

14

IRREVERSIBLE THERMODYNAMICS

14-1 GENERAL REMARKS

As useful as the characterization of equilibrium states by thermostatic theory has proven to be, it must be conceded that our primary interest is frequently in processes rather than in states. In biology, particularly, it is the life process that captures our imagination, rather than the eventual equilibrium state to which each organism inevitably proceeds. Thermostatistics does provide two methods that permit us to infer some limited information about processes, but each of these methods is indirect and each yields only the most meager return. First, by studying the initial and terminal equilibrium states it is possible to bracket a process and thence to determine the effect of the process in its totality. Second, if some process occurs *extremely* slowly, we may compare it with an idealized, nonphysical, quasistatic process. But neither of these methods confronts the central problem of *rates* of real physical processes.

The extension of thermodynamics that has reference to the rates of physical processes is the theory of *irreversible thermodynamics*.

Irreversible thermodynamics is based on the postulates of equilibrium thermostatics plus the additional postulate of *time reversal symmetry of physical laws*. This additional postulate states that *the laws of physics remain unchanged if the time t is everywhere replaced by its negative $-t$, and if simultaneously the magnetic field B_e is replaced by its negative $-B_e$* (and, if the process of interest is one involving the transmutation of fundamental particles, that the charge and "parity" of the particles also be reversed in sign). For macroscopic processes the parenthetical restriction has no observable consequences, and we shall henceforth refer to time reversal symmetry in its simpler form.

The thermodynamic theory of irreversible processes is based on the Onsager Reciprocity Theorem, formulated by Lars Onsager¹ in brilliant

¹Lars Onsager, *Physical Review* 37, 405 (1931); 38, 2265 (1931).

pioneering papers published in 1931, but not widely recognized for almost 20 years thereafter. Powerful statistical mechanical theorems also exist; the “fluctuation-dissipation theorem”,² the “Kubo relations,” and the formalism of “linear response theory” based on the foregoing theorems³. We review only the thermodynamic theory, rooted in the Onsager theorem.

14-2 AFFINITIES AND FLUXES

Preparatory to our discussion of the Onsager theorem, we define certain quantities that appropriately describe irreversible processes. Basically we require two types of parameters: one to describe the “force” that drives a process and one to describe the response to this force.

The processes of most general interest occur in continuous systems, such as the flow of energy in a bar with a continuous temperature gradient. However, to suggest the proper way to choose parameters in such continuous systems, we first consider the relatively simple case of a discrete system. A typical process in a discrete system would be the flow of energy from one homogeneous subsystem to another through an infinitely thin diathermal partition.

Consider a composite system composed of two subsystems. An extensive parameter has values X_k and X'_k in the two subsystems, and the closure condition requires that

$$X_k + X'_k = X_k^{\circ}, \quad \text{a constant} \quad (14.1)$$

If X_k and X'_k are unconstrained, their equilibrium values are determined by the vanishing of the quantity

$$\mathcal{F}_k \equiv \left(\frac{\partial S^{\circ}}{\partial X_k} \right)_{X_k^{\circ}} = \left(\frac{\partial (S + S')}{\partial X_k} \right)_{X_k^{\circ}} = \frac{\partial S}{\partial X_k} - \frac{\partial S'}{\partial X'_k} = F_k - F'_k \quad (14.2)$$

Thus, if \mathcal{F}_k is zero the system is in equilibrium, but if \mathcal{F}_k is nonzero an irreversible process occurs, taking the system toward the equilibrium state. The quantity \mathcal{F}_k , which is the difference in the entropy-representation intensive parameters, acts as a “generalized force” which “drives” the process. Such generalized forces are called *affinities*.

²H. Callen and T. Welton, *Phys. Rev.* **83**, 34 (1951).

³c.f. R. Kubo, *Lectures in Theoretical Physics*, vol. 1 (Interscience, New York, 1959, p. 120–203.)

For definiteness, consider two systems separated by a diathermal wall, and let X_k be the energy U . Then the affinity is

$$\mathcal{F}_k = \frac{1}{T} - \frac{1}{T'} \quad (14.3)$$

No heat flows across the diathermal wall if the difference in inverse temperatures vanishes. But a nonzero difference in inverse temperature, acting as a generalized force, drives a flow of heat between the subsystems.

Similarly, if X_k is the volume the affinity \mathcal{F}_k is $[P/T - (P'/T')]$, and if X_k is a mole number the associated affinity is $[\mu'_k/T' - (\mu_k/T)]$.

We characterize the response to the applied force by the rate of change of the extensive parameter X_k . The flux J_k is then defined by

$$J_k \equiv \frac{dX_k}{dt} \quad (14.4)$$

Therefore, the flux vanishes if the affinity vanishes, and a nonzero affinity leads to a nonzero flux. It is the relationship between fluxes and affinities that characterizes the rates of irreversible processes.

The identification of the affinities in a particular type of system is frequently rendered more convenient by considering the rate of production of entropy. Differentiating the entropy $S(X_0, X_1, \dots)$ with respect to the time, we have

$$\frac{dS}{dt} = \sum_k \frac{\partial S}{\partial X_k} \frac{dX_k}{dt} \quad (14.5)$$

or

$$\dot{S} = \sum_k \mathcal{F}_k J_k \quad (14.6)$$

Thus *the rate of production of entropy is the sum of products of each flux with its associated affinity.*

The entropy production equation is particularly useful in extending the definition of affinities to continuous systems rather than to discrete systems. If heat flows from one homogeneous subsystem to another, through an infinitely thin diathermal partition, the generalized force is the difference $[1/T - (1/T')]$; but if heat flows along a metal rod, in which the temperature varies in a continuous fashion, it is difficult to apply our previous definition of the affinity. Nevertheless we can compute the rate of production of entropy, and thereby we can identify the affinity.

With the foregoing considerations to guide us, we now turn our attention to continuous systems. We consider a three-dimensional system in

which energy and matter flow, driven by appropriate forces. We choose the components of the vector current densities of energy and matter as fluxes. Thus, associated with the energy U we have the three energy fluxes J_{ox}, J_{oy}, J_{oz} . These quantities are the x , y , and z components of the vector current density \mathbf{J}_o . By definition the magnitude of \mathbf{J}_o is the amount of energy that flows across the unit area in unit time, and the direction of \mathbf{J}_o is the direction of this energy flow. Similarly, the current density \mathbf{J}_k may describe the flow of a particular chemical component per unit area and per unit time; the components $J_{kx}, J_{ky},$ and J_{kz} are fluxes.

In order to identify the affinities, we now seek to write the rate of production of entropy in a form analogous to equation 14.6. One problem that immediately arises is that of defining entropy in a nonequilibrium system. This problem is solved in a formal manner as follows.

To any infinitesimal region we associate a local entropy $S(X_0, X_1, \dots)$, where, *by definition, the functional dependence of S on the local extensive parameters X_0, X_1, \dots is taken to be identical to the dependence in equilibrium.* That is, we merely adopt the equilibrium fundamental equation to associate a local entropy with the local parameters X_0, X_1, \dots . Then

$$dS = \sum_k F_k dX_k \quad (14.7)$$

or, taking all quantities per unit volume,⁴

$$ds = \sum_k F_k dx_k \quad (14.8)$$

The summation in this equation omits the term for volume and consequently has one less term than that in equation 14.7.

Again, the local intensive parameter F_k is taken to be the same function of the local extensive parameters as it would be in equilibrium. It is because of this convention, incidentally, that we can speak of the temperature varying continuously in a bar, despite the fact that thermostatics implies the existence of temperature only in equilibrium systems.

Equation 14.7 immediately suggests a reasonable definition of the entropy current density \mathbf{J}_S

$$\mathbf{J}_S = \sum F_k \mathbf{J}_k \quad (14.9)$$

in which \mathbf{J}_k is the current density of the extensive parameter X_k . The magnitude of the entropy flux \mathbf{J}_S is the entropy transported through unit area per unit time.

⁴It should be noted that in the remainder of this chapter we use lowercase letters to indicate extensive parameters *per unit volume* rather than *per mole*.

The rate of local production of entropy is equal to the entropy leaving the region, plus the rate of increase of entropy within the region. If \dot{s} denotes the rate of production of entropy per unit volume and $\partial s/\partial t$ denotes the increase in entropy per unit volume, then

$$\dot{s} = \frac{\partial s}{\partial t} + \nabla \cdot \mathbf{J}_s \quad (14.10)$$

If the extensive parameters of interest are *conserved*, as are the energy and (in the absence of chemical reactions) the mole numbers, the equations of continuity for these parameters become

$$0 = \frac{\partial x_k}{\partial t} + \nabla \cdot \mathbf{J}_k \quad (14.11)$$

We are now prepared to compute \dot{s} explicitly and thence to identify the affinities in continuous systems.

The first term in equation 14.10 is easily computed from equation 14.8.

$$\frac{\partial s}{\partial t} = \sum_k F_k \frac{\partial x_k}{\partial t} \quad (14.12)$$

The second term in equation 14.10 is computed by taking the divergence of equation 14.9

$$\nabla \cdot \mathbf{J}_s = \nabla \cdot \left(\sum_k F_k \mathbf{J}_k \right) = \sum_k \nabla F_k \cdot \mathbf{J}_k + \sum_k F_k \nabla \cdot \mathbf{J}_k \quad (14.13)$$

Thus equation 14.10 becomes

$$\dot{s} = \sum_k F_k \frac{\partial x_k}{\partial t} + \sum_k \nabla F \cdot \mathbf{J}_k + \sum_k F_k \nabla \cdot \mathbf{J}_k \quad (14.14)$$

Finally, by equation 14.11, we observe that the first and third terms cancel, giving

$$\dot{s} = \sum_k \nabla F_k \cdot \mathbf{J}_k \quad (14.15)$$

Although the affinity is defined as the difference in the entropy-representation intensive parameters for discrete systems, it is the gradient of the entropy-representation intensive parameters in continuous systems.

If \mathbf{J}_{oz} denotes the z component of the energy current density, the associated affinity \mathcal{F}_{oz} is $\nabla_z(1/T)$, the z component of the gradient of the inverse temperature. And if \mathbf{J}_k denotes the k th mole number current

density (the number of moles of the k th component flowing through unit area per second), the affinity associated with J_{kz} is $\mathcal{F}_{kz} = -\nabla_z(\mu_k/T)$.

14-3 PURELY RESISTIVE AND LINEAR SYSTEMS

For certain systems the fluxes at a given instant depend only on the values of the affinities at that instant. Such systems are referred to as "purely resistive."

For other than purely resistive systems the fluxes may depend upon the values of the affinities at previous times as well as upon the instantaneous values. In the electrical case a "resistor" is a purely resistive system, whereas a circuit containing an inductance or a capacitance is not purely resistive. A non-purely-resistive system has a "memory."

Although it might appear that the restriction to purely resistive systems is very severe, it is found in practice that a very large fraction of the systems of interest, other than electrical systems, are purely resistive. Extensions to non-purely-resistive systems do exist, based on the fluctuation-dissipation theorem or Kubo formula referred to in Section 14.1.

For a purely resistive system, by definition, each local flux depends only upon the instantaneous local affinities and upon the local intensive parameters. That is, dropping the indices denoting vector components

$$J_k = J_k(\mathcal{F}_0, \mathcal{F}_1, \dots, \mathcal{F}_j, \dots; F_0, F_1, \dots, F_j, \dots) \quad (14.16)$$

Thus, the local mole number current density of the k th component depends on the gradient of the inverse temperature, on the gradients of μ_j/T for each component, and upon the local temperature, pressure, and so forth. It should be noted that we do not assume that each flux depends only on its own affinity but rather that each flux depends on *all* affinities. It is true that each flux tends to depend most strongly on its own associated affinity, but the dependence of a flux on other affinities as well is the source of some of the most interesting phenomena in the field of irreversibility.

Each flux J_k is known to vanish as the affinities vanish, so we can expand J_k in powers of the affinities with no constant term

$$J_k = \sum_j L_{jk} \mathcal{F}_j + \frac{1}{2!} \sum_i \sum_j L_{ijk} \mathcal{F}_i \mathcal{F}_j + \dots \quad (14.17)$$

where

$$L_{jk} = \left(\frac{\partial J_k}{\partial \mathcal{F}_j} \right)_0 \quad (14.18)$$

and

$$L_{ijk} = \left(\frac{\partial^2 J_k}{\partial \mathcal{F}_i \partial \mathcal{F}_j} \right)_0 \quad (14.19)$$

The functions L_{jk} are called *kinetic coefficients*. They are functions of the local intensive parameters

$$L_{jk} = L_{jk}(F_0, F_1, \dots) \quad (14.20)$$

The functions L_{ijk} are called *second-order kinetic coefficients*, and they are also functions of the local intensive parameters. Third-order and higher-order kinetic coefficients are similarly defined.

For the purposes of the Onsager theorem, which we are about to enunciate, it is convenient to adopt a notation that exhibits the functional dependence of the kinetic coefficients on an externally applied magnetic field \mathbf{B}_e , suppressing the dependence on the other intensive parameters

$$L_{jk} = L_{jk}(\mathbf{B}_e) \quad (14.21)$$

The Onsager theorem states that

$$L_{jk}(\mathbf{B}_e) = L_{kj}(-\mathbf{B}_e) \quad (14.22)$$

That is, the value of the kinetic coefficient L_{jk} measured in an external magnetic field \mathbf{B}_e is identical to the value of L_{kj} measured in the reversed magnetic field $-\mathbf{B}_e$.

The Onsager theorem states a symmetry between the linear effect of the j th affinity on the k th flux and the linear effect of the k th affinity on the j th flux when these effects are measured in opposite magnetic fields.

A situation of great practical interest arises if the affinities are so small that all quadratic and higher-order terms in equation 14.17 can be neglected. A process that can be adequately described by the truncated approximate equations

$$J_k = \sum_j L_{jk} \mathcal{F}_j \quad (14.23)$$

is called a *linear* purely resistive process. For the analysis of such processes the Onsager theorem is a particularly powerful tool.

It is perhaps surprising that so many physical processes of interest are linear. But the affinities that we commonly encounter in the laboratory are quite small in the sense of equation 14.17, and we therefore recognize that we generally deal with systems that deviate only slightly from equilibrium.

Phenomenologically, it is found that the flow of energy in a thermally conducting body is proportional to the gradient of the temperature. Denoting the energy current density by \mathbf{J}_o , we find that experiment yields the linear law

$$\mathbf{J}_o = -\kappa \nabla T \quad (14.24)$$

in which κ is the thermal conductivity of the body. We can rewrite this in the more appropriate form

$$\mathbf{J}_{oz} = \kappa T^2 \nabla_z \left(\frac{1}{T} \right) \quad (14.25)$$

and similarly for x and y components, and we see that (κT^2) is the kinetic coefficient. The absence of higher-order terms, such as $[\nabla(1/T)]^2$ and $[\nabla(1/T)]^3$, in the phenomenological law shows that commonly employed temperature gradients are small in the sense of equation 14.17.

Ohm's law of electrical conduction and Fick's law of diffusion are other linear phenomenological laws which demonstrate that for the common values of the affinities in these processes higher-order terms are negligible. On the other hand, both the linear region and the nonlinear region can be realized easily in chemical systems, depending upon the deviations of the molar concentrations from their equilibrium values. Although the class of linear processes is sufficiently common to merit special attention, it is by no means all inclusive, and the Onsager theorem is *not* restricted to this special class of systems.

14-4 THE THEORETICAL BASIS OF THE ONSAGER RECIPROCIDY

The Onsager reciprocity theorem has been stated but not proved in the preceding sections. Before turning to applications in the following sections we indicate the relationship of the theorem to the underlying principle of time reversal symmetry of physical laws.

From the purely thermodynamic point of view, the extensive parameters of a system in contact with a reservoir are constants. In fact, if an extensive parameter (such as the energy) is permitted to flow to and from a reservoir, it does so in continual spontaneous fluctuations. These fluctuations tend to be very rapid, and macroscopic observations average over the fluctuations (as discussed in some detail in Chapter 1). Occasionally a large fluctuation occurs, depleting the energy of the system by a non-negligible amount. If the system were to be decoupled from the reservoir before this rare large fluctuation were to decay, we would then associate a lower temperature to the system. But if the system were *not* decoupled,

the fluctuation would decay by the spontaneous flow of energy from the reservoir to the system.

Onsager connected the theory of macroscopic processes to thermodynamic theory by the assumption that *the decay of a spontaneous fluctuation is identical to the macroscopic process of flow of energy or other analogous quantity between the reservoir and the system of depleted energy.*

We consider a system in equilibrium with a pair of reservoirs corresponding to the extensive parameters X_j and X_k . Let the instantaneous values of these parameters be denoted by \hat{X}_j and \hat{X}_k , and let $\delta\hat{X}_j$ denote the deviation of \hat{X}_j from its average value. Thus $\delta\hat{X}_j$ describes a fluctuation, and the average value of $\delta\hat{X}_j$ is zero. Nevertheless the average value of $(\delta\hat{X}_j)^2$, denoted by $\langle(\delta\hat{X}_j)^2\rangle$, is not zero. Nor is the correlation moment $\langle\delta\hat{X}_j\delta\hat{X}_k\rangle$. A very slight extension of the thermodynamic formalism, invoking only very general features of statistical mechanics, permits exact evaluation of the correlation moments of the fluctuations (as we shall see in Chapter 19).

More general than the correlation moment $\langle\delta\hat{X}_j\delta\hat{X}_k\rangle$ is the *delayed correlation moment* $\langle\delta\hat{X}_j\delta\hat{X}_k(\tau)\rangle$, which is the average product of the deviations $\delta\hat{X}_j$ and $\delta\hat{X}_k$, with the latter being observed a time τ after the former. It is this delayed correlation moment upon which Onsager focused attention.

The delayed correlation moment is subject to certain symmetries that follow from the time reversal symmetry of physical laws. In particular, assuming no magnetic field to be present, the delayed correlation moment must be unchanged under the replacement of τ by $-\tau$

$$\langle\delta\hat{X}_j\delta\hat{X}_k(\tau)\rangle = \langle\delta\hat{X}_j\delta\hat{X}_k(-\tau)\rangle \tag{14.26}$$

or, since only the relative times in the two factors are significant,

$$\langle\delta\hat{X}_j\delta\hat{X}_k(\tau)\rangle = \langle\delta\hat{X}_j(\tau)\delta\hat{X}_k\rangle \tag{14.27}$$

If we now subtract $\langle\delta\hat{X}_j\delta\hat{X}_k\rangle$ from each side of the equation and divide by τ , we find

$$\left\langle\delta\hat{X}_j\frac{\delta\hat{X}_k(\tau) - \delta\hat{X}_k}{\tau}\right\rangle = \left\langle\frac{\delta\hat{X}_j(\tau) - \delta\hat{X}_j}{\tau}\delta\hat{X}_k\right\rangle \tag{14.28}$$

In the limit as $\tau \rightarrow 0$ we can write the foregoing equation in terms of time derivatives.

$$\langle\delta\hat{X}_j\delta\dot{\hat{X}}_k\rangle = \langle\dot{\delta\hat{X}}_j\delta\hat{X}_k\rangle \tag{14.29}$$

Now we *assume* that the decay of a fluctuation $\delta\hat{X}_k$ is governed by the *same* linear dynamical laws as are macroscopic processes

$$\delta\hat{X}_k = \sum_i L_{ik} \delta\hat{\mathcal{F}}_i \quad (14.30)$$

Inserting these equations in equation 14.29 gives

$$\sum_i L_{ik} \langle \delta\hat{X}_j \delta\hat{\mathcal{F}}_i \rangle = \sum_i L_{ij} \langle \delta\hat{\mathcal{F}}_i \delta\hat{X}_k \rangle \quad (14.31)$$

The theory of fluctuations reveals (Chapter 19) the plausible result that in the absence of a magnetic field the fluctuation of each affinity is associated only with the fluctuation of its own extensive parameter; *there are no cross-correlation terms of the form $\langle \delta\hat{X}_j \delta\hat{\mathcal{F}}_i \rangle$ with $i \neq j$* . Furthermore it will be shown that the “diagonal” correlation function (with $i = j$) has the value $-k_B$ (though the specific value is not of importance for our present purposes)

$$\langle \delta\hat{X}_j \delta\hat{\mathcal{F}}_i \rangle = \begin{cases} -k_B & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases} \quad \mathbf{B}_e = 0 \quad (14.32)$$

It follows that in the absence of a magnetic field $L_{ij} = L_{ji}$, which is the Onsager reciprocity theorem (equation 14.22).

In the presence of a magnetic field the proof follows in similar fashion, depending upon a similar symmetry in the correlation functions of the spontaneous fluctuations.

Despite this fundamental basis in fluctuation theory, the applications of the Onsager theory are purely macroscopic, expressed in terms of phenomenological dynamical equations. This thermodynamic emphasis of application has motivated interjection of the subject prior to the statistical mechanical chapters to follow. Accordingly we turn to thermoelectric effects as an illustrative application of the Onsager theorem.

14-5 THERMOELECTRIC EFFECTS

Thermoelectric effects are phenomena associated with the simultaneous flow of electric current and “heat current” in a system. Relationships among various such phenomena were proposed in 1854 by Lord Kelvin on the basis of empirical observations. Kelvin also presented a heuristic argument leading to the relations, carefully pointing out, however, that the argument was not only unjustified but that it could be made to yield

incorrect relations as well as correct ones. Unfortunately the argument continually resurfaces with renewed claims of rigor—of which the reader of the thermodynamic literature should be forewarned.

To analyze the thermoelectric effects in terms of the Onsager reciprocity we focus attention on a conductor in which both electric current and heat current flow in one dimension, and we describe the electric current as being carried by electrons. Then if s is the local entropy density

$$ds = \frac{1}{T} du - \sum_k \left(\frac{\mu_k}{T} \right) dn_k \quad (14.33)$$

in which u is the local energy density, μ is the electrochemical potential (per particle) of the electrons, n is the number of electrons per unit volume, and in which the sum refers to other “components.” These other components are the various types of atomic nuclei that together with the electrons constitute the solid. It will be noted that we have taken n as the number of electrons rather than the number of moles of electrons, and μ is accordingly the electrochemical potential per particle rather than per mole. In this regard we deviate from the more usual parameters merely by multiplication and division by Avogadro’s number, respectively.

Just as equation 14.7 led to equation 14.9, equation 14.33 now leads to

$$\mathbf{J}_S = \frac{1}{T} \mathbf{J}_U - \frac{\mu}{T} \mathbf{J}_N \quad (14.34)$$

in which \mathbf{J}_S , \mathbf{J}_U , and \mathbf{J}_N are current densities of entropy, energy, and number of electrons, respectively. The other components in equation 14.33 are assumed immobile and consequently do not contribute flux terms to equation 14.34.

Repeating the logic leading to equation 14.15, we find

$$\dot{s} = \nabla \cdot \frac{1}{T} \mathbf{J}_U - \nabla \cdot \frac{\mu}{T} \mathbf{J}_N \quad (14.35)$$

Thus if the components of \mathbf{J}_U and $-\mathbf{J}_N$ are taken as fluxes, the associated affinities are the components of $\nabla(1/T)$ and $\nabla\mu/T$. Assuming for simplicity that all flows and forces are parallel to the x -direction, and omitting the subscript x , the linear dynamical laws become

$$-J_N = L'_{11} \nabla \frac{\mu}{T} + L'_{12} \nabla \frac{1}{T} \quad (14.36)$$

$$J_U = L'_{21} \nabla \frac{\mu}{T} + L'_{22} \nabla \frac{1}{T} \quad (14.37)$$

and the Onsager theorem gives the relation

$$L'_{12}(\mathbf{B}_e) = L'_{21}(-\mathbf{B}_e) \quad (14.38)$$

Before drawing physical conclusions from equation 14.38 we recast the dynamical equations into an equivalent but instructive form. Although \mathbf{J}_U is a current density of total internal energy, we generally prefer to discuss the current density of heat. In analogy with the relation $dQ = T dS$ we therefore define a heat current density \mathbf{J}_Q by the relation

$$\mathbf{J}_Q = T\mathbf{J}_S \quad (14.39)$$

or, by equation 14.34,

$$\mathbf{J}_Q = \mathbf{J}_U - \mu\mathbf{J}_N \quad (14.40)$$

In a very rough intuitive way we can look on μ as the potential energy per particle and on $\mu\mathbf{J}_N$ as a current density of potential energy; subtraction of the potential energy current density from the total energy current density yields the heat current density as a sort of kinetic energy current density. At any rate, eliminating \mathbf{J}_U in favor of \mathbf{J}_Q from equation 14.34 gives

$$\dot{s} = \nabla \cdot \frac{1}{T} \cdot \mathbf{J}_Q - \frac{1}{T} \nabla \mu \cdot \mathbf{J}_N \quad (14.41)$$

It follows from this equation that if the components of \mathbf{J}_Q and of $-\mathbf{J}_N$ are chosen as fluxes the associated affinities are the corresponding components of $\nabla(1/T)$ and of $(1/T)\nabla\mu$, respectively. The dynamical equations can then be written, in the one-dimensional case, as

$$-J_N = L_{11} \frac{1}{T} \nabla \mu + L_{12} \nabla \frac{1}{T} \quad (14.42)$$

$$J_Q = L_{21} \frac{1}{T} \nabla \mu + L_{22} \nabla \frac{1}{T} \quad (14.43)$$

and the Onsager relation is

$$L_{12}(\mathbf{B}_e) = L_{21}(-\mathbf{B}_e) \quad (14.44)$$

The reader should verify that the dynamical equations 14.42 and 14.43 can also be obtained by direct substitution of equation 14.40 into the previous pair of dynamical equations 14.36 and 14.37 without recourse to the entropy production equation 14.41.

The significance of the heat current can be exhibited in another manner. We consider, for a moment, a steady-state flow. Then both \mathbf{J}_U and \mathbf{J}_N are divergenceless and taking the divergence of equation 14.40 gives

$$\nabla \cdot \mathbf{J}_Q = -\nabla \mu \cdot \mathbf{J}_N \quad (\text{in the steady state}) \quad (14.45)$$

which states that in the steady state the rate of increase in heat current is equal to the rate of decrease in the potential energy current. Furthermore, the insertion of this equation into equation 14.41 gives

$$\dot{s} = \nabla \cdot \frac{1}{T} \cdot \mathbf{J}_Q + \frac{1}{T} \nabla \cdot \mathbf{J}_Q \quad (14.46)$$

which can be interpreted as stating that the production of entropy is due to two causes: The first term is the production of entropy due to the flow of heat from high to low temperature, and the second term is the increase in entropy due to the appearance of heat current.

We now accept the dynamical equations 14.42 and 14.43 and the symmetry condition (equation 14.44) as the basic equations with which to study the flow of heat and electric current in a system.

14-6 THE CONDUCTIVITIES

We consider a system in which an electric current and a heat current flow parallel to the x -axis in a steady state, with no applied magnetic field. Then omitting the subscript x

$$-J_N = L_{11} \frac{1}{T} \nabla \mu + L_{12} \nabla \frac{1}{T} \quad (14.47)$$

$$J_Q = L_{12} \frac{1}{T} \nabla \mu + L_{22} \nabla \frac{1}{T} \quad (14.48)$$

where the Onsager theorem has reduced to the simple symmetry

$$L_{12} = L_{21} \quad (14.49)$$

The three kinetic coefficients appearing in the dynamical equations can be related to more familiar quantities, such as conductivities. In developing this connection we first comment briefly on the nature of the electrochemical potential μ of the electrons. We can consider μ as being composed of two parts, a chemical portion μ_c and an electrical portion μ_e

$$\mu = \mu_c + \mu_e \quad (14.50)$$

If the charge on an electron is e , then μ_e is simply $e\phi$, where ϕ is the ordinary electrostatic potential. The chemical potential μ_c is a function of the temperature and of the electron concentration. Restating these facts in terms of gradients, the electrochemical potential *per unit charge* is $(1/e)\mu$; its gradient $(1/e)\nabla\mu$ is the sum of the *electric field* $(1/e)\nabla\mu_e$, plus an effective driving force $(1/e)\nabla\mu_c$ arising from a concentration gradient.

The *electric conductivity* σ is defined as the electric current density (eJ_N) per unit potential gradient $(1/e)\nabla\mu$ in an isothermal system. It is easily seen that $(1/e)\nabla\mu$ is actually the emf, for in a homogeneous isothermal system $\nabla\mu_c = 0$ and $\nabla\mu = \nabla\mu_e$. Thus, by definition

$$\sigma \equiv -eJ_N / \frac{1}{e} \nabla\mu \quad \text{for } \nabla T = 0 \quad (14.51)$$

whence equation 14.47 gives

$$\sigma = e^2 L_{11} / T \quad (14.52)$$

Similarly the *heat conductivity* κ is defined as the heat current density per unit temperature gradient for zero electric current

$$\kappa \equiv -J_Q / \nabla T \quad \text{for } J_N = 0 \quad (14.53)$$

Solving the two kinetic equations simultaneously, we find

$$\kappa = \frac{D}{T^2 L_{11}} \quad (14.54)$$

where D denotes the determinant of the kinetic coefficients

$$D \equiv L_{11}L_{22} - L_{12}^2 \quad (14.55)$$

14-7 THE SEEBECK EFFECT AND THE THERMOELECTRIC POWER

The Seebeck effect refers to the production of an electromotive force in a thermocouple under conditions of zero electric current.

Consider a thermocouple with junctions at temperatures T_1 and T_2 ($T_2 > T_1$), as indicated in Fig. 14.1. A voltmeter is inserted in one arm of the thermocouple at a point at which the temperature is T' . This voltmeter is such that it allows no passage of electric current but offers no resistance to the flow of heat. We designate the two materials composing the

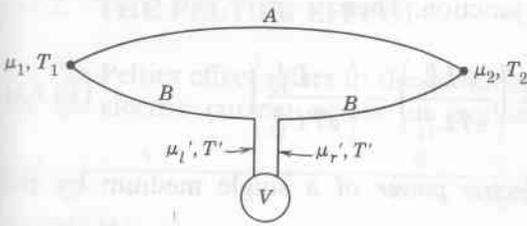


FIGURE 14.1

thermocouple by A and B . With $J_N = 0$, we obtain from the kinetic equations, for either conductor

$$\nabla\mu = \frac{L_{12}}{TL_{11}} \nabla T \tag{14.56}$$

Thus

$$\mu_2 - \mu_1 = \int_1^2 \frac{L_{12}^A}{TL_{11}^A} dT \tag{14.57}$$

$$\mu_2 - \mu'_r = \int_r^2 \frac{L_{12}^B}{TL_{11}^B} dT \tag{14.58}$$

$$\mu'_l - \mu_1 = \int_1^l \frac{L_{12}^B}{TL_{11}^B} dT \tag{14.59}$$

Eliminating μ_1 and μ_2 from these equations

$$\mu'_r - \mu'_l = \int_1^2 \left(\frac{L_{12}^A}{TL_{11}^A} - \frac{L_{12}^B}{TL_{11}^B} \right) dT \tag{14.60}$$

But, because there is no temperature difference across the voltmeter, the voltage is simply

$$V = \frac{1}{e} (\mu'_r - \mu'_l) = \int_1^2 \left(\frac{L_{12}^A}{eTL_{11}^A} - \frac{L_{12}^B}{eTL_{11}^B} \right) dT \tag{14.61}$$

The *thermoelectric power* of the thermocouple, ϵ_{AB} , is defined as the change in voltage per unit change in temperature difference. The sign of ϵ_{AB} is chosen as positive if the voltage increment is such as to drive the

current from A to B at the hot junction. Then

$$\varepsilon_{AB} = \frac{\partial V}{\partial T_2} = \left(\frac{-L_{12}^B}{eTL_{11}^B} \right) - \left(\frac{-L_{12}^A}{eTL_{11}^A} \right) \quad (14.62)$$

Defining the *absolute thermoelectric power* of a single medium by the relation

$$\varepsilon_A \equiv \frac{-L_{12}^A}{eTL_{11}^A} \quad (14.63)$$

the thermoelectric power of the thermocouple is

$$\varepsilon_{AB} = \varepsilon_B - \varepsilon_A \quad (14.64)$$

If we accept the electric conductivity σ , the heat conductivity κ , and the absolute thermoelectric power ε as the three physically significant dynamical properties of a medium, we can eliminate the three kinetic coefficients in favor of these quantities and rewrite the kinetic equations in the following form

$$-J_N = \left(\frac{T\sigma}{e^2} \right) \frac{1}{T} \nabla \mu - \left(\frac{T^2 \sigma \varepsilon}{e} \right) \nabla \frac{1}{T} \quad (14.65)$$

$$J_Q = - \left(\frac{T^2 \sigma \varepsilon}{e} \right) \frac{1}{T} \nabla \mu + (T^3 \sigma \varepsilon^2 + T^2 \kappa) \nabla \frac{1}{T} \quad (14.66)$$

An interesting insight to the physical meaning of the absolute thermoelectric power can be obtained by eliminating $(1/T)\nabla\mu$ between the two foregoing dynamical equations and writing J_Q in terms of J_N and $\nabla(1/T)$

$$J_Q = T\varepsilon e J_N + T^2 \kappa \nabla \frac{1}{T} \quad (14.67)$$

or, recalling that $J_S = J_Q/T$

$$J_S = \varepsilon e J_N + T \kappa \nabla \frac{1}{T} \quad (14.68)$$

According to this equation, each electron involved in the electric current carries with it an entropy of εe . This flow of entropy is in addition to the entropy current $T\kappa\nabla(1/T)$, which is independent of the electronic current. The thermoelectric power can be looked on as the entropy transported per coulomb by the electron flow.

14-8 THE PELTIER EFFECT

The Peltier effect refers to the evolution of heat accompanying the flow of an electric current across an isothermal junction of two materials.



FIGURE 14.2

Consider an isothermal junction of two conductors A and B and an electric current eJ_N to flow as indicated in Fig. 14.2. Then the total energy current will be discontinuous across the junction, and the energy difference appears as *Peltier heat* at the junction. We have $J_U = J_Q + \mu J_N$, and since both μ and J_N are continuous across the junction it follows that the discontinuity in J_U is equal to the discontinuity in J_Q

$$J_U^A - J_U^B = J_Q^A - J_Q^B \quad (14.69)$$

Because of the isothermal condition, the dynamical equations 14.65 and 14.66 give, in either conductor

$$J_Q = T\epsilon(eJ_N) \quad (14.70)$$

whence

$$J_Q^B - J_Q^A = T(\epsilon_B - \epsilon_A)(eJ_N) \quad (14.71)$$

The *Peltier coefficient* π_{AB} is defined as the heat that must be supplied to the junction when unit electric current passes from conductor A to conductor B . Thus

$$\pi_{AB} \equiv (J_Q^B - J_Q^A)/eJ_N = T(\epsilon_B - \epsilon_A) \quad (14.72)$$

Equation 14.72, which relates the Peltier coefficient to the absolute thermoelectric powers, is one of the relations presented on empirical evidence by Kelvin in 1854. It is called the *second Kelvin relation*.

The method by which we have derived equation 14.72 is typical of all applications of the Onsager relations, so that it may be appropriate to review the procedure. We first write the linear dynamical equations, reducing the number of kinetic coefficients appearing therein by invoking the Onsager relations. We then proceed to analyze various effects, expressing each in terms of the kinetic coefficients. When we have analyzed as many effects as there are kinetic coefficients, we rewrite the dynamical equations in terms of those effects rather than in terms of the kinetic coefficients (as in equations 14.65 and 14.66). Thereafter every additional

effect analyzed on the basis of the dynamical equations results in a relation analogous to equation 14.72 and expresses this new effect in terms of the coefficients in the dynamical equation.

14-9 THE THOMSON EFFECT

The Thomson effect refers to the evolution of heat as an electric current traverses a temperature gradient in a material.

Consider a conductor carrying a heat current but no electric current. A temperature distribution governed by the temperature dependence of the kinetic coefficients will be set up. Let the conductor now be placed in contact at each point with a heat reservoir of the same temperature as that point, so that there is no heat interchange between conductor and reservoirs. Now let an electric current pass through the conductor. An interchange of heat will take place between conductor and reservoirs. This heat exchange consists of two parts—the *Joule heat* and the *Thomson heat*.

As the electric current passes along the conductor, any change in total energy flow must be supplied by an energy interchange with the reservoirs. Thus we must compute $\nabla \cdot \mathbf{J}_U$

$$\nabla \cdot \mathbf{J}_U = \nabla \cdot (\mathbf{J}_Q + \mu \mathbf{J}_N) = \nabla \cdot \mathbf{J}_Q + \nabla \mu \cdot \mathbf{J}_N \quad (14.73)$$

which can be expressed in terms of \mathbf{J}_N and $\nabla(1/T)$ by using equations 14.67 and 14.68

$$\nabla \cdot \mathbf{J}_U = \nabla \cdot \left(T \epsilon e \mathbf{J}_N + T^2 \kappa \nabla \frac{1}{T} \right) + \left(-\frac{e^2}{\sigma} \mathbf{J}_N + T^2 e \epsilon \nabla \frac{1}{T} \right) \cdot \mathbf{J}_N \quad (14.74)$$

or

$$\nabla \cdot \mathbf{J}_U = T \nabla \epsilon \cdot (e \mathbf{J}_N) + \nabla \cdot \left(T^2 \kappa \nabla \frac{1}{T} \right) - \frac{e^2}{\sigma} \mathbf{J}_N \quad (14.75)$$

However the temperature distribution is that which is determined by the steady state with no electric current, and we know that $\nabla \cdot \mathbf{J}_U$ vanishes in that state. By putting $\mathbf{J}_N = 0$ and $\nabla \cdot \mathbf{J}_U = 0$ in equation 14.75 we conclude that the temperature distribution is such as to make the second term vanish, and consequently

$$\nabla \cdot \mathbf{J}_U = T \nabla \epsilon \cdot (e \mathbf{J}_N) - \frac{1}{\sigma} (e \mathbf{J}_N)^2 \quad (14.76)$$

Furthermore, noting that the thermoelectric power is a function of the local temperature, we write

$$\nabla \varepsilon = \frac{d\varepsilon}{dT} \nabla T \quad (14.77)$$

and

$$\nabla \cdot \mathbf{J}_U = T \frac{d\varepsilon}{dT} \nabla T \cdot (e\mathbf{J}_N) - \frac{1}{\sigma} (e\mathbf{J}_N)^2 \quad (14.78)$$

The second term is the Joule heat, produced by the flow of electric current even in the absence of a temperature gradient. The first term represents the Thomson heat, absorbed from the heat reservoirs when the current $e\mathbf{J}_N$ traverses the temperature gradient ∇T . The Thomson coefficient τ is defined as the Thomson heat absorbed per unit electric current and per unit temperature gradient

$$\tau \equiv \frac{\text{Thomson heat}}{\nabla T \cdot (e\mathbf{J}_N)} = T \frac{d\varepsilon}{dT} \quad (14.79)$$

Thus the coefficient of the Thomson effect is related to the temperature derivative of the thermoelectric power.

Equations 14.72 and 14.79 imply the "first Kelvin relation"

$$\frac{d\tau_{AB}}{dT} + \tau_A - \tau_B = \varepsilon_A - \varepsilon_B \quad (14.80)$$

which was obtained by Kelvin on the basis of energy conservation alone.

Various other thermoelectric effects can be defined, and each can be expressed in terms of the three independent coefficients L_{11} , L_{12} , and L_{22} , or in terms of α , κ , and ε .

In the presence of an orthogonal magnetic field the number of "thermodynamic" effects becomes quite large. If the field is in the z -direction an x -directed electric current produces a y -directed gradient of the electrochemical potential; this is the "Hall effect." Similarly an x -directed thermal gradient produces a y -directed gradient of the electrochemical potential; the Nernst effect. The method of analysis⁵ is identical to that of the thermoelectric effects, with the addition of the field dependence (equation 14.22) of the Onsager reciprocity theorem.

⁵H. Callen, *Phys. Rev.* **73**, 1349 (1948).