta G_f^0[Z, T] - \Delta G_f^0[X, T] - \Delta G_f^0[Y, T] \end{aligned} \quad (9.3.9)$$

The equilibrium constant is then written as

$$\begin{aligned} K(T) &= \exp(-\Delta G_r^0/RT) \\ &= \exp[-(\Delta H_r^0 - T\Delta S_r^0)/RT] \end{aligned} \quad (9.3.10)$$

in which  $\Delta G_r^0$ ,  $\Delta H_r^0$  and  $\Delta S_r^0$  are respectively the standard Gibbs energy, enthalpy and entropy of the reaction at temperature  $T$ , though their temperature dependence is usually not explicitly indicated. The activities in Equation (9.3.8) can be written in terms of partial pressures  $p_k$  or mole fractions  $x_k$ . If reaction (9.3.1) were an ideal-gas reaction, then  $a_k = p_k/p_0$ . With  $p_0 = 1$  bar and  $p_k$  measured in bars, the equilibrium constant takes the form

$$\frac{p_{Z,\text{eq}}^2}{p_{X,\text{eq}} p_{Y,\text{eq}}} = K_p(T) = \exp(-\Delta G_r^0/RT) \quad (9.3.11)$$

At a given temperature, regardless of the initial partial pressures, the chemical reaction (9.3.1) will irreversibly evolve towards the state of equilibrium in which the partial pressures will satisfy Equation (9.3.11). This is one form of the *law of mass action*.  $K_p$  is the *equilibrium constant* expressed in terms of the partial pressures. Since in an ideal gas mixture  $p_k = (N_k/V)RT = [k]RT$  (in which  $R$  is in units of bar L mol<sup>-1</sup> K<sup>-1</sup>), the law of mass action can also be expressed in terms of the concentrations of the reactants and products:

$$\frac{[Z]_{\text{eq}}^2}{[X]_{\text{eq}}[Y]_{\text{eq}}} = K_c(T) \quad (9.3.12)$$

in which  $K_c$  is the equilibrium constant expressed in terms of the concentrations. In general, for a reaction of the form,  $aX + bY \rightleftharpoons cZ$  it is easy to obtain the relation  $K_c = (RT)^\alpha K_p$ , where  $\alpha = a + b - c$  (Exercise 9.14). In the particular case of reaction (9.3.1)  $\alpha$  happens to be zero.

If one of the reactants were a pure liquid or a solid, then the equilibrium constant will not contain corresponding 'concentration' terms. For example, let us consider the reaction



Since  $a_{\text{C(s)}} \approx 1$  for the solid phase, the equilibrium constant in this case is written as

$$\frac{a_{\text{CO,eq}}^2}{a_{\text{O}_2,\text{eq}} a_{\text{C,eq}}^2} = \frac{p_{\text{CO,eq}}^2}{p_{\text{O}_2,\text{eq}}} = K_p(T) \quad (9.3.14)$$

Equations (9.3.9) and (9.3.10) provide us with the means of calculating the equilibrium constant  $K(T)$  using the tabulated values of  $\Delta G_f^0[k]$ . If the activities are expressed in terms of partial pressures, then we have  $K_p$ . Some examples are shown in Box 9.5.

### Box 9.5 The equilibrium constant

A basic result of equilibrium chemical thermodynamics is that the equilibrium constant  $K(T)$  is a function of only temperature. It can be expressed in terms of the standard Gibbs energy of reaction  $\Delta G_r^0$  (Equations (9.3.9) and (9.3.10)):

$$K(T) = \exp[-\Delta G_r^0/RT]$$

For a reaction such as  $\text{O}_2(\text{g}) + 2\text{C}(\text{s}) \rightleftharpoons 2\text{CO}(\text{g})$  the equilibrium constant at 298.15 K can be calculated using the tabulated values of standard Gibbs energy of formation  $\Delta G_f^0$  at  $T = 298.15$  K:

$$\begin{aligned} \Delta G_r^0 &= 2\Delta G_f^0[\text{CO}] - 2\Delta G_f^0[\text{C}] - \Delta G_f^0[\text{O}_2] \\ &= -2(137.2) \text{ kJ mol}^{-1} - 2(0) - (0) = -274.4 \text{ kJ mol}^{-1} \end{aligned}$$

Using this value in the expression  $K(T) = \exp[-\Delta G_r^0/RT]$  we can calculate  $K(T)$  at  $T = 298.15$ :

$$K(T) = \exp[-\Delta G_r^0/RT] = \exp[274.4 \times 10^3 / (8.314 \times 298.15)] = 1.18 \times 10^{48}$$

Similarly, for the reaction  $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$ , at  $T = 298.15$  K,

$$\begin{aligned} \Delta G_r^0 &= \Delta G_f^0[\text{CH}_3\text{OH}] - \Delta G_f^0[\text{CO}] - 2\Delta G_f^0[\text{H}_2] \\ &= -161.96 \text{ kJ mol}^{-1} - (-137.2 \text{ kJ mol}^{-1}) - 2(0) = -24.76 \text{ kJ mol}^{-1} \end{aligned}$$

The equilibrium constant is

$$K(T) = \exp[-\Delta G_r^0/RT] = \exp[24.76 \times 10^3 / (8.314 \times 298.15)] = 2.18 \times 10^4.$$

### 9.3.1 Relation between the Equilibrium Constants and the Rate Constants

Chemical equilibrium can also be described as a state in which the forward rate of every reaction equals its reverse rate. If the reaction  $\text{X} + \text{Y} \rightleftharpoons 2\text{Z}$  is an elementary step, and if we express the reaction rates in terms of the activities, then when the velocity of the reaction is zero we have

$$k_f a_X a_Y = k_r a_Z^2 \quad (9.3.15)$$

From a theoretical viewpoint, writing the reaction rates in terms of activities rather than concentrations is better because the state of equilibrium is directly related to activities, not concentrations.

Comparing Equation (9.3.15) and the equilibrium constant (9.3.8), we see that

$$K(T) = \frac{a_Z^2}{a_X a_Y} = \frac{k_f}{k_r} \quad (9.3.16)$$

Thus, the equilibrium constant can also be related to the rate constants  $k_r$  and  $k_f$  when the rates are expressed in terms of the activities. It must be emphasized that Equation (9.3.8) is valid even if the forward and reverse rates do not have the form shown in Equation (9.3.15); in other words, Equation (9.3.8) is valid whether the reaction  $X + Y \rightleftharpoons 2Z$  is an elementary reaction step or not. *The relation between the activities and the equilibrium constant is entirely a consequence of the laws of thermodynamics; it is independent of the kinetic rates of the forward and reverse reactions.*

### 9.3.2 The van't Hoff Equation

Using Equation (9.3.10), the temperature variation of the equilibrium constant  $K(T)$  can be related to the enthalpy of reaction  $\Delta H_r$ . From Equation (9.3.10) it follows that

$$\frac{d \ln K(T)}{dT} = -\frac{d}{dT} \frac{\Delta G_r}{RT} \quad (9.3.17)$$

However, according to the Gibbs–Helmholtz equation (5.2.14), the variation of  $\Delta G$  with temperature is related to  $\Delta H$  by  $[\partial(\Delta G/T)/\partial T] = -\Delta H/T^2$ . Using this in the above equation we have

$$\boxed{\frac{d \ln K(T)}{dT} = \frac{\Delta H_r}{RT^2}} \quad (9.3.18)$$

This relation enables us to deduce how the equilibrium constant  $K(T)$  depends on the temperature. It is called the **van't Hoff equation**. In many situations of interest, the heat of reaction  $\Delta H_r$  changes very little with temperature and may be assumed to be a constant equal to the standard enthalpy of reaction at 298.15 K, which we denote by  $\Delta H_r^0$ . Thus, we may integrate Equation (9.3.18) and obtain

$$\ln K(T) = \frac{-\Delta H_r^0}{RT} + C \quad (9.3.19)$$

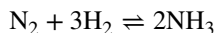
Experimentally,  $K(T)$  can be obtained at various temperatures. According to Equation (9.3.19), a plot of  $\ln K(T)$  versus  $1/T$  should result in a straight line with a slope equal to  $-\Delta H_r^0/R$ . This method can be used to obtain the values of  $\Delta H_r^0$ .

### 9.3.3 Response to Perturbation from Equilibrium: The Le Chatelier–Braun Principle

When a system is perturbed from its state of equilibrium, it will relax to a new state of equilibrium. Le Chatelier and Braun noted in 1888 that a simple principle may be used to predict the direction of the response to a perturbation from equilibrium. Le Chatelier stated this principle thus:

Any system in chemical equilibrium undergoes, as a result of a variation in one of the factors governing the equilibrium, a compensating change in a direction such that, had this change occurred alone it would have produced a variation of the factors considered in the *opposite* direction.

To illustrate this principle, let us consider the reaction



in equilibrium. In this reaction, the total molar amount of all components decreases when the reactants convert to products. If the pressure of this system is suddenly increased, then the system's response will be the production of more  $\text{NH}_3$ , which decreases the total molar amount and thus the pressure. The compensating change in the system is in a direction *opposite* to that of the perturbation. The new state of equilibrium will

contain more  $\text{NH}_3$ . Similarly, if a reaction is exothermic, if heat is supplied to the system, then the product will be converted to reactants, which has the effect of opposing the increase in temperature. Though this principle has its usefulness, it does not always give unambiguous results. For this reason, a more general approach under the name ‘theorems of moderation’ has been developed [7]. This approach provides a very precise and accurate description of the response of a system in equilibrium to a perturbation from this state, which is always the evolution to another state of equilibrium.

Le Chatelier’s principle only describes the response of a system in thermodynamic equilibrium; it says nothing about the response of a system that is maintained in a nonequilibrium state. Indeed, the response of a nonequilibrium system to small changes in temperature could be extraordinarily complex. This is obviously evident in living organisms, which are nonequilibrium systems. In the case of alligators, for example, the sex of an offspring depends on the incubation temperature of the eggs [8]: temperatures below  $30^\circ\text{C}$  produce all females, while temperatures above  $34^\circ\text{C}$  produce all males.

## 9.4 The Principle of Detailed Balance

There is an important aspect of the state of chemical equilibrium, and the state of thermodynamic equilibrium in general, that must be noted, namely the **principle of detailed balance**.

We observed earlier that, for a given reaction, the state of equilibrium depends only on the stoichiometry of the reaction, not its actual mechanism. For example, in the reaction  $\text{X} + \text{Y} \rightleftharpoons 2\text{Z}$  considered above, if the forward and reverse reaction rates were given by

$$R_f = k_f a_X a_Y \quad \text{and} \quad R_r = k_r a_Z^2 \quad (9.4.1)$$

respectively, then the result that  $a_Z^2/a_X a_Y = K(T)$  is at equilibrium can be interpreted as the balance between forward and reverse reactions:

$$R_f = k_f a_X a_Y = R_r = k_r a_Z^2$$

so that

$$\frac{a_Z^2}{a_X a_Y} = K(T) = \frac{k_f}{k_r} \quad (9.4.2)$$

However, the equilibrium relation  $a_Z^2/a_X a_Y = K(T)$  was not obtained using any assumption regarding the kinetic mechanism of the reaction. It remains valid even if there was a complex set of intermediate reactions that result in the overall reaction  $\text{X} + \text{Y} \rightleftharpoons 2\text{Z}$ . This feature could be understood through the **principle of detailed balance**, according to which:

In the state of equilibrium, every transformation is balanced by its exact opposite or reverse.

That the principle of detailed balance implies that  $a_Z^2/a_X a_Y = K(T)$  regardless of the mechanism can be seen through the following example. Assume that the reaction really consists of two steps:



which results in the net reaction  $X + Y \rightleftharpoons 2Z$ . According to the principle of detailed balance, at equilibrium we must have

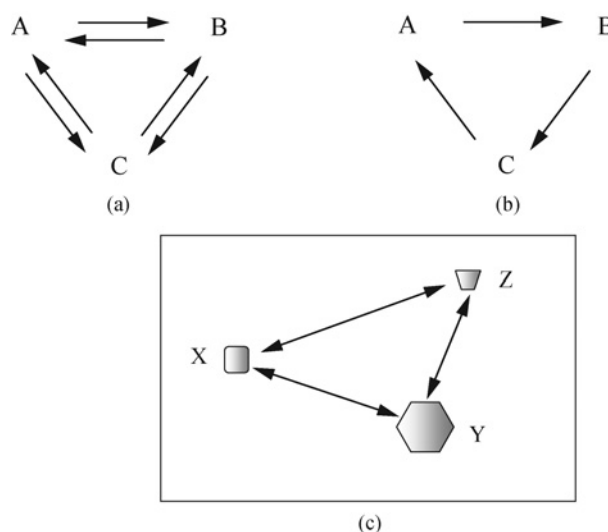
$$\frac{a_W}{a_X^2} = \frac{k_{fa}}{k_{ra}} \equiv K_a, \quad \frac{a_Z^2 a_X}{a_W a_Y} = \frac{k_{fb}}{k_{rb}} \equiv K_b \quad (9.4.5)$$

in which the subscripts  $a$  and  $b$  stand for reactions (9.4.3) and (9.4.4) respectively. The thermodynamic equation for equilibrium  $a_Z^2/a_X a_Y = K(T)$  can now be obtained as the product of  $K_a$  and  $K_b$ :

$$K_a K_b = \frac{a_W a_Z^2 a_X}{a_X^2 a_W a_Y} = \frac{a_Z^2}{a_X a_Y} = K \quad (9.4.6)$$

From this derivation it is clear that this result will be valid for an arbitrary set of intermediate reactions.

The principle of detailed balance is a very general principle, valid for all transformations. It is in fact valid for the exchange of matter and energy between any two volume elements of a system in equilibrium. The amount of matter and energy transferred from volume element X to volume element Y exactly balances the energy and matter transferred from volume element Y to volume element X (see Figure 9.1). The same can be said of the interaction between the volume elements Y and Z and X and Z. One important consequence of this type of balance is that the removal or isolation of one of the volume elements from the system, say Z, does not alter the states of X or Y or the interaction between them. This is another way of saying that there is no long-range correlation between the various volume elements. As we shall see in later chapters, the principle of detailed balance is not valid in nonequilibrium systems that make a transition to organized dissipative structures. Consequently, the removal or isolation of a volume element at one part will alter the



**Figure 9.1** The principle of detailed balance. (a) The equilibrium between three interconverting compounds A, B and C is a result of ‘detailed balance’ between each pair of compounds. (b) Though a cyclic conversion from one compound to another as shown can also result in concentrations that remain constant in time, such a state is not the equilibrium state. (c) The principle of detailed balance has a more general validity. The exchange of matter (or energy) between any two regions of a system is balanced in detail; the amount of matter going from X to Y is balanced by exactly the reverse process.

state of a volume element located elsewhere. It is then said to have long-range correlations. We can see this clearly if we compare a droplet of water that contains carbon compounds in thermal equilibrium and a living cell that is in an organized state far from thermodynamic equilibrium. Removal of a small part of the water droplet does not change the state of other parts of the droplet, whereas removing a small part of a living cell is likely to have a drastic influence on other parts of the cell.

## 9.5 Entropy Production due to Chemical Reactions

The formalism of the previous sections can now be used to relate entropy production to reaction rates more explicitly. In Chapter 4 we saw that the entropy production rate due to a chemical reaction is given by

$$\frac{d_i S}{dt} = \frac{A}{T} \frac{d\xi}{dt} \geq 0 \quad (9.5.1)$$

Our objective is to relate the affinity  $A$  and  $d\xi/dt$  to the reaction rates, so that the entropy production is written in terms of the reaction rates. In order to do this, let us consider the reaction that we have considered before:



Assuming that this is an elementary step, we have for the forward and reverse rates

$$R_f = k_f a_X a_Y \quad \text{and} \quad R_r = k_r a_Z^2 \quad (9.5.3)$$

Since the forward and reverse rates must be equal at equilibrium, we have seen from Equation (9.4.2) that

$$K(T) = \frac{k_f}{k_r} \quad (9.5.4)$$

The velocity of reaction  $v$ , which is simply the difference between the forward and reverse reaction rates, is related to  $d\xi/dt$  as shown in Equation (9.2.6). The reaction rates  $R_f$  and  $R_r$  can themselves be expressed as functions of the extent of reaction  $\xi$ , as was shown in Section 9.2:

$$\frac{1}{V} \frac{d\xi}{dt} = [R_f(\xi) - R_r(\xi)] \quad (9.5.5)$$

To obtain the velocity of reaction as a function of time, this differential equation has to be solved. An example is presented below.

Turning now to the affinity  $A$ , we can relate it to the reaction rates in the following manner. By definition, the affinity of the reaction (9.5.2) is

$$\begin{aligned} A &= \mu_X + \mu_Y - 2\mu_Z \\ &= \mu_X^0(T) + RT \ln(a_X) + \mu_Y^0(T) + RT \ln(a_Y) - 2[\mu_Z^0(T) + RT \ln(a_Z)] \\ &= [\mu_X^0(T) + \mu_Y^0(T) - 2\mu_Z^0(T)] + RT \ln(a_X) + RT \ln(a_Y) - 2RT \ln(a_Z) \end{aligned} \quad (9.5.6)$$

Since  $[\mu_X^0(T) + \mu_Y^0(T) - 2\mu_Z^0(T)] = -\Delta G_r^0 = RT \ln K(T)$ , the above equation can be written as

$$A = RT \ln K(T) + RT \ln \left( \frac{a_X a_Y}{a_Z^2} \right) \quad (9.5.7)$$

This is an alternative way of writing the affinity. At equilibrium,  $A = 0$ . To relate  $A$  to the reaction rates, we use Equation (9.5.4) and combine the two logarithm terms:

$$A = RT \ln \frac{k_f}{k_r} + RT \ln \left( \frac{a_X a_Y}{a_Z^2} \right) = RT \ln \left( \frac{k_f a_X a_Y}{k_r a_Z^2} \right) \quad (9.5.8)$$

This leads us to the relations we are seeking if we use the expressions in (9.5.3) to write this expression in terms of the reaction rates:

$$A = RT \ln \left( \frac{R_f}{R_r} \right) \quad (9.5.9)$$

Clearly, this equation is valid for any elementary step because the rates of elementary steps are directly related to the stoichiometry. Now we can substitute Equations (9.5.5) and (9.5.9) in the expression for the entropy production rate (Equation (9.5.1)) and obtain

$$\frac{1}{V} \frac{d_i S}{dt} = \frac{1}{V} \frac{A}{T} \frac{d\xi}{dt} = R(R_f - R_r) \ln(R_f/R_r) \geq 0 \quad (9.5.10)$$

which is an expression that relates *entropy production rate per unit volume* to the reaction rates. (Note that  $R$  is the gas constant.) Also, as required by the Second Law, the right-hand side of this equation is positive, whether  $R_f > R_r$  or  $R_f < R_r$ . Another point to note is that in Equation (9.5.10) the forward and reverse rates  $R_f$  and  $R_r$  can be expressed in terms of concentrations, partial pressures of the reactants or other convenient variables; the reaction rates need not be expressed only in terms of activities, as in Equation (9.5.3).

The above equation can be generalized to several simultaneous reactions, each indexed by the subscript  $k$ . The rate of total entropy production per unit volume is the sum of the rates at which entropy is produced in each reaction:

$$\frac{1}{V} \frac{d_i S}{dt} = \frac{1}{V} \sum_k \frac{A_k}{T} \frac{d\xi_k}{dt} = R \sum_k (R_{kf} - R_{kr}) \ln(R_{kf}/R_{kr}) \quad (9.5.11)$$

in which  $R_{kf}$  and  $R_{kr}$  are the forward and reverse reaction rates of the  $k$ th reaction. This expression is useful for computing the entropy production rate in terms of the reaction rates, but *it is valid only for elementary steps whose reaction rates are specified by the stoichiometry*. This is not a serious limitation, however, because every reaction is ultimately the result of many elementary steps. If the detailed mechanism of a reaction is known, then an expression for the entropy production rate can be written for any chemical reaction.

### 9.5.1 An Example

As an example of entropy production due to an irreversible chemical reaction, consider the simple reaction:



which is the interconversion or ‘racemization’ of molecules with mirror-image structures. Molecules that are not identical to their mirror image are said to be *chiral* and the two mirror-image forms are called *enantiomers*.



Let  $[L]$  and  $[D]$  be the concentrations of the enantiomers of a chiral molecule. If at time  $t = 0$  the concentrations are  $[L] = L_0$  and  $[D] = D_0$ , and  $\xi(0) = 0$ , then we have the following relations:

$$\frac{d[L]}{-1} = \frac{d[D]}{+1} = \frac{d\xi}{V} \quad (9.5.13)$$

$$[L] = L_0 - (\xi/V), \quad [D] = D_0 + (\xi/V) \quad (9.5.14)$$

Relations (9.5.14) are obtained by integrating (9.5.13) and using the initial conditions. For notational convenience we shall assume  $V = 1$ . At the end of the calculation we can reintroduce the  $V$  factor. Racemization can be an elementary first-order reaction for which the forward and reverse reactions are

$$R_f = k[L] = k(L_0 - \xi), \quad R_r = k[D] = k(D_0 + \xi) \quad (9.5.15)$$

Note that the rate constants for the forward and reverse reactions are the same due to symmetry:  $L$  must convert to  $D$  with the same rate constant as  $D$  to  $L$ . Also, from Equations (9.5.15) and (9.5.9) one can see that the affinity is a function of the state variable  $\xi$  for a given set of initial concentrations.

To obtain the entropy production as an explicit function of time, we must obtain  $R_f$  and  $R_r$  as functions of time. This can be done by solving the differential equation defining the velocity of this reaction:

$$\frac{d\xi}{dt} = R_f - R_r = k(L_0 - \xi) - k(D_0 + \xi)$$

i.e.

$$\frac{d\xi}{dt} = 2k \left( \frac{L_0 - D_0}{2} - \xi \right) \quad (9.5.16)$$

This first-order differential equation can be easily solved by defining  $x = [(L_0 - D_0)/2] - \xi$  so that the equation reduces to  $dx/dt = -2kx$ . The solution is

$$\xi(t) = \frac{L_0 - D_0}{2} (1 - e^{-2kt}) \quad (9.5.17)$$

With this expression for  $\xi(t)$ , the rates in Equation (9.5.15) can be written as explicit functions of time:

$$R_f = \frac{k(L_0 + D_0)}{2} + \frac{k(L_0 - D_0)}{2} e^{-2kt} \quad (9.5.18)$$

$$R_r = \frac{k(L_0 + D_0)}{2} - \frac{k(L_0 - D_0)}{2} e^{-2kt} \quad (9.5.19)$$

With Equations (9.5.18) and (9.5.19), we can now also write the rate of entropy production (9.5.10) as an explicit function of time:

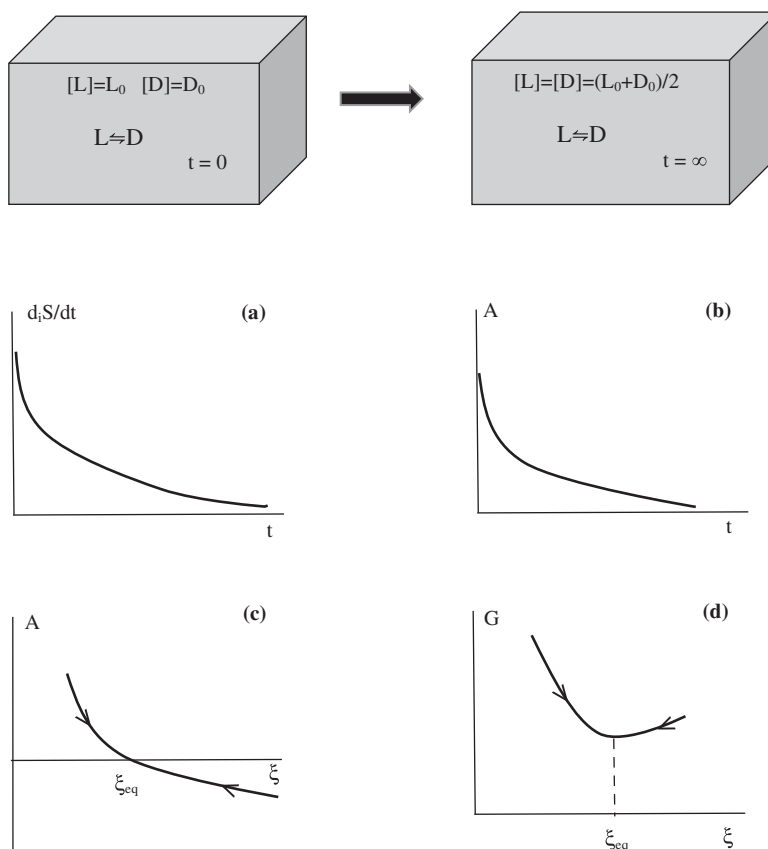
$$\begin{aligned} \frac{1}{V} \frac{d_r S}{dt} &= R(R_f - R_r) \ln(R_f/R_r) \\ \frac{1}{V} \frac{d_r S}{dt} &= R[k(L_0 - D_0)e^{-2kt}] \ln \left[ \frac{(L_0 + D_0) + (L_0 - D_0)e^{-2kt}}{(L_0 + D_0) - (L_0 - D_0)e^{-2kt}} \right] \end{aligned} \quad (9.5.20)$$

As  $t \rightarrow \infty$ , the system reaches equilibrium, at which

$$\xi_{eq} = \frac{L_0 - D_0}{2} \quad \text{and} \quad [L]_{eq} = [D]_{eq} = \frac{L_0 + D_0}{2} \quad (9.5.21)$$

The volume term can be reintroduced by replacing  $\xi_{eq}$  by  $\xi_{eq}/V$ .

In Chapter 5 (see Equation (5.1.12)) we noted the relation between affinity  $A$  and the Gibbs energy  $G$ :  $A = -(\partial G/\partial \xi)_{p,T}$ . Both  $A$  and  $G$  are functions of state, which can be expressed as functions of  $\xi$  and the initial



**Figure 9.2** Racemization of enantiomers as an example of a chemical reaction. The associated entropy production, the time variations of  $A$ , are shown in (a) and (b). State functions  $A$  and  $G$  as functions of  $\xi$  are shown in (c) and (d).

molar amounts of reactants and products. As  $\xi$  approaches its equilibrium value  $\xi_{eq}$ , the Gibbs energy reaches its minimum value and the affinity  $A$  goes to zero, as shown in Figure 9.2.

The entropy production for more complex reactions can be obtained numerically using computers. *Mathematica* codes for the above example are given in Appendix 9.1. The student is encouraged to expand these codes for more complex reactions.

## 9.6 Elementary Theory of Chemical Reaction Rates

The rates of chemical reactions depend on several factors. In previous sections we discussed the dependence of rates on concentrations and introduced the Arrhenius and transition-state rate constants. According to the Arrhenius theory, the rate constant has the form  $k_0 \exp(-E_a/RT)$ , whereas transition-state theory gives a rate constant of the form  $k_0 \exp(-\Delta G^\ddagger/RT)$ . In this section we will introduce the reader to the theoretical basis that leads to these expressions.

### 9.6.1 The Arrhenius Theory of Rates

When the molecular nature of compounds became established, theories of rates of chemical reactions began to emerge. That molecules were in incessant and rapid chaotic motion was established by the kinetic theory of gases. A natural consequence was a view that chemical reactions were a consequence of molecular collisions. When molecules collide, somehow an atomic rearrangement occurs and the products are formed. However, not every collision between reacting molecules results in the formation of products. In fact, quantitative estimates indicated that only a very small fraction of the collisions were ‘reactive collisions’. This naturally raised the question as to why only certain collisions between reactant molecules resulted in the formation of products.

One of the first successful theories of reaction rates is due to the Swedish chemist Svante Arrhenius (1859–1927), but it is noted that others, especially van’t Hoff, also made important contributions to this theory [5,6]. The success of the Arrhenius theory is mainly in explaining the temperature dependence of reaction rates. To explain why only a small fraction of molecular collisions resulted in reactions, the concept of ‘activation energy’ was introduced. This is the idea that the colliding molecules must have sufficient energy to activate the reaction, i.e. the breaking of bonds and formation of new bonds. That only a small fraction of molecules have the required activation energy was proposed by the German chemist L. Pfundler. To compute the probability that the collision has the required activation energy, the Boltzmann principle is taken as a guide. We recall that, according to the Maxwell–Boltzmann probability distribution, the probability that a molecule has energy  $E$  is proportional to  $\exp(-E/RT)$ . Using this principle, it could be argued that if a certain activation energy  $E_a$  is required in a collision between reacting molecules to generate the product, this will happen with a probability proportional to  $\exp(-E_a/RT)$ . Thus, the reaction rate must be proportional to a factor  $\exp(-E_a/RT)$ ; that is, of all the collisions that occur in a unit volume in unit time, a fraction  $k_0 \exp(-E_a/RT)$  will be reactive collisions. Thus, the Arrhenius rate constant

$$k = k_0 e^{-E_a/RT}$$

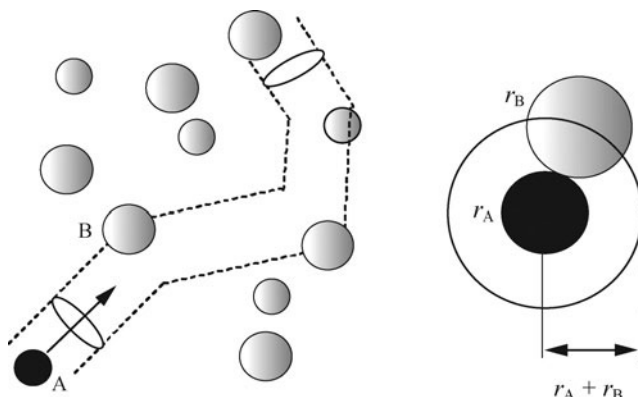
where  $k_0$  is called the **pre-exponential factor**.

The next step is to compute the number of collisions that occur in unit time in a unit volume. For gases, this can be done using the Maxwell–Boltzmann distribution (Section 1.6). Let us consider the reaction  $A + B \rightarrow \text{Products}$ . Let  $r_A$  and  $r_B$  be the radii of the A and B molecules respectively. For small molecules, radii can be estimated from tabulated bond lengths. Figure 9.3 shows the path of a molecule of A as it undergoes collisions with molecules in its path. An observer located on the molecule A will observe a stream of molecules; collisions with molecules of B occur when the distance between the center of A and the center of a streaming B is equal to or less than the sum  $r_A + r_B$ . Consider a cylinder of radius  $r_A + r_B$  with the path of the molecule A as its axis. Molecule A will collide with all B molecules in such a cylinder. From the viewpoint of an observer on A, molecules will be streaming at an average speed  $v_r$ , which is equal to the average relative velocity between A and B molecules. Thus, in unit time, on the average, a molecule of A will collide with all B molecules in the volume  $\pi(r_A + r_B)^2 v_r$ . The term  $\pi(r_A + r_B)^2$  is called the **collision cross-section**. If  $n_B$  is the moles of B molecules per unit volume, then a single A molecule will collide with  $\pi(r_A + r_B)^2 v_r n_B N_A$  molecules of B per unit time. Thus, the average total number of collisions between A and B molecules per unit volume per unit time, called the **collision frequency**  $z_{AB}$ , equals

$$z_{AB} = \pi(r_A + r_B)^2 v_r n_B n_A N_A^2 \quad (9.6.1)$$

in which  $n_A$  is the moles of A molecules per unit volume. Using the Maxwell–Boltzmann distribution it can be shown that the average relative velocity between A and B molecules is given by

$$v_r = \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} \quad \text{in which} \quad \mu = \frac{m_A m_B}{m_A + m_B} \quad (9.6.2)$$



**Figure 9.3** The elementary bimolecular reaction  $A + B \rightarrow \text{Products}$  is a result of collisions between the molecules of A and B. Approximating the molecule's shape to be spherical, we assume the radii of molecules of A and B are  $r_A$  and  $r_B$  respectively. As shown, on average, in unit time, a molecule of A (filled sphere) will collide with all molecules in the cylinder of cross-section  $\pi(r_A + r_B)^2$  and length  $v_r$ .

where  $m_A$  and  $m_B$  are the masses of molecules A and B respectively. The factor  $\mu$  is called the **reduced mass**. Of all the collisions, only a fraction  $\exp(-E_a/RT)$  are reactive collisions that result in the formation of products. Hence, the reaction rate (number of reactive collisions per unit time per unit volume) equals

$$\begin{aligned} \text{Rate} &= z_{AB} \exp(-E_a/RT) \\ &= N_A^2 \pi (r_A + r_B)^2 \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} n_B n_A \exp(-E_a/RT) \end{aligned} \quad (9.6.3)$$

To specify the rate in moles per unit volume per unit time, we divide the above expression by  $N_A$ :

$$\text{Rate}(\text{mol m}^{-3} \text{ s}^{-1}) = N_A (r_A + r_B)^2 \left( \frac{8\pi k_B T}{\mu} \right)^{1/2} \exp(-E_a/RT) n_A n_B \quad (9.6.4)$$

in which all quantities are in SI units. If the unit of length is taken to be decimeters, then the concentrations will be molarities  $[A]$  and  $[B]$  and the rate will be in the units of moles per liter. We can now identify the pre-exponential factor  $k_0$  in the Arrhenius rate:

$$k_0 = N_A (r_A + r_B)^2 \left( \frac{8\pi k_B T}{\mu} \right)^{1/2} \quad (9.6.5)$$

At  $T = 300 \text{ K}$ , the value of  $k_0$  is of the order of  $10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} = 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$ . The changes in  $k_0$  due to changes in  $T$  are small compared with the corresponding changes in the exponential factor in the rate constant.

A number of other expressions were also suggested to explain the temperature dependence of reaction rates, as Laidler notes [6], but they found less and less support as experimental data were gathered. In addition, the expression suggested by Arrhenius had a strong theoretical basis that the other expressions lacked.

### 9.6.2 The Transition State Theory

Transition state theory postulates the existence of a transition state which is in equilibrium with the reactants. The transition state has an unstable mode that results in conversion to products. For a reaction  $X + Y \rightarrow Z + W$ , the transition-state mechanism is



The rate of product formation is  $k_{2f}[XY^{\ddagger}]$ . The assumption that the transition state is in equilibrium with the reactants implies that

$$[(XY)^{\ddagger}]/[X][Y] = k_{1f}/k_{1r} = K_1(T) = \exp(-\Delta G^{\ddagger}/RT) \quad (9.6.7)$$

in which  $K_1(T)$  is the equilibrium constant and  $\Delta G^{\ddagger}$  is the Gibbs energy of reaction. The reaction rate can now be written as

$$\text{Rate} = k_{2f}[(XY)^{\ddagger}] = k_{2f}K_1(T)[X][Y] \quad (9.6.8)$$

The use of statistical thermodynamics and quantum mechanics to calculate the rate constant gives  $k_{2f} = \kappa(k_B T/h)$ , in which  $\kappa$  is a term of the order of unity and  $h$  is the Planck's constant (see Box 9.3). Therefore, the rate constant has the form

$$k = \kappa \left( \frac{k_B T}{h} \right) \exp(-\Delta G^{\ddagger}/RT) \quad (9.6.9)$$

In contrast to the Arrhenius theory, the transition state theory has a *thermodynamic basis* and predicts the existence of a transition state. The pre-exponential factor it predicts is proportional to  $T$ ; this is in contrast to the Arrhenius theory, which predicts a  $T^{1/2}$  dependence. The transition state theory predicts a change in the rate of reaction due to factors that might change  $\Delta G^{\ddagger}$ . One such factor is the effect of solvents. In solutions, if the reactants are ionic, then it is observed that the reaction rate depends on the dielectric constant of the solvent. This effect, called the 'solvent effect', can be explained by noting that a change in the dielectric constant changes the value of  $\Delta G^{\ddagger}$ . In general, the transition state theory gives more insight into the nature of a chemical reaction than the Arrhenius theory and is widely used.

## 9.7 Coupled Reactions and Flow Reactors

In the previous sections we discussed some basic aspects of chemical kinetics. In this section, we shall look at more complex reactions. Box 9.4 summarizes the main aspects of first- and second-order reactions. In these cases, the reverse reactions were not considered, but in many cases the reverse reaction cannot be ignored. We shall now consider some examples below.

### 9.7.1 Zero-Order Reactions

In certain conditions, the rate of a reaction can be essentially independent of the concentration of the initial reactants. For example, a reaction such as



could have a rate of product formation that is given by

$$\frac{d[Y]}{dt} = k \quad (9.7.2)$$

in which  $k$  is a constant. Such a reaction may be said to be of ‘zero order’ in the reactant X. Such a rate law clearly indicates that the reaction mechanism that controls the conversion of X to Y depends on the concentration of another compound and that increasing the amount of X does not increase the rate of conversion to Y. For example, let us assume that the formation of Y depends on X binding to a catalyst C to form a complex CX and that the complex CX converts to C and Y:



The rate of product formation depends on the amount of the complex CX. If all the catalyst is bound to the reactant X, then increasing the amount of X does not increase the rate of product formation. If  $[C]_T$  is the total amount of C, then the rate of reaction when the complex is saturated is

$$\frac{d[Y]}{dt} = k_{2f}[C]_T \quad (9.7.4)$$

Such rates can be observed in reactions catalyzed by solid catalysts and in enzymes. The solution to Equation (9.7.2) is  $[Y] = [Y]_0 + kt$ .

## 9.7.2 Reversible First-Order Reaction

In general, the forward and the reverse rate constants are not equal and the rate equations are of the form



$$\frac{d[A]}{dt} = -R_f + R_r = -k_f[A] + k_r[B] \quad (9.7.6)$$

in which  $R_f$  and  $R_r$  are the forward and reverse reactions rates. Let  $[A]_0$  and  $[B]_0$  be the initial concentrations. In the above reaction, the total concentration, which we shall denote as  $T = [A] + [B] = [A]_0 + [B]_0$ , remains constant. Hence, the above rate equation can be rewritten as

$$\frac{d[A]}{dt} = -k_f[A] + k_r(T - [A]) = -(k_f + k_r)[A] + k_rT \quad (9.7.7)$$

The solution to this equation is

$$[A] = \frac{k_r}{k_f + k_r}T + \left([A]_0 - \frac{k_r}{k_f + k_r}T\right)e^{-(k_f + k_r)t} \quad (9.7.8)$$

The reaction could also be described in terms of the extent of reaction  $\xi$ , as was done in Section 9.5 for the racemization reaction  $L \rightleftharpoons D$ . This is left as an exercise for the student.

## 9.7.3 Consecutive First-Order Reactions

Sequential conversion of compounds is quite common in natural and industrial processes. Sequential transformations in Nature more often than not are cyclical. Let us consider a very simple example: conversion of A to B to C, in which the reverse reactions have negligible rates:



We assume that all the rates are first order and that, at  $t = 0$ ,  $[A] = [A]_0$ ,  $[B] = 0$  and  $[C] = 0$ . The kinetic equations for the concentrations of A, B and C are

$$R_{1f} = k_{1f}[A], \quad R_{2f} = k_{2f}[B] \quad (9.7.10)$$

$$\frac{d[A]}{dt} = -R_{1f} = -k_{1f}[A] \quad (9.7.11)$$

$$\frac{d[B]}{dt} = R_{1f} - R_{2f} = k_{1f}[A] - k_{2f}[B] \quad (9.7.12)$$

$$\frac{d[C]}{dt} = R_{2f} = k_{2f}[B] \quad (9.7.13)$$

This set of coupled equations can be solved analytically. The solution to Equation (9.7.11) is

$$[A] = [A]_0 \exp(-k_{1f}t) \quad (9.7.14)$$

This solution can be substituted into the equation for [B], (9.7.12); we get

$$\frac{d[B]}{dt} + k_{2f}[B] = k_{1f}[A]_0 \exp(-k_{1f}t) \quad (9.7.15)$$

This is a first-order differential equation of the form  $(dX/dt) + cX = f(t)$  in which  $c$  is a constant and  $f(t)$  is a function of time. The general solution to such an equation is

$$X(t) = X(0)e^{-ct} + e^{-ct} \int_0^t e^{ct'} f(t') dt' \quad (9.7.16)$$

Using this general solution, we can write the solution to Equation (9.7.15) and show that

$$[B] = \frac{k_{1f}[A]_0}{k_{2f} - k_{1f}} (e^{-k_{1f}t} - e^{-k_{2f}t}) \quad (9.7.17)$$

in which we have used  $[B]_0 = 0$ . If the initial concentration  $[C]_0 = 0$ , then the total amount  $[A] + [B] + [C] = [A]_0$ . Using this relation, one can obtain the time variation of [C]:

$$\begin{aligned} [C] &= [A]_0 - [A] - [B] \\ &= [A]_0 \left[ 1 - e^{-k_{1f}t} - \frac{k_{1f}}{k_{2f} - k_{1f}} (e^{-k_{1f}t} - e^{-k_{2f}t}) \right] \end{aligned} \quad (9.7.18)$$

Alternatively, the rate equations can be written and solved in terms of the extents of reaction  $\xi_1$  and  $\xi_2$  of the two reactions (9.7.9). For simplicity, and without loss of generality, we shall assume the system volume  $V = 1$  so that concentrations and  $\xi$  values can be related without explicitly including  $V$ . The extent of reaction for the two reactions and the corresponding changes in concentrations are related by

$$\frac{d[A_1]}{-1} = \frac{d[B_1]}{+1} = d\xi_1, \quad \frac{d[B_2]}{-1} = \frac{d[C_2]}{+1} = d\xi_2 \quad (9.7.19)$$

in which the subscripts indicate changes due to the first and second reactions in the consecutive reactions (9.7.9). The total change in the concentration of A is only due to the reaction  $A \rightarrow B$  and that of C is only due to  $B \rightarrow C$ , i.e.

$$d[A] = d[A_1] = -d\xi_1 \quad \text{or} \quad [A] = [A]_0 - \xi_1 \quad (9.7.20)$$

and

$$d[C] = d[C_2] = +d\xi_2 \quad \text{or} \quad [C] = [C]_0 + \xi_2 \quad (9.7.21)$$

where we have assumed  $\xi = 0$  at  $t = 0$  (the subscript 0 indicates values at  $t = 0$ ). Since the change in the intermediate [B] is due to both reactions, we write:

$$d[B] = d[B_1] + d[B_2] = d\xi_1 - d\xi_2 \quad \text{or} \quad [B] = [B]_0 + \xi_1 - \xi_2 \quad (9.7.22)$$

The velocities of the two reactions are

$$\frac{d\xi_1}{dt} = R_{1f} - R_{1r} = k_{1f}[A] = k_{1f}([A]_0 - \xi_1) \quad (9.7.23)$$

$$\frac{d\xi_2}{dt} = R_{2f} - R_{2r} = k_{2f}[B] = k_{2f}([B]_0 + \xi_1 - \xi_2) \quad (9.7.24)$$

These two first-order linear differential equations could be solved using the methods outlined above. By substituting the solutions  $\xi_1(t)$  and  $\xi_2(t)$  into Equations (9.7.20) to (9.7.22), the time variation of concentrations [A], [B] and [C] can be obtained (Exercise 9.20). Describing the kinetics of reactions using extents of reaction has some notable aspects:

- Each extent of reaction is an independent variable and the number of independent variables in a set of reactions is equal to the number of extents of reaction. The time variations of all reacting species are expressed in terms of these independent variables.
- The initial values of all reactants appear explicitly in the equations and the initial values of all extents of reaction may be assumed to be zero.
- The rate of entropy production can be conveniently expressed in terms of the velocities  $d\xi_k/dt$  and the chemical potentials of the reacting species.

#### 9.7.4 The Steady-State Assumption

In many chemical reactions, the concentration of an intermediate compound or complex may be approximated to be constant. Take, for example, the following **Michaelis–Menten mechanism**, which describes enzyme reactions:



Enzyme E complexes with the substrate S to form the complex ES, which in turn transforms to product P and the enzyme. The complexation of E and S to form ES occurs very rapidly and reversibly. In contrast, the conversion of ES to P and E happens relatively slowly. The rapidity of the reaction  $E + S \rightleftharpoons ES$  keeps the concentration of ES essentially a constant close to its equilibrium value; any decrease in [ES] due to product formation is quickly compensated by the production of ES. Hence, we can assume that [ES] is in a *steady state*, i.e. its time derivative is zero. Taking the two steps of the reaction (9.7.25), the steady-state assumption can be expressed as

$$\frac{d[ES]}{dt} = k_{1f}[E][S] - k_{1r}[ES] - k_{2f}[ES] = 0 \quad (9.7.26)$$

In the above reaction, the total concentration of enzyme  $[E_0]$ , in the free and complex form, is a constant:

$$[E] + [ES] = [E_0] \quad (9.7.27)$$



Combining Equations (9.7.26) and (9.7.27) we can write  $k_{1f}([E_0] - [ES])[S] - k_{1r}[ES] - k_{2f}[ES] = 0$ . From this, it follows that

$$[ES] = \frac{k_{1f}[E_0][S]}{k_{1f}[S] + (k_{1r} + k_{2f})} \quad (9.7.28)$$

The rate of formation of the product P is  $k_{2f}[ES]$  and is usually written in the following form:

$$R = \frac{d[P]}{dt} = k_{2f}[ES] = \frac{k_{2f}[E_0][S]}{[S] + (k_{1r} + k_{2f})/k_{1f}} = \frac{R_{\max}[S]}{[S] + K_m} \quad (9.7.29)$$

in which  $R_{\max} = k_{2f}[E_0]$  is the maximum rate of product formation and  $K_m = (k_{1r} + k_{2f})/k_{1f}$ . It can be seen from Equation (9.7.29) that the rate at which P is generated has the following properties:

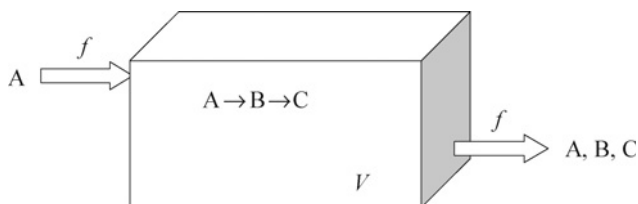
- When  $[S] \ll K_m$ , the rate is proportional to  $[S]$ .
- When  $[S] \gg K_m$ , the rate reaches its maximum value and is independent of  $[S]$ .
- When  $[S] = K_m$ , that rate reaches half the maximum value.

### 9.7.5 Flow Reactors

Many industrial chemical reactions take place in a flow reactor into which reactants flow and from which products are removed. The kinetic equations for such systems must consider the inflow and outflow. To see how the kinetic equations are written for a flow reactor, let us consider the following reaction, which we assume requires a catalyst:



We assume that the reaction takes place in a solution. The solution containing A flows into the reactor (Figure 9.4) of volume  $V$ . In the reactor, activated by a catalyst, the conversion from A to B and C takes place. The fluid in the reactor is rapidly stirred so that we may assume that it is homogeneous. The outflow is a solution containing B, C and unconverted A. If the objective is to produce B and C, then the reaction should be rapid enough so that very little A is in the outflow. We consider a flow rate of  $f$  liters per second of a solution of concentration  $[A]_{\text{in}}$  mol L<sup>-1</sup>. Moles of A flowing into the reactor per second equals  $[A]_{\text{in}}f$ . Hence, the rate at which the concentration of A increases due to the inflow into the reactor of volume  $V$  is  $[A]_{\text{in}}f/V$ . Similarly, the rate of decrease in concentrations of A, B and C due to the outflow are  $[A]f/V$ ,  $[B]f/V$  and  $[C]f/V$  respectively. The term  $f/V$  has units of s<sup>-1</sup>. Its inverse,  $V/f \equiv \tau$ , is called the **residence time** (because



**Figure 9.4** A flow reactor into which fluid containing A flows. Owing to a catalyst in the reactor, conversion of  $A \rightarrow B \rightarrow C$  takes place in the reactor. The outflow consists of unconverted A and the products B and C. The amount of fluid flowing into the reactor per unit time is  $f$ . The inflow rate equals the outflow rate at steady state.

it roughly corresponds to the time the flowing fluid resides in the reactor before it flows out). Taking the flow into consideration, the kinetic equations for the reactor can be written as

$$\frac{d[A]}{dt} = [A]_{\text{in}}(f/V) - k_{1f}[A] - [A](f/V) \quad (9.7.31)$$

$$\frac{d[B]}{dt} = k_{1f}[A] - k_{2f}[B] - [B](f/V) \quad (9.7.32)$$

$$\frac{d[C]}{dt} = k_{2f}[B] - [C](f/V) \quad (9.7.33)$$

This set of linear coupled equations can be solved for steady states by setting  $d[A]/dt = d[B]/dt = d[C]/dt = 0$ . If, initially, the reactor contains no A, B or C, then the flow will result in an initial increase in the concentration of the three reactants and then the reactor will approach a steady state in which the concentrations are constant. The steady states, which we identify with a subscript 's', are easily calculated:

$$[A]_s = \frac{[A]_{\text{in}}(f/V)}{k_{1f} + (f/V)} \quad (9.7.34)$$

$$[B]_s = \frac{k_{1f}[A]_s}{k_{2f} + (f/V)} \quad (9.7.35)$$

$$[C]_s = \frac{k_{2f}[B]_s}{f/V} \quad (9.7.36)$$

If the rate constants  $k_{1f}$  and  $k_{2f}$  are large compared with  $f/V$ , then the steady-state concentrations  $[A]_s$  and  $[B]_s$  will be small and  $[C]_s$  will be large. This corresponds to almost complete conversion of A into product C, which will flow out of the reactor. On the other hand, if the flow rate is high, then the conversion in the reactor will only be partial. Because they are coupled linear equations, (9.7.31) to (9.7.33) can also be solved analytically; generally, however, chemical kinetics leads to coupled nonlinear equations, which cannot be solved analytically. They can, of course, be solved numerically.

The above simple example illustrates how kinetic equations for a reactor can be written. Generalizing it to reactions more complex than Equation (9.7.30) is straightforward. The purpose of some reactors is to combust fuel and generate heat. At the steady state, heat is generated at a constant rate. If the enthalpies of the reactions are known, then at a steady state, the rate at which heat is generated in the reactor can be calculated.

## Appendix 9.1 Mathematica Codes

In *Mathematica*, numerical solutions to the rate equation can be obtained using the **NDSolve** command. Examples of the use of this command in solving simple rate equations are given below. The results can be plotted using the **Plot** command. Numerical output can be exported to graphing software using the **Export** command.

### CODE A: LINEAR KINETICS $X \rightarrow \text{PRODUCTS}$

```
(* Linear Kinetics *)

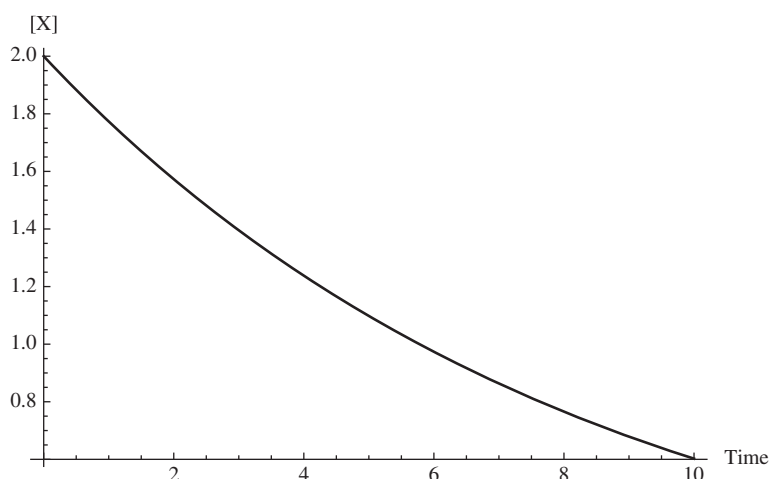
k=0.12;
```

```
Soln1=NDSolve[{X'[t]== -k*X[t], X[0]==2.0},X,{t,0,10}]
```

```
{X->InterpolatingFunction[{{0.,10.}},<>]}
```

The above output indicates that the solution as an interpolating function has been generated. The solution can be plotted using the following command. Here ' $\text{/.Soln1}$ ' specifies that the values of  $X[t]$  are to be calculated using the interpolation function generated by Soln1.

```
Plot[Evaluate[X[t]/.Soln1],{t,0,10},
     PlotStyle->{{Black,Thick}},
     AxesLabel->{Time,"[X]"}]
```



To write output files for spreadsheets use the 'Export' command and the file format List. For more detail see the *Mathematica* help file for the Export command. In the command below, the output filename is: data1.txt. This file can be read by most spreadsheets and graphing software. The command ' $X[t]/\text{.Soln1}$ ' specifies that  $X[t]$  is to be evaluated using Soln1 defined above. TableForm outputs data in a convenient form.

```
Export["data1.txt", Table[{t,X[t]/.Soln1},{t,1,10}]]//TableForm,"List"]
```

```
data1.txt
```

To obtain a table of  $t$  and  $X(t)$  the following command can be used.

```
Table[{t,X[t]/.Soln1},{t,1,5}]]//TableForm
```

```
1    1.77384
2    1.57326
3    1.39535
4    1.23757
5    1.09762
```

**CODE B: Mathematica CODE FOR THE REACTION  $X + 2Y \rightleftharpoons 2Z$** 

In writing codes for kinetic equations, we shall define the forward and reverse rates,  $R_f$  and  $R_r$  respectively, and use these in the rate equations. Thus we avoid typing the same expression many times.

```
(* Reaction  X+2Y  $\rightleftharpoons$  2Z *)

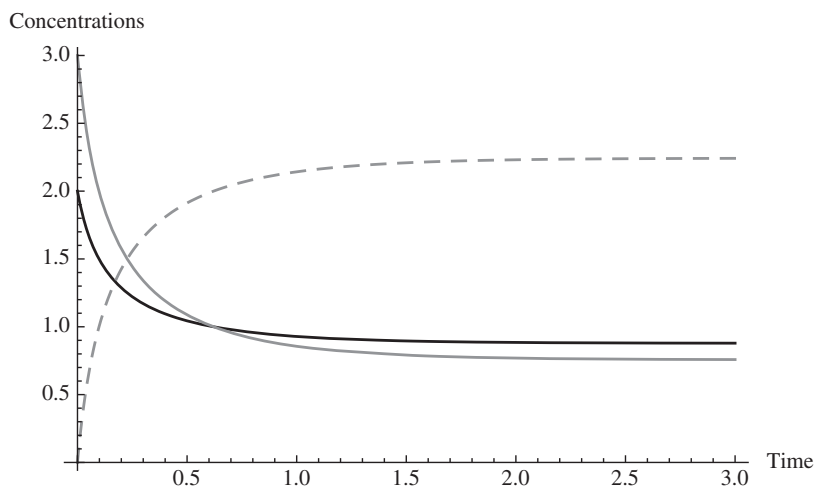
kf=0.5;kr=0.05;
Rf:=kf*X[t]*(Y[t]^2); Rr:=kr*Z[t]^2;

Soln2=NDSolve[{ X'[t]== -Rf+Rr,
                 Y'[t]== 2*(-Rf+Rr),
                 Z'[t]== 2*(Rf-Rr),
                 X[0]==2.0,Y[0]==3.0,Z[0]==0.0},
               {X,Y,Z},{t,0,3}]

{{X->InterpolatingFunction[{{0.,3.}},<>],
  Y->InterpolatingFunction[{{0.,3.}},<>],
  Z->InterpolatingFunction[{{0.,3.}},<>]}}
```

The above output indicates that the solution as an interpolating function has been generated. The solution can be plotted using the following command:

```
Plot[Evaluate[{X[t],Y[t],Z[t]}/.Soln2},{t,0,3},
      AxesLabel->{Time,Concentrations},
      PlotStyle->{{Black,Thick},{GrayLevel[.5],Thick},
                  {Dashed,Gray,Thick}}]
```



As shown in Code A, the data could be written to an output file that graphing software can read using the Export command.

**CODE C: Mathematica CODE FOR RACEMIZATION REACTION  $L \rightleftharpoons D$  AND CONSEQUENT ENTROPY PRODUCTION**

```
(* Racemization Kinetics:  L  $\rightleftharpoons$  D *)

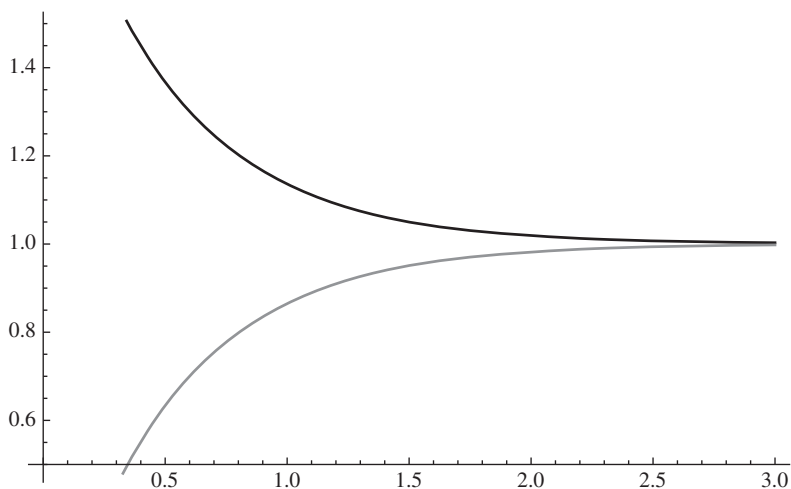
kf=1.0;kr=1.0;
Rf:=kf*XL[t]; Rr:=kr*XD[t];

Soln3=NDSolve[{ XL'[t]== -Rf+Rr,
                 XD'[t]== Rf-Rr,
                 XL[0]==2.0,XD[0]==0.001},
               {XL,XD},{t,0,3}]

{{XL->InterpolatingFunction[{{0.,3.}},<>],
  XD->InterpolatingFunction[{{0.,3.}},<>]}}
```

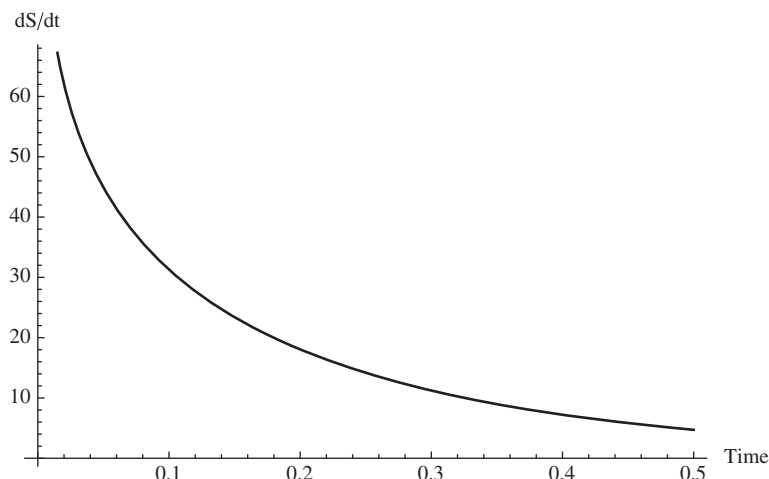
The output indicates an interpolating function has been generated. As before, the solution can be plotted.

```
Plot[Evaluate[{XL[t],XD[t]}/.Soln3},{t,0,3},
      PlotStyle->{{Black,Thick},{Gray,Thick}}]
```



The rate of entropy production can be obtained from the interpolating functions and the first equation in (9.5.20). Note: in *Mathematica*, log is ln.

```
(*Calculation of entropy production "sigma"*)
R=8.314; sigma=R*(Rf-Rr)*Log[Rf/Rr];
Plot[Evaluate[sigma/.Soln3},{t,0,0.5},
      PlotStyle->{Thick},AxesLabel->{"Time","dS/dt"}]
```



## References

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## Examples

**Example 9.1** At a temperature  $T$ , the average energy  $h\nu$  of a thermal photon is roughly equal to  $kT$ . As discussed in Chapter 2, at high temperatures electron–positron pairs will be spontaneously produced when the energy of photons is larger than rest energy  $2mc^2$  of an electron positron pair (where  $m$  is the mass of the electron). Calculate the temperature at which electron–positron pair production occurs.

**Solution** For pair production:

$$h\nu = k_B T = 2mc^2 = (2 \times 9.10 \times 10^{-31} \text{ kg})(3.0 \times 10^8 \text{ m s}^{-1})^2 = 1.64 \times 10^{-13} \text{ J}$$

Hence, the corresponding  $T = (1.64 \times 10^{-13} \text{ J}) / (1.38 \times 10^{-23} \text{ J K}^{-1}) = 1.19 \times 10^{10} \text{ K}$ .

**Example 9.2** Consider a second-order reaction  $2X \rightarrow \text{Products}$  whose rate equation is  $d[X]/dt = -2k_f[X]^2 = -k[X]^2$  in which we set  $k = 2k_f$ . (a) Show that the half-life  $t_{1/2}$  for this reaction depends on the initial value of  $[X]$  and is equal to  $1/([X]_0 k)$ . (b) Assume that  $k = 2.3 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$  and obtain the value of  $[X]$  at a time  $t = 60.0 \text{ s}$  if the initial concentration  $[X]_0 = 0.50 \text{ M}$ .

**Solution**

- a. As shown in Box 9.4, the solution to the rate equation is

$$\frac{1}{[X]} - \frac{1}{[X]_0} = kt$$

Multiplying both sides by  $[X]_0$  we obtain

$$\frac{[X]_0}{[X]} = 1 + [X]_0 kt$$

Since at  $t = t_{1/2}$  the ratio  $[X]_0/[X] = 2$ , we must have  $[X]_0 kt_{1/2} = 1$  or  $t_{1/2} = 1/([X]_0 k)$ .

- b. If the initial concentration  $[X]_0 = 0.50 \text{ M}$ ,  $k = 0.23 \text{ M}^{-1} \text{ s}^{-1}$  and  $t = 60.0 \text{ s}$  we have

$$\frac{1}{[X]} - \frac{1}{0.50} = 0.23 \times 60 \text{ mol L}^{-1}$$

Solving for  $[X]$  we get  $[X] = 0.063 \text{ mol L}^{-1}$ .

**Example 9.3** For the water dissociation reaction  $\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+$  the enthalpy of reaction  $\Delta H_r = 55.84 \text{ kJ mol}^{-1}$ . At  $25^\circ\text{C}$ , the value of the equilibrium constant  $K = 1.00 \times 10^{-14}$  and pH is 7.0. At  $50^\circ\text{C}$ , what will the pH be?

**Solution** Given  $K(T)$  at one temperature  $T_1$ , its value at another temperature  $T_2$  can be obtained using the van't Hoff equation (9.3.19):

$$\ln K(T_1) - \ln K(T_2) = \frac{-\Delta H_r}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

For this example, we have, for  $K$  at  $50^\circ\text{C}$ ,

$$\ln K = \ln(1.0 \times 10^{-14}) - \frac{55.84 \times 10^3}{8.314} \left( \frac{1}{323} - \frac{1}{298} \right) = -30.49$$

Hence,  $K$  at  $50^\circ\text{C}$  is equal to  $\exp(-30.49) = 5.73 \times 10^{-14}$ . Since the equilibrium constant  $K = [\text{OH}^-][\text{H}^+]$  and because  $[\text{OH}^-] = [\text{H}^+]$ , we have

$$\text{pH} = -\log[\text{H}^+] = -\log[\sqrt{K}] = -\frac{1}{2} \log[5.73 \times 10^{-14}] = 6.62$$

**Exercises**

- 9.1** When the average kinetic energy of molecules is nearly equal to the chemical bond energy, molecular collisions will begin to break the bonds. (a) The C–H bond energy is about  $414 \text{ kJ mol}^{-1}$ . At what temperature will the C–H bonds in methane begin to break? (b) The average binding energy per nucleon (neutron or proton) is in the range  $(6.0\text{--}9.0) \times 10^6 \text{ eV}$  or  $(6.0\text{--}9.0) \times 10^8 \text{ kJ mol}^{-1}$ . At what temperature do you expect nuclear reactions to take place?
- 9.2** For the reaction  $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$ , the activation energy  $E_a = 23.0 \text{ kJ mol}^{-1}$  and  $k_0 = 7.9 \times 10^{10} \text{ mol}^{-1} \text{ L s}^{-1}$ . What is the value of the rate constant at  $T = 300.0 \text{ K}$ ? If  $[\text{Cl}] = 1.5 \times 10^{-4} \text{ mol L}^{-1}$  and  $[\text{H}_2] = 1.0 \times 10^{-5} \text{ mol L}^{-1}$ , what is the forward reaction rate at  $T = 350.0 \text{ K}$ ?

- 9.3** For the decomposition of urea in an acidic medium, the following data were obtained for rate constants at various temperatures:

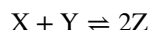
Temperature (°C)	50	55	60	65	70
Rate constant $k$ ( $10^{-8} \text{ s}^{-1}$ )	2.29	4.63	9.52	18.7	37.2

- (a) Using an Arrhenius plot, obtain the activation energy  $E_a$  and the pre-exponential factor  $k_0$ .  
 (b) Apply the transition state theory to the same data, plot  $\ln(k/T)$  versus  $1/T$  and obtain  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  of the transition state.
- 9.4** Consider the dimerization of the triphenylmethyl radical  $\text{Ph}_3\text{C}^\bullet$ , which can be written as the reaction



The forward and reverse rate constants for this reaction at 300 K are found to be  $k_f = 0.406 \text{ s}^{-1}$  and  $k_r = 3.83 \times 10^2 \text{ mol}^{-1} \text{ L s}^{-1}$ . Assume that this reaction is an elementary step. At  $t = 0$  the initial concentration of A and B are  $[\text{A}]_0 = 0.041 \text{ M}$  and  $[\text{B}]_0 = 0.015 \text{ M}$ .

- (a) What is the velocity of the reaction at  $t = 0$ ?  
 (b) If  $\xi_{\text{eq}}$  is the extent of reaction at equilibrium ( $\xi = 0$  at  $t = 0$ ), write the equilibrium concentrations of A and B in terms of  $[\text{A}]_0$ ,  $[\text{B}]_0$  and  $\xi_{\text{eq}}$ .  
 (c) Use (b) to obtain the value of  $\xi_{\text{eq}}$  by solving the appropriate quadratic equation and obtain the equilibrium concentrations of [A] and [B].
- 9.5** (a) Write the rate equations for the concentrations of X, Y and Z in the following reaction:



- (b) Write the rate equation for the extent of reaction  $\xi$ .  
 (c) When the system reaches thermal equilibrium,  $\xi = \xi_{\text{eq}}$ . If  $[\text{X}]_0$ ,  $[\text{Y}]_0$  and  $[\text{Z}]_0$  are the initial concentrations, write the equilibrium concentrations in terms of the initial concentrations and  $\xi_{\text{eq}}$ .
- 9.6** Radioactive decay is a first-order reaction. If  $N$  is the number of radioactive nuclei at any time, then  $dN/dt = -kN$ .  $^{14}\text{C}$  is radioactive with a half-life of 5730 years. What is the value of  $k$ ? For this process, do you expect  $k$  to change with temperature?
- 9.7** If  $d[\text{A}]/dt = -k[\text{A}]^\alpha$ , show that the half-life is

$$t_{1/2} = \frac{2^{\alpha-1} - 1}{(\alpha - 1)k[\text{A}]_0^{\alpha-1}}$$

- 9.8** Find an analytical solution to the reversible reaction  $[\text{L}] \xrightleftharpoons[k_r]{k_f} [\text{D}]$ , in which L and D are enantiomers. Enantiomeric excess (EE) is defined as

$$\text{EE} \equiv \frac{|[\text{L}] - [\text{D}]|}{[\text{L}] + [\text{D}]}$$

If the initial  $\text{EE} = 1.0$ , how long does it take for it to reach 0.5? (Amino acid racemization is used in dating of biological samples.)



- 9.9 (a)** For the bimolecular reaction  $A + B \xrightarrow{k_f} P$  the rate equation is

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

When  $[A]_0$  and  $[B]_0$  are the initial concentrations, show that

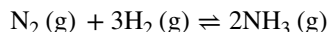
$$\frac{1}{[B]_0 - [A]_0} \ln \left( \frac{[A][B]_0}{[B][A]_0} \right) = -k_f t$$

- (b)** Write the above rate equation in terms of the extent of reaction  $\xi$  and solve it.
- 9.10** The chirping rate of crickets depends on temperature. When the chirping rate is plotted against  $1/T$  it is observed to follow the Arrhenius law (see K.J. Laidler, *J. Chem. Ed.*, **49** (1972), 343). How would you explain this observation?
- 9.11** Consider the reaction  $X + Y \rightleftharpoons 2Z$  in the gas phase. Write the reaction rates in terms of the concentrations  $[X]$ ,  $[Y]$  and  $[Z]$  as well as in terms of the activities. Find the relation between the rate constants in the two ways of writing the reaction rates.
- 9.12** When atmospheric  $\text{CO}_2$  dissolves in water it produces carbonic acid  $\text{H}_2\text{CO}_3$  (which causes natural rain to be slightly acidic). At  $25.0^\circ\text{C}$  the equilibrium constant  $K_a$  for the reaction  $\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$  is specified by  $\text{p}K_a = 6.63$ . The enthalpy of this reaction  $\Delta H_r = 7.66 \text{ kJ mol}^{-1}$ . Calculate the pH at  $25^\circ\text{C}$  and at  $35^\circ\text{C}$ . (Use Henry's law to obtain  $[\text{H}_2\text{CO}_3]$ .)
- 9.13** Equilibrium constants can vary over an extraordinary range, as the following examples demonstrate. Obtain the equilibrium constants for the following reactions at  $T = 298.15 \text{ K}$ , using the tables for  $\mu(p_0, T_0) = \Delta G_f^0$ :
- (a)**  $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$
  - (b)**  $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}_2(\text{g})$
  - (c)**  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
- 9.14 (a)** For a reaction of the form  $aX + bY \rightleftharpoons cZ$ , show that the equilibrium constants  $K_c$  and  $K_p$  are related by  $K_c = (RT)^\alpha K_p$  where  $\alpha = a + b - c$ .
- (b)** Using the definition of enthalpy  $H = U + pV$ , show that the van't Hoff equation for a gas-phase reaction can also be written as

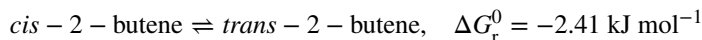
$$\frac{d \ln K_c}{dT} = \frac{\Delta U_r}{RT^2}$$

in which  $K_c$  is the equilibrium constant expressed in terms of concentrations.

- 9.15** Ammonia may be produced through the reaction of  $\text{N}_2(\text{g})$  with  $\text{H}_2(\text{g})$ :



- (a)** Calculate the equilibrium constant of this reaction at  $25^\circ\text{C}$  using the thermodynamic tables.
  - (b)** Assuming that there is no significant change in the enthalpy of reaction  $\Delta H_r$ , use the van't Hoff equation to obtain the approximate  $\Delta G_r$  and the equilibrium constant at  $400^\circ\text{C}$ .
- 9.16** 2-Butene is a gas that has two isomeric forms, cis and trans. For the reaction:



calculate the equilibrium constant at  $T = 298.15 \text{ K}$ . If the total amount of butene is  $2.5 \text{ mol}$ , then, assuming ideal gas behavior, determine the molar amounts of each isomer.

**9.17** Determine if the introduction of a catalyst will alter the affinity of a reaction or not.

**9.18** For the reaction  $A \xrightleftharpoons[k_r]{k_f} B$ , write the equation for the velocity of reaction  $d\xi/dt$  in terms of the initial values  $[A]_0$  and  $[B]_0$  and obtain the solution  $\xi(t)$ .

**9.19** For the reaction  $X + 2Y \rightleftharpoons 2Z$ , write explicitly the expression for the entropy production in terms of the rates and as a function of  $\xi$ .

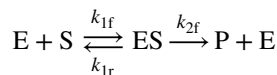
**9.20** As shown in Section 9.7, for the reaction  $A \xrightarrow{k_{1f}} B \xrightarrow{k_{2f}} C$  the extents of reaction obey the equations

$$\begin{aligned}\frac{d\xi_1}{dt} &= R_{1f} - R_{1r} = k_{1f}[A] = k_{1f}([A]_0 - \xi_1) \\ \frac{d\xi_2}{dt} &= R_{2f} - R_{2r} = k_{2f}[B] = k_{2f}([B]_0 + \xi_1 - \xi_2)\end{aligned}$$

Solve these equations with initial conditions  $\xi_1 = \xi_2 = 0$  at  $t = 0$ . Assume  $[A] = [A]_0$ ,  $[B] = 0$  and  $[C] = 0$  and show that

$$[C] = [A]_0 \left[ 1 - e^{-k_{1f}t} - \frac{k_{1f}}{k_{2f} - k_{1f}} (e^{-k_{1f}t} - e^{-k_{2f}t}) \right]$$

**9.21** Write the complete set of rate equations for all the species in the Michaelis–Menten reaction mechanism:



Write *Mathematical/Maple* code to solve them numerically with the following numerical values for the rate constants and initial values (assuming all quantities are in appropriate units):  $k_{1f} = 1.0 \times 10^2$ ,  $k_{1r} = 5.0 \times 10^3$ ,  $k_{2f} = 2.0 \times 10^3$  and, at  $t = 0$ ,  $[E] = 3.0 \times 10^{-4}$ ,  $[S] = 2 \times 10^{-2}$ ,  $[ES] = 0$ ,  $[P] = 0$ . Using the numerical solutions, check the validity of the steady-state assumption.

**9.22** Calculate  $k_0$  for the reaction between  $H_2$  and  $O_2$  at  $T = 298$  K using the bond lengths 74 pm for H–H and 121 pm for O=O.