

12

Steady-State Systems

What an organism feeds upon is negative entropy.

Erwin Schrodinger¹

The time invariance of steady-state systems depends on flows of energy, matter, and charge between the system and the surroundings. Intensive properties of such systems are not uniform but can be represented as functions of position. The net transfer of a conservative quantity, such as energy, through the boundaries of the system must be zero. Entropy is a nonconservative property and is always generated in systems undergoing flow (irreversible) processes. In processes involving steady-state systems, entropy generation is most conveniently measured as the entropy increase of the surroundings. Formulas are developed for the rate of entropy generation per unit volume in heat transfer, mechanical work, electric current, diffusion, chemical reaction, and phase transfer, in terms of flows and their conjugate forces. The flows are expressed as linear functions of the forces, including terms involving nonconjugate forces. The symmetries of the coefficients relating flows to forces, including Onsager's relation, are discussed. Forces with no conjugate flows adjust so that entropy production is a minimum in the steady state. A number of irreversible processes are considered.

12.1 Steady-State Systems

Up to this point, our thermodynamic analyses have dealt with systems at equilibrium or in transition between equilibrium states. Systems in equilibrium states have no tendency to change with time and retain this characteristic when the influence of their surroundings is removed. Steady-state systems also have no tendency to change with time. However, in the steady state, the static condition depends on the surroundings. If the interaction with the surroundings is removed, the system will change with time as it progresses toward a different static state, namely that of equilibrium. Steady-state systems may be open or closed, but not isolated. They are of great practical importance; to a good approximation, they encompass almost the entire biological world and many industrial processes.²

A steady-state system is not in equilibrium with the surroundings and may not be in internal mechanical, thermal or material equilibrium. Differences in pressure, temperature, and chemical and electrical potential between the system and surroundings are the driving forces for the bulk flow of material³ and the flow of energy, species, and charge, respectively, between the system and the surroundings. These driving forces create nonuniform thermodynamic properties within steady-state systems. Thus, although steady-state systems are unchanging in time, they are not uniform in space.

Because we have adopted the philosophy that intensive systems properties, such as temperature and pressure, are measured in the surroundings, we should consider under what conditions it is appropriate to assign such thermodynamic properties to steady-state systems. Usually, we will be able to regard a steady-state system as composed of numerous smaller systems, over each of which intensive properties can be treated as uniform, with negligible error. If these smaller systems are large enough for these properties to be statistically determined with negligible fluctuations, we can treat intensive properties as functions of positions in a steady-state system. This approach will fail if systems are far from equilibrium and properties vary abruptly with position, such as occur in some regions of flames. Although properties vary abruptly at phase boundaries, these can be handled by considering the system as composed of separate subsystems for different phases. Extensive thermodynamic properties, such as U , can be handled by treating related intensive properties, such as the molar energy, U_m or the *energy per unit volume*, u . The intensive variables are functions of position, and the energy of the entire system can be obtained by a volume integral of u over the system.

12.2 Conservative and Nonconservative Properties

Extensive quantities, such as energy, entropy, and charge, can be transported through the boundaries of both closed and open systems; chemical species can be

transported only through the boundaries of open systems. In analogy to what was done for heat and work, we will use the symbol δ to indicate a small amount of these quantities transported, with the convention that positive transport indicates transport into the system. Some quantities, such as chemical species and entropy, can also be generated within a system. We will use the symbol d_{int} to indicate a small amount of a quantity generated within a system. As usual d without a subscript indicates the change of quantity of a variable in the system. For any extensive property, X , we can write

$$dX = \sum_i \delta X_i + d_{\text{int}} X^{\text{ss}} = 0 \quad (1)$$

where a summation is included because we may want to treat transport that occurs at different boundaries separately.⁴ We have equated dX to zero because we are treating only steady-state systems, which have time-invariant properties. Rearranging gives

$$d_{\text{int}} X^{\text{ss}} = - \sum_i \delta X_i \quad (2)$$

the net X that is produced in a steady-state system must be transported out of the system.

Some extensive quantities can be neither created nor destroyed. They are called *conservative quantities*, and the d_{int} of these are zero. Among these are total mass, charge, and energy, and the mass of each element.⁵ For these quantities,

$$\sum_i \delta X_i^{\text{cons}} = 0 \quad (3)$$

Each δX_i of a conservative quantity is matched by a corresponding decrease in X in the surroundings; thus, for conservative quantities,

$$\sum_i dX_{\text{sur},i}^{\text{cons}} = 0 \quad (4)$$

(Because we deal exclusively with steady-state systems in this chapter, the “ss” designation will henceforth be omitted in equations.)

When chemical reactions occur in a system, the number of moles of the various compounds (but not the elements) may be *nonconservative*. Another very important nonconservative quantity is entropy, the production of which is the hallmark of real processes. In a steady-state system,

$$dS = d_{\text{int}} S + \sum_i \delta S_i = 0 \quad (5)$$

$$dS_{\text{univ}} = dS + \sum_i dS_{\text{sur},i} = d_{\text{int}} S + \sum_i \delta S_i + \sum_i dS_{\text{sur},i} > 0 \quad (6)$$

Although, in general, transports are not reversible, we can idealize them as being reversible from the point of view of the system. This is because, by definition, we are not interested in the details of the processes that occur in the surroundings. Thus, we can imagine heat transfer to occur from a heat reservoir, which is constructed of a material with infinite heat conductivity, so that it maintains a uniform temperature as heat is withdrawn from it. Moreover, the reservoir is in contact with the boundary of the system sufficiently long so that the boundary is at the temperature of the reservoir. In this case, the decrease of the entropy of the reservoir is exactly equal to the entropy transported to the system:

$$\delta S_i = -dS_{\text{sur},i,\text{rev}} \quad (7)$$

Because this can be idealized to occur for each transport to the system, we can write

$$d_{\text{int}}S + \sum_i (\delta S_i + dS_{\text{sur},i}) = d_{\text{int}}S > 0 \quad (8)$$

because each term in the summation is zero. Entropy is always produced in systems undergoing flow processes.

Calculation of the entropy produced in systems undergoing different flow processes (called *irreversible processes*) is key for considering steady-state systems. In order to measure the entropy produced in the system, we think of it as transported to the surroundings in a reversible manner and measure the entropy changes in the surroundings. From Eqs. (5) and (7),

$$dS_{\text{int}} = \sum_i dS_{\text{sur},i,\text{rev}} \quad (9)$$

The entropy generated in a steady-state system is the entropy added to the surroundings, if this entropy is transported in a reversible manner. This is a convenient operational principle, because the surroundings can be idealized as composed of reservoirs, each with uniform intensive properties.

12.3 Entropy Generation in Some Simple Processes in Steady-State Systems

12.3.1 Heat Flow

We consider a system of uniform area and thickness dx , between and in contact with heat reservoirs at temperatures T and $T + dT$, as shown in Fig. 1.

Because energy is conserved, the heat flows into and out of the system are equal. Using Eq. (9), we have, for the entropy generated in the system,

$$d_{\text{int}}S = \sum_i dS_{\text{sur},i,\text{rev}} = \frac{\delta q}{T + dT} - \frac{\delta q}{T} = \delta q \left(\frac{1}{T + dT} - \frac{1}{T} \right) \quad (10)$$

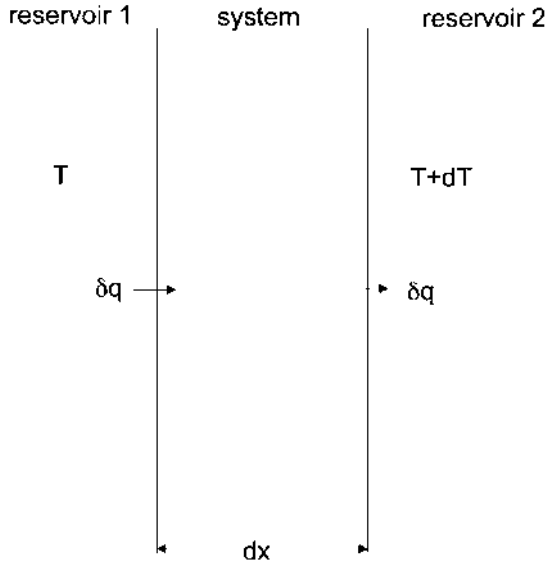


Figure 1 Heat transfer.

which can be written as

$$d_{\text{int}}S = \delta q d\left(\frac{1}{T}\right) = \delta q \frac{d(T^{-1})}{dx} dx \quad (11)$$

Of particular interest is Θ , the *rate of entropy generation per unit volume of the system*, which must always be positive:

$$\Theta \equiv \frac{1}{V} \frac{d_{\text{int}}S}{dt} > 0 \quad (12)$$

For heat transfer, this becomes

$$\Theta_q = \frac{1}{A} \frac{\delta q}{dx} \frac{d(T^{-1})}{dt} dx = J_q \frac{d(T^{-1})}{dx} \quad (13)$$

where J_q is the *heat flux* (heat flow per unit area per unit time). Readers with some exposure to vector calculus can generalize Eq. (13) to three dimensions as

$$\Theta_q = \mathbf{J}_q \cdot \nabla(T^{-1}) \quad (14)$$

where ∇ refers to the gradient of a scalar function.⁶ In this derivation, we have considered heat reservoirs, so that temperatures upstream and downstream of the system are constant during the heat flow. However, in a steady-state system, the

temperatures upstream and downstream of *any small part* of the system are constant. The results of Eqs. (13) and (14) thus hold for all parts of such systems.

The forms of Eqs. (13) and (14) are called *bilinear*, giving the entropy generation as the product of a flux and the gradient of temperature. The flux must be related to the gradient, because Θ is always positive, requiring heat flux in the opposite direction of the temperature gradient [$\nabla(T^{-1}) = -(1/T^2)\nabla T$]. We define the quantity multiplying a flux in the bilinear expression for entropy as the *force conjugate to the flux*. $\nabla(T^{-1})$ is, therefore, the “force” driving heat flux.

The *dissipation*, Φ , is defined as

$$\Phi \equiv T\Theta \quad (15)$$

and is an alternative way of defining forces (the product of a force and flux being Φ). Forces defined in this manner will differ from those used here by a factor of T . The reader should be wary of such differences in pursuing further readings in the field. The dissipation function is the rate of destruction of free energy in the system by irreversible processes.

12.3.2 Mechanical or Electrical Energy

In many industrial processes, mechanical energy is continuously added to stir a system. Because we regard mechanical energy as completely nondegraded, its addition does not transport any entropy. At the steady state, however, the input of mechanical work δw must be balanced by an equal magnitude of heat flowing to the surroundings (assumed at constant temperature T). This gives

$$\Theta_{\text{mech}} \equiv \frac{1}{V} \frac{d_{\text{int}}S}{dt} = \frac{1}{V} \frac{dS_{\text{sur,rev}}}{dt} = \frac{1}{T} \frac{1}{V} \frac{\delta w_{\text{mech}}}{dt} \quad (16)$$

where $(1/V)(\delta w_{\text{mech}}/dt)$ is the rate per unit volume at which mechanical energy is added to the system. Expression of Θ_{mech} in terms of the product of a force and a flux requires specification of additional details of the mechanical system.

Exactly similar considerations hold for electrical energy, where the volumetric production of entropy in the system is

$$\Theta_{\text{elec}} = \frac{1}{T} \frac{1}{V} \frac{\delta w_{\text{elec}}}{dt} \quad (17)$$

$\delta w_{\text{elec}}/dt$ is the electrical power dissipated by a current flow through a drop in electrical potential $d\phi$ over the system of width dx :

$$\frac{\delta w_{\text{elec}}}{dt} = -Id\phi \quad (18)$$

Substituting into Eq. (17) gives

$$\Theta_{\text{elec}} = -\frac{1}{T} \frac{I}{A} \frac{d\phi}{dx} = -\frac{J_e}{T} \left(\frac{d\phi}{dx} \right) \quad (19)$$

where J_e is the flux of electric current. Θ_{elec} must be greater than zero, indicating that current flows in the direction of decreasing electric potential. In three dimensions, Eq. (19) becomes

$$\Theta_{\text{elec}} = -\frac{\mathbf{J}_e}{T} \cdot \nabla\phi, \quad (20)$$

where $\nabla\phi$ is the gradient of the electrical potential. The force driving the flow of electric charge is therefore $-(1/T)\nabla\phi$.

12.3.3 Diffusion

Figure 2 describes diffusion of a component through a system of width dx and constant area, A . The entropy generated in the system is by Eq. (9), using Eq. (19) of [Chapter 6](#) to calculate the entropy change of the constant temperature and pressure reservoirs:

$$d_{\text{int}}S = \sum_i dS_{\text{sur},i,\text{rev}} = \frac{1}{T} (\delta q_{\text{tot},2} - \delta q_{\text{tot},1})_{\text{rev}} - \frac{1}{T} (\mu_i + d\mu_i - \mu_i) \delta n_i \quad (21)$$

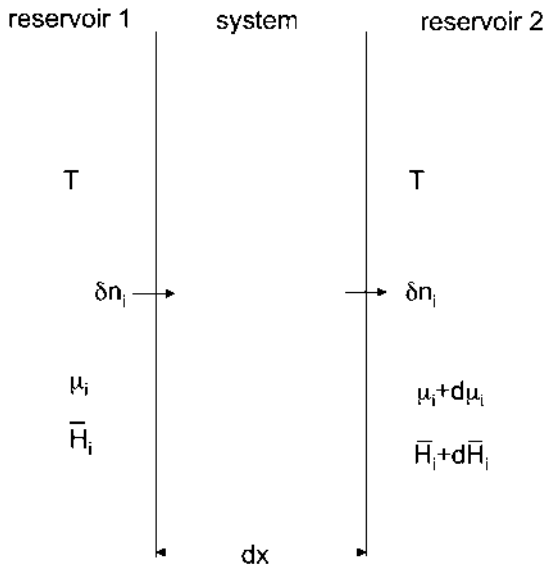


Figure 2 Diffusion.

Because P is constant, the first term is the enthalpy change of the reservoirs. However, because enthalpy is a conserved quantity in this case,⁷ this term is zero by Eq. (4), and

$$d_{\text{int}}S = -\frac{1}{T} \left(\frac{\partial \mu_i}{\partial x} \right) dx \delta n_i \quad (22)$$

$$\Theta_i \equiv \frac{1}{V} \frac{d_{\text{int}}S}{dt} = -\frac{1}{T} \left(\frac{\partial \mu_i}{\partial x} \right) \frac{\delta n_i}{A dt} = -\frac{1}{T} \left(\frac{\partial \mu_i}{\partial x} \right) J_i \quad (23)$$

where J_i is the flux of component i . In three dimensions, this becomes

$$\Theta_i = -\frac{\mathbf{J}_i}{T} \cdot \nabla \mu_i \quad (24)$$

For charged particles (ions), there is an additional electrostatic energy $z\mathcal{F}\phi$ transported, which is incorporated by using the electrochemical potential, $\tilde{\mu}_i$, defined in Eq. (35) of [Chapter 10](#). Equation (24) then becomes

$$\Theta_i = -\frac{\mathbf{J}_i}{T} \cdot \nabla \tilde{\mu}_i = \mathbf{J}_i \cdot \left(-\frac{1}{T} \nabla \tilde{\mu}_i \right) \quad (25)$$

The total entropy generation due to the diffusion of a number of species is

$$\Theta_{\text{dif}} = \sum_i \mathbf{J}_i \cdot \left(-\frac{1}{T} \nabla \tilde{\mu}_i \right) \quad (26)$$

The force driving the diffusive flow of component i is therefore $-(1/T)(\nabla \tilde{\mu}_i)_T$, where we have indicated that this result is for a constant-temperature situation.

12.3.4 Chemical Reactions and Phase Transfer

When a chemical reaction occurs in a steady-state system, products must be transferred out of the system and reactants must be transferred into the system. To avoid additional entropy generation, we take these transfers as being transfers by diffusion to reservoirs at material equilibrium with the system. The entropy generated in the system by the chemical reaction is then, by Eq. (9), the entropy increase of the reservoirs:

$$dS_{\text{int}} = \sum_i dS_{\text{sur},i} = \frac{1}{T} \sum_i \delta q_{\text{tot},\text{sur}} - \sum_i \frac{1}{T} \mu_i \delta n_i = -\frac{1}{T} \sum_i \mu_i dn_i \quad (27)$$

As discussed in Section 12.2, we can drop the first summation in a process in which enthalpy is conserved. Following Eq. (5) of [Chapter 7](#), we have $dn_i = v_i d\xi$, giving

$$dS_{\text{int}} = -\frac{1}{T} \sum_i v_i \mu_i d\xi = \frac{1}{T} A d\xi, \quad (28)$$

where $A \equiv -\sum_i v_i \mu_i$ is called the *affinity* of the chemical reaction. The volumetric rate of entropy production is then

$$\Theta_{\text{react}} = \frac{1}{T} A \frac{1}{V} \frac{d\xi}{dt} = \frac{A}{T} v_{\text{react}} \quad (29)$$

where v_{react} is the *volumetric rate of the reaction* (defined as the rate of production of a product with unit stoichiometric coefficient). A/T is, therefore, the “force” driving the chemical reaction, and “motion” of the reaction is along the coordinate of ξ , the extent of the reaction. Because the entropy generated within a system must be positive, if a single reaction can occur in a system, v_{react} is positive [i.e., toward products, if the affinity of the reaction is positive ($\Delta_{\text{react}} G = \sum_i v_i \mu_i < 0$)]. This is a generalization of a principle derived in [Chapter 7](#) for the special cases of reactions occurring at constant T and V or constant T and P .

With j chemical reactions occurring in a system, the total rate of entropy generation by chemical reactions is

$$\Theta_{\text{react}} = \sum_j (A_j/T) v_{\text{react},j} \quad (30)$$

If the reactions are independent, each term in the sum must be positive. However, if the reactions are “coupled,” most simply by having reactants and products in common, only the total entropy generation must be positive. Thus, as is well known in biochemical systems, it is possible for reactions with negative affinity (positive free-energy change) to be “driven” to products by reactions with positive affinity.

Phase transfer ($\alpha \rightarrow \beta$) can be treated exactly as for chemical reactions, with the affinity of phase transfer equal to the difference in chemical potentials of the phases:

$$A_\phi = -(\mu_\beta - \mu_\alpha) = -\Delta_\phi G \quad (31)$$

For charged particles (ions), the electrostatic energy of the transfer is incorporated by using the electrochemical potential defined in Eq. (35) of [Chapter 10](#). The electrochemical affinity is

$$\tilde{A}_\phi = -(\tilde{\mu}_\beta - \tilde{\mu}_\alpha) \quad (32)$$

and is used in Eq. (30) or (31).

12.3.5 Simultaneous Flows

As an example of simultaneous flows, we will consider simultaneous diffusion and heat transfer. This is illustrated in [Fig. 3](#).

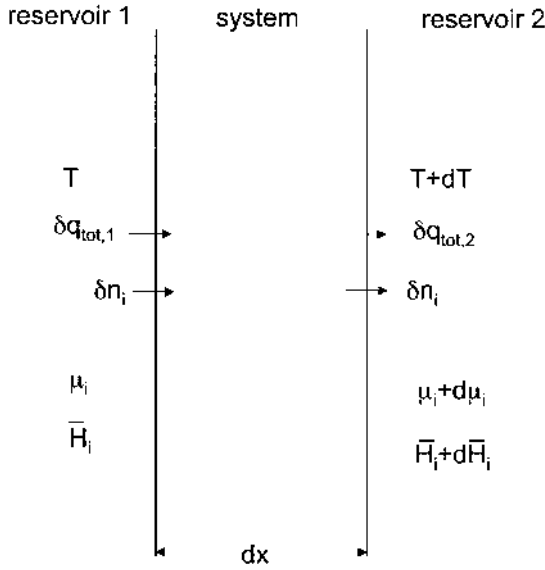


Figure 3 Simultaneous heat transfer and diffusion.

As in the previous examples, we calculate the entropy generated in the steady-state system by the entropy increase of the reservoirs:

$$\begin{aligned}
 d_{\text{int}}S &= dS_{\text{res 1,rev}} + dS_{\text{res 2,rev}} \\
 &= -\frac{1}{T}\delta q_{\text{tot 1}} - \frac{\tilde{\mu}_i}{T}(-\delta n_i) + \left[\frac{1}{T} + d\left(\frac{1}{T}\right)\right]\delta q_{\text{tot 2}} - \left[\frac{\tilde{\mu}_i}{T} + d\left(\frac{\tilde{\mu}_i}{T}\right)\right]\delta n_i
 \end{aligned} \tag{33}$$

Because enthalpy is conserved in heat transfer and diffusion, $\delta q_{\text{tot 1}} = \delta q_{\text{tot 2}} = \delta q_{\text{tot}}$, giving

$$d_{\text{int}}S = \delta q_{\text{tot}}d(1/T) - \delta n_id(\tilde{\mu}_i/T) \tag{34}$$

$$\Theta \equiv \frac{1}{V} \frac{d_{\text{int}}S}{dt} = J_{q_{\text{tot}}} \frac{d(1/T)}{dx} - J_i \frac{d(\tilde{\mu}_i/T)}{dx} \tag{35}$$

or, in three dimensions,

$$\Theta = \mathbf{J}_{q_{\text{tot}}} \cdot \nabla \left(\frac{1}{T}\right) - \mathbf{J}_i \cdot \nabla \left(\frac{\tilde{\mu}_i}{T}\right) \tag{36}$$

We write $\mathbf{J}_{q \text{ tot}} = \mathbf{J}_q + \bar{H}_i \mathbf{J}_i$ and use Eq. 12A in [Appendix A](#) to write a component of the gradient as

$$\begin{aligned} \frac{d}{dx}(T^{-1}\mu_i) = & \left(\frac{\partial(T^{-1}\mu_i)}{\partial x} \right)_{T^{-1}} + \left(\frac{\partial(T^{-1}\mu_i)}{\partial T^{-1}} \right)_x \frac{dT^{-1}}{dx} = \frac{1}{T} \left(\frac{\partial\mu_i}{\partial x} \right)_{T^{-1}} \\ & + \bar{H}_i \frac{dT^{-1}}{dx} \end{aligned} \quad (37)$$

where the Gibbs–Helmholtz equation, Eq. (29) of [Chapter 4](#), has been used in this constant-pressure system. Substituting into Eq. (35) gives⁸

$$\Theta = \mathbf{J}_q \cdot \nabla \left(\frac{1}{T} \right) - \mathbf{J}_i \cdot \frac{1}{T} (\nabla \mu_i)_T \quad (38)$$

which is the superposition of entropy generations for heat flow and diffusion, Eqs. (14) and (24). We will accept as a general principle that when a number of simultaneous irreversible processes are occurring in a system, the entropy generation and dissipation can both be written as the sum of terms, one for each of the processes, and the forms of terms are analogous to that obtained when the processes are considered individually. Either Eq. (36) or Eq. (38) can be used to analyze systems undergoing heat transfer and diffusion simultaneously. The choice is usually based on which provides a simpler calculation.

12.4 The Phenomenological Equations Relating Flows and Forces

Although it may be interesting to compare the entropy generated by various irreversible processes in a given system, in order to make real progress with the theory, we must postulate relations between the flows and forces that we have discussed in the last section. Assuming that the flows depend on the forces, we can expand the functional relationship between a flow, J_k , and the forces, X_i , in a multivariable power series:

$$J_k = J_k(0) + \sum_i L_{ki} X_i + \text{h.o.} \quad (39)$$

Because there are no flows at equilibrium, where the forces are zero, $J_k(0) = 0$. We will explore the regime, not too far from equilibrium, where the higher-order (h.o.) terms can be ignored, giving

$$J_k = \sum_i L_{ki} X_i \quad (40)$$

Flow processes have been studied experimentally for quite some time and these phenomena have often been found to follow Eq. (40). For example, Ohm's law for the flow of charge is

$$\mathbf{J}_e = -k_e \nabla \phi \quad (41)$$

where k_e is the electrical conductivity. Because, from Eq. (20), $X_e = -(1/T)\nabla\phi$, we have

$$\mathbf{J}_e = -k_e \nabla \phi = L_{ee} \left(-\frac{1}{T} \nabla \phi \right) \quad (42)$$

or

$$L_{ee} = T k_e \quad (43)$$

Similarly, for heat flow, we have Fourier's law,

$$\mathbf{J}_q = -k_q \nabla T \quad (44)$$

where k_q is the thermal conductivity. Because, from Eq. (14),

$$\begin{aligned} X_q &= \nabla(1/T) = -(1/T^2) \nabla T, \\ \mathbf{J}_q &= -k_q \nabla T = -L_{qq} \frac{1}{T^2} \nabla T \end{aligned} \quad (45)$$

or

$$L_{qq} = T^2 k_q \quad (46)$$

For diffusion, we have Fick's law:

$$\mathbf{J}_i = -D_i \nabla c_i \quad (47)$$

where D_i is the diffusion coefficient. However, the force conjugate to the diffusion flow is, from Eq. (26), $X_i = -(1/T)(\nabla\mu_i)_T$. At uniform temperature, using a 1.0 *m* standard state, this can be written as

$$X_i = -R \nabla \ln c_i = -\frac{R}{c_i} \nabla c_i \quad (48)$$

giving

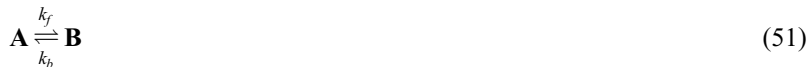
$$\mathbf{J}_i = -D_i \nabla c_i = -L_{ii} \frac{R}{c_i} \nabla c_i \quad (49)$$

from which

$$L_{ii} = \frac{c_i D_i}{R} \quad (50)$$

For some irreversible processes, it is not obvious that fluxes are proportional to thermodynamic driving forces. For example, in chemical kinetics, the

flux of a chemical reaction (its reaction rate) is expressed in terms of concentration, because it is proportional to the collision rate, whereas the thermodynamic driving force is expressed in terms of chemical potentials, which determine the affinity. However, it has been shown that near equilibrium, the kinetic and thermodynamic forms for the rates of chemical reactions become identical (i.e., both are proportional to the deviation of a concentration variable from its equilibrium value). For example, for the simple monatomic reversible reaction,



use of Eq. (40) gives

$$J_{\text{react}} = L_{\text{react}} X_{\text{react}} = L_{\text{react}} \frac{A}{T} = \frac{L_{\text{react}}}{T} (\mu_A - \mu_B) \quad (52)$$

Because at equilibrium the chemical potential of A and B are equal, this can be written as

$$\begin{aligned} J_{\text{react}} &= \frac{L_{\text{react}}}{T} [(\mu_A - \mu_{A,\text{eq}}) - (\mu_B - \mu_{B,\text{eq}})] \\ &= L_{\text{react}} R \left[\ln \left(\frac{c_A}{c_{A,\text{eq}}} \right) - \ln \left(\frac{c_B}{c_{B,\text{eq}}} \right) \right] \end{aligned} \quad (53)$$

Writing this in terms of the deviation of concentrations from their equilibrium values,

$$\Delta c_A = c_A - c_{A,\text{eq}} = -\Delta c_B = c_{B,\text{eq}} - c_B \quad (54)$$

gives

$$J_{\text{react}} = L_{\text{react}} R \left[\ln \left(1 + \frac{\Delta c_A}{c_{A,\text{eq}}} \right) - \ln \left(1 + \frac{\Delta c_B}{c_{B,\text{eq}}} \right) \right] \quad (55)$$

After expanding the logarithms in Taylor series,

$$J_{\text{react}} = L_{\text{react}} R \Delta c_A \left(\frac{1}{c_{A,\text{eq}}} + \frac{1}{c_{B,\text{eq}}} \right) \quad (56)$$

Problem 2 deals with showing that this is identical to the kinetic expression for the volumetric rate of the reaction if

$$L_{\text{react}} = \frac{k_f c_{A,\text{eq}}}{R} \quad (57)$$

This analysis suggests that, for a general reaction, the expression for L_{react} is $\text{Rate}_{\text{eq}}/R$.

12.5 Fluxes Produced by Nonconjugate Forces

Equation (40) is of the form of the multiplication of a second-order tensor by a vector. However, the equations of Ohm, Fourier, and Fick relate a flux only to its conjugate force (i.e., involve only the diagonal elements of the tensor \mathbf{L}). The question immediately arises of whether the nondiagonal elements of this tensor can be nonzero (i.e., whether a flow can depend on nonconjugate forces). There is abundant evidence that, indeed, this does occur. In [Chapter 5](#), thermal transpiration was presented as an example of a diffusive flow resulting from a temperature difference. Another example is the thermoelectric effect, on which the operation of thermocouples is based. Thus, when using Eq. (40), it is important to include the nonconjugate forces, which produce “coupling” between irreversible processes. In fact, it is in the consideration of such “nondiagonal terms” that steady-state thermodynamics provides its most interesting results.

Although nonconjugate forces must be considered, certain limitations can be placed on the coefficients in Eq. (40). This can be seen by considering the case of two forces and two flows⁹:

$$\begin{aligned}\mathbf{J}_1 &= L_{11}\mathbf{X}_1 + L_{12}\mathbf{X}_2 \\ \mathbf{J}_2 &= L_{21}\mathbf{X}_1 + L_{22}\mathbf{X}_2\end{aligned}\tag{58}$$

Suppose process 1 is heat flow and process 2 is the rate of a chemical reaction: Eqs. (58) then become

$$\begin{aligned}\mathbf{J}_q &= L_{11}\nabla\left(\frac{1}{T}\right) + L_{12}\frac{\mathbf{A}}{T} \\ J_{\text{react}} &= L_{21}\nabla\left(\frac{1}{T}\right) + L_{22}\frac{\mathbf{A}}{T}\end{aligned}$$

Now assume that we treat a case in which a chemical reaction is occurring in a system with uniform temperature, the first of Eqs. (59) becomes

$$\mathbf{J}_q = L_{12}\frac{\mathbf{A}}{T}\tag{60}$$

However, \mathbf{A} and T are scalar quantities, and because L_{12} is only a property of the medium, in an isotropic medium it must also be a scalar. Because there is no way to define a direction for the vector heat flow, $L_{12} = 0$ is required. *There can be no coupling between vector and scalar irreversible flow processes in isotropic media.*^{10,11} This is known as the Curie–Prigogine principle.

A very important relationship between the coefficients in Eq. (40) was derived by Onsager.¹² Starting with the concept of *microscopic reversibility*,¹³ Onsager treated the fluctuations around the equilibrium state. Then, reasoning

that macroscopic irreversible flows should behave in the same way as these fluctuations, he showed that

$$L_{12} = L_{21} \quad (61)$$

(i.e., *the matrix of coupling coefficients is symmetric*).

Equation (58) indicates that in order for only a single flux, \mathbf{J}_1 , to result from a force \mathbf{X}_1 , either L_{21} must be zero or \mathbf{X}_2 must be adjusted to keep \mathbf{J}_2 zero. Because we are exploring the consequences of “cross coupling,” we must assume the latter situation. An example of this was seen in [Chapter 5](#), where we used statistical mechanics to investigate thermal diffusion. Here, we had a temperature gradient, which drives a heat flux through the system. This is the only flux occurring in the system at steady state, because a pressure gradient is established that balances the tendency of molecules to diffuse under the influence of the thermal gradient. This pressure gradient is an example of an *uncontrolled force*, as it is not exerted by action external to the system.

Prigogine¹⁴ has proved an important theorem regarding uncontrolled forces in systems with single irreversible flows. To derive this theorem, we write the entropy generation in terms of forces as

$$\Theta = \mathbf{J}_1 \mathbf{X}_1 + \mathbf{J}_2 \mathbf{X}_2 = L_{11} \mathbf{X}_1^2 + (L_{12} + L_{21}) \mathbf{X}_1 \mathbf{X}_2 + L_{22} \mathbf{X}_2^2 \quad (62)$$

From this, we obtain

$$\left(\frac{\partial \Theta}{\partial \mathbf{X}_2} \right)_{\mathbf{X}_1} = (L_{12} + L_{21}) \mathbf{X}_1 + 2L_{22} \mathbf{X}_2 = 2(L_{21} \mathbf{X}_1 + L_{22} \mathbf{X}_2) = 2\mathbf{J}_2 \quad (63)$$

because $L_{12} = L_{21}$. Thus, for a given value of the controlled force, \mathbf{X}_1 , the variation of entropy generation with respect to the uncontrolled force, \mathbf{X}_2 , is proportional to the flux conjugate to the uncontrolled force. When this flux is zero, $(\partial \Theta / \partial \mathbf{X}_2)_{\mathbf{X}_1} = 0$ (i.e., the entropy generation is an extremum). Because entropy generation is always positive, the single extremum is a minimum. *In steady-state systems, uncontrolled forces with zero conjugate fluxes adjust so that entropy production is a minimum.* This is the principle of minimum entropy production first developed by Prigogine.

12.6 Thermal Diffusion

In Chapter 5, we used an approach based on microscopic velocity distributions to investigate the ideal gas pressure difference established between two chambers held at different temperatures at steady state. The chambers were separated by a partition containing a hole small enough that effusive flow existed between the chambers. We will now apply steady-state thermodynamics to the same system. Because, in Eq. (62) of Chapter 5, we calculated the total energy flow between the

chambers, we will analyze the problem using the approach of Eq. (36) (where the fluxes are taken as the mass flow and the *total* energy flow). We write Eq. (58) as

$$\begin{aligned}\mathbf{J}_{q \text{ tot}} &= L_{qq} \nabla \left(\frac{1}{T} \right) - L_{qi} \nabla \left(\frac{\mu}{T} \right) \\ \mathbf{J}_i &= L_{iq} \nabla \left(\frac{1}{T} \right) - L_{ii} \nabla \left(\frac{\mu}{T} \right)\end{aligned}\tag{64}$$

In thermal transpiration, we have a flow of energy, but no flow of matter; therefore, $\mathbf{J}_i = 0$ and

$$\nabla \left(\frac{\mu}{T} \right) = \frac{L_{iq}}{L_{ii}} \nabla \left(\frac{1}{T} \right)\tag{65}$$

For a one-dimensional system, we can substitute the differential for the gradient:

$$d \left(\frac{\mu}{T} \right) = \mu d \left(\frac{1}{T} \right) + \frac{1}{T} d\mu = \frac{L_{iq}}{L_{ii}} d \left(\frac{1}{T} \right) = \frac{L_{qi}}{L_{ii}} d \left(\frac{1}{T} \right)\tag{66}$$

the last step resulting from the application of Onsager's relation [Equation (61)]. Substituting for the chemical potential,

$$(H_m - TS_m) \left(-\frac{1}{T^2} \right) dT + \left(\frac{1}{T} \right) (V_m dP - S_m dT) = -\frac{L_{qi}}{L_{ii} T^2} dT\tag{67}$$

$$\left(\frac{L_{qi}}{L_{ii}} - H_m \right) \frac{dT}{T^2} = -R \frac{dP}{P}\tag{68}$$

where use has been made of the ideal gas equation. The quantity $L_{qi}/L_{ii} \equiv Q^*$ is the *energy of transport*, the total energy transported per mole of gas that passes through the hole connecting the chambers. In Eq. (62) of [Chapter 5](#), this was shown to be $2RT$. The molar enthalpy of these molecules is $(5/2)RT$, giving

$$\frac{1}{2} \frac{dT}{T} = \frac{dP}{P}\tag{69}$$

Upon integration, we get

$$\frac{P_1}{P_2} = \sqrt{\frac{T_1}{T_2}}\tag{70}$$

which is identical to the result obtained in Eq. (65) of Chapter 5.

A solution normally has uniform concentration. However, if a temperature gradient is established in a solution, a concentration gradient will result, a

phenomenon that is called the *Soret effect*. For analysis, we employ Eq. (58), which in a binary solution leads to the coupled flux equations:

$$\begin{aligned}\mathbf{J}_q &= L_{qq} \nabla \left(\frac{1}{T} \right) - L_{qi} \frac{1}{T} (\nabla \mu_i)_T - L_{qA} \frac{1}{T} (\nabla \mu_A)_T \\ \mathbf{J}_i &= L_{iq} \nabla \left(\frac{1}{T} \right) - L_{ii} \frac{1}{T} (\nabla \mu_i)_T - L_{iA} \frac{1}{T} (\nabla \mu_A)_T \\ \mathbf{J}_A &= L_{Aq} \nabla \left(\frac{1}{T} \right) - L_{Ai} \frac{1}{T} (\nabla \mu_i)_T - L_{AA} \frac{1}{T} (\nabla \mu_A)_T\end{aligned}\quad (71)$$

where A is the solvent and i is the solute.

Using the Gibbs–Duhem equation [Chapter 8, Eq. (15)] in the form

$$(\nabla \mu_A)_T = - \frac{x_i}{x_A} (\nabla \mu_i)_T = - \frac{c_i}{c_A} (\nabla \mu_i)_T \quad (72)$$

and applying the second of Eqs. (71) to the case of no material flux through the system, gives, with the use of Onsager's relation,

$$L_{iq} \nabla \left(\frac{1}{T} \right) = \frac{1}{T} \left(L_{ii} - \frac{c_i}{c_A} L_{Ai} \right) (\nabla \mu_i)_T \quad (73)$$

We note that

$$\mathbf{J}_i - \frac{c_i}{c_A} \mathbf{J}_A = c_i \left(\frac{\mathbf{J}_i}{c_i} - \frac{\mathbf{J}_A}{c_A} \right) = c_i (\mathbf{v}_i - \mathbf{v}_A) \equiv c_i \mathbf{v}_i^{\text{rel}} \equiv \mathbf{J}_i^{\text{rel}} \quad (74)$$

where $\mathbf{v}_i^{\text{rel}}$ and $\mathbf{J}_i^{\text{rel}}$ are the velocity and flux of the solute relative to the solvent. Equation (73) can therefore be written as

$$L_{iq} \nabla \left(\frac{1}{T} \right) = \frac{1}{T} L_{it}^{\text{rel}} (\nabla \mu_i)_T \quad (75)$$

where L_{it}^{rel} is the relative coupling constant in the case of a pure heat flow.

Using a 1.0 M standard state for chemical potentials, this becomes, for one-dimensional variation,

$$L_{iq} \frac{dT^{-1}}{dx} = L_{it}^{\text{rel}} R \frac{d \ln c_i}{dx} \quad (76)$$

Making use of Onsager's relation and rearranging,

$$\frac{d \ln c_i}{dT^{-1}} = \frac{L_{qi}}{RL_{it}^{\text{rel}}} = \frac{Q^*}{R} \quad (77)$$

which shows obvious similarity to the Clausius–Clapeyron equation [Eq. (44), Chapter 6].

12.7 Thermoelectric Effects

The most familiar thermoelectric effect is the generation of Ohmic heat due to current flow, discussed in Section 12.3.2. Less well known is the Thomson heat, produced or absorbed when a current flows in a temperature gradient. The *Thomson coefficient*, σ , can be defined as

$$\sigma \equiv -\frac{\delta q}{\delta Q dT} \quad (78)$$

It is the heat emitted per unit charge passing through unit temperature difference. This is a reversible effect; identical heat must be absorbed if the charge passes through the temperature gradient in the opposite direction.

There are also two well-known thermoelectric effects resulting from the joining of dissimilar materials (forming a junction): the *Seebeck effect*, on which thermocouples are based, and the *Peltier effect*, used for thermopiles. The Seebeck effect results when the two junctions of the dissimilar materials are held at different temperatures. The *Seebeck coefficient*, ϵ , is defined as the open-circuit voltage generated per unit temperature differential of the two junctions:

$$\epsilon \equiv \left(\frac{\partial \phi}{\partial T} \right)_{J_{\text{elec}}=0} \quad (79)$$

The *Peltier effect*, on which thermopiles are based, is the heat released or taken up when a current flows through an isothermal junction. In a thermopile, the current flows in the opposite direction through the two junctions and, thus, transfers heat from one junction to the other. The *Peltier coefficient*, Π , is defined as the heat absorbed per unit charge flow:

$$\Pi \equiv \frac{\delta q}{\delta Q} \Big|_T = \left(\frac{\partial J_q}{\partial J_{\text{elec}}} \right)_T \quad (80)$$

Thomson applied the first law of thermodynamics to a virtual charge of magnitude δQ passing through the circuit at equilibrium shown in Fig. 4. Equating the reversible work needed to drive the charge to the heat emitted gives

$$\delta w_{\text{rev}} = \delta Q d\phi = \Pi(T + dT)\delta Q - \Pi(T)\delta Q + (\sigma_A - \sigma_B) \delta Q dT \quad (81)$$

or

$$\frac{d\phi}{dT} = \frac{d\Pi}{dT} + (\sigma_A - \sigma_B) \quad (82)$$

Note that when there is no temperature gradient, the Thomson effect vanishes and the Peltier effects cancel. By considering the test charge to flow in infinite time,

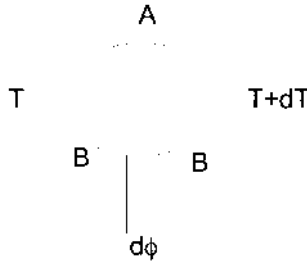


Figure 4 Thomson's circuit.

the current and the Ohmic heat go to zero and the potential becomes that for the open circuit, which is how the Seebeck coefficient is defined. We get

$$\epsilon = \frac{d\Pi}{dT} + (\sigma_A - \sigma_B) \quad (83)$$

which is Thomson's equation. Additional results can be obtained from the equations for coupled heat and charge flows:

$$\begin{aligned} \mathbf{J}_q &= L_{qq} \nabla \left(\frac{1}{T} \right) - \frac{L_{qe}}{T} \nabla \phi \\ \mathbf{J}_e &= L_{eq} \nabla \left(\frac{1}{T} \right) - \frac{L_{ee}}{T} \nabla \phi \end{aligned} \quad (84)$$

The Peltier coefficient is obtained by dropping the temperature gradient terms:

$$\Pi = \left. \frac{\mathbf{J}_q}{\mathbf{J}_e} \right|_{\nabla T=0} = \frac{L_{qe}}{L_{ee}} \quad (85)$$

The Seebeck coefficient results from setting the electric current equal to zero:

$$0 = -\frac{L_{eq}}{T^2} \left(\frac{\partial T}{\partial x} \right)_{\mathbf{J}_e=0} - \frac{L_{ee}}{T} \left(\frac{\partial \phi}{\partial x} \right)_{\mathbf{J}_e=0} \quad (86)$$

$$\epsilon \equiv \left(\frac{\partial \phi}{\partial T} \right)_{\mathbf{J}_e=0} = -\frac{L_{eq}}{L_{ee} T} = -\frac{L_{qe}}{L_{ee} T} = -\frac{\Pi}{T} \quad (87)$$

where we have used Onsager's equation in the next to last step.

Questions

1. Can a steady-state system that is not in equilibrium with its surroundings be in internal mechanical, thermal, and material equilibrium?

2. Apply Eq. (1) to the total mass of carbon in the atmosphere
 - (a) over a short time period (days)
 - (b) over a long time period (decades).
3. How would you obtain the internal energy, U , of a steady-state system from u_m , the energy per unit mass as a function of position in the system?
4. Must each irreversible process occurring in a steady-state system produce entropy?
5. What are the forces conjugate to the flux of heat, electric current, diffusion and chemical reaction if the dissipation function is used to define the forces?
6. If mechanical energy enters a system at a shaft of radius R , which rotates at an angular velocity, ω , exerting a torque, τ , what is the mechanical energy flux added to the system? What is the force conjugate to this flux?
7. The second law of thermodynamics not only gives us a direction for time but also gives us a macroscopic explanation for the direction for irreversible processes in steady-state systems. For heat flow and diffusion, give a *microscopic* reason why the flows are in the direction opposite to the gradient of temperature and concentration, respectively.
8. If a temperature gradient is established across a single chamber, will there be a resulting pressure gradient, as we obtained for the case of thermal transpiration? Why are different results obtained in these two cases?
9. If a temperature gradient is established in a two-chamber system, with the chambers connected by an orifice through which Joule–Thomson type flow occurs, will there be a resulting pressure gradient? Explain your answer?
10. Discuss similarities and differences between Eq. (77) and the Clausius–Clapeyron equation and the phenomena underlying each of these.
11. A reservoir of saltwater and a reservoir of pure water are connected by a tube. The system is well insulated so that no heat transfer will occur between it and the surroundings or directly between the two reservoirs. Describe what will happen.
12. Which of the following must be zero: $L_{\text{react},i}$, $L_{\text{react},q}$, and $L_{q,i}$?
13. If a chemical reaction cannot couple with heat flow in an isotropic medium, how does the heat produced in an exothermic reaction get out of the system?
14. Give a *microscopic* explanation for the Seebeck effect and for Thomson heat generation.

Problems

1. Show that enthalpy is not a conserved quantity in a steady-state system when an electric current is flowing. (Compare with Note 7.)
2. The chemical kinetics expression for the rate of the chemical reaction given in Eq. (51) is $J_B \equiv dc_B/dt = k_f c_A - k_b c_B$. Show that the requirement that the thermodynamic reaction

flux, Eq. (52), be the same as that given by chemical kinetics is that L_{react} be given by Eq. (57), for the case of reversible first-order reactions.

3.* Solve Eq. (58) for the forces in terms of J_1 and J_2 and express Θ in terms of the flows only. Show that, with Onsager's relation, $(\partial\Theta/\partial J_1)_{J_2} = 2X_1$ and $(\partial\Theta/\partial J_2)_{J_1} = 2X_2$.

4. A mixture of He and Ne is held in a one-dimensional temperature gradient. The mole fraction of He is 0.500, where the temperature is 373 K, and the mole fraction of He is 0.512, where the temperature is 288 K. Estimate the heat of transfer for diffusion of He through Ne.

Notes

1. E. Schrodinger. What Is Life? Cambridge: Cambridge University Press, 1974, p 76.
2. Assuming that the rate of change of the biological system or the industrial reactor can be neglected.
3. We will not consider bulk flow in this volume.
4. In cases in which there is continuous variation of the transport over the boundary of the system, integration, rather than summation, is required.
5. In the realm of chemistry, where nuclear transformations are not considered.
6. In Cartesian coordinates, with unit vectors, $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$, and $\hat{\mathbf{k}}$,

$$\nabla f = \hat{\mathbf{i}} \frac{df}{dx} + \hat{\mathbf{j}} \frac{df}{dy} + \hat{\mathbf{k}} \frac{df}{dz}$$

Boldface type indicates vector quantities.

7. Because U is always conserved, $\Delta U_1 + \Delta U_2 = 0$ in a steady-state process. Because the boundaries of the system and pressure are unchanging $\Delta(PV)_1 + \Delta(PV)_2$ is also zero.
8. Constant T^{-1} implies constant T .
9. The forces and flows are written in boldface because they may be vector quantities, as is the case with heat flow and diffusion.
10. Such coupling is possible in anisotropic media, such as in active transport at membranes in biological systems.
11. In general, there can be no coupling between flow processes represented by tensors of different orders.
12. Lars Onsager, Nobel laureate.
13. Microscopic processes are reversible, because they depend on Newton's laws of motion, which contain only a *second* derivative with respect to time.
14. Ilya Prigogine, Nobel prize in chemistry, 1977.