Nonequilibrium Thermodynamics: A Survey

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This paper presents a review of the field of thermodynamics of irreversible processes. The three essential steps in the use of this form of thermodynamics are the calculation of the entropy production, the setting up of the linear phenomenological equations, and the use of the Onsager reciprocal relation. The most important applications are to the transport processes, especially to the coupling phenomena which occur when two or more such processes take place in the same system.

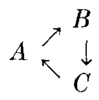
To a classical thermodynamicist, such as Clausius or Willard Gibbs, the existence many years later of a flourishing branch of thermodynamics which purports to deal with nonequilibrium states might have seemed very unlikely. To be sure the first law applies equally to equilibrium and nonequilibrium but is very limited in its scope. The most interesting parts of classical thermodynamics were based on the use of the second law as much as on the first. As such its results were applicable only to equilibrium, for it is only for reversible processes that the second law gives equations as distinct from inequalities. For all irreversible change the relation $dS > 0$ can be used only for the derivation of other inequalities, and these are comparatively unimportant. (For example, viscosities, conductivities, etc., cannot be negative.)

Thus at the time of Gibbs, and indeed up to 1931, what was called thermodynamics was essentially an equilibrium thermodynamics. However there had been one conspicuous exception: the derivation by William Thomson, Lord Kelvin (*11*), of the equation relating the Peltier heat to the electromotive force in a thermoelectric circuit, a system which is certainly not at equilibrium because of the temperature gradients. In this derivation Thomson was well aware that he was using a new hypothesis which could not be justified on the basis of the first and second laws; what it amounts to is the statement that an infinitesimal displacement from a steady state creates no entropy. To the thermodynamics of Clausius and Gibbs this would have appeared quite inadmissible unless the words *steady state* were replaced by the more restricted *condition of equilibrium*.

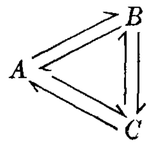
Nevertheless the equation obtained as a result of Thomson's intuitive genius was substantially confirmed by experiment, and the same hypothesis was subsequently used by Eastman (*9*) and Wagner (*20*) as a basis for the theory of thermal diffusion and thermocells*.

However the real breakthrough into a fully fledged nonequilibrium thermodynamics came in 1931 as a result of Onsager's famous papers (*14, 12*). The essential feature was the use of a third physical principle, microscopic reversibility, in addition to the first and second laws. By using all three together, Onsager was able to establish entirely new relations, applicable to any system in which there are two or more irreversible processes between which there is some mechanism of coupling. Many of these relations have been verified experimentally. Their great merit—and among them are included the thermoelectric equations—is that they are based on three well-established principles and not, as in Thomson's derivation, on two such principles together with a new hypothesis.

The starting point of Onsager's work was his observation that the chemist makes implicit use of the principle of microscopic reversibility whenever he asserts the detailed balancing of reactions in a system at equilibrium in which several reactions are coupled.† One should consider a substance which can exist in three tautomeric forms, *A*, *B*, and *C*, between which there is interconversion. A state of equilibrium could be maintained if there were a steady flow, at the molecular level, round the cycle:



The chemist rather believes that each of the three reactions, at equilibrium, takes place with equal frequency in the forward and backward directions. This is expressed symbolically:



In the case of coupled reactions, such as those above, this assertion of detailed balancing is not deducible from classical thermodynamics but is a special case of the principle of microscopic reversibility which has its origin in quantum mechanics. It has been expressed by Tolman (*19*) as follows: ". . . under equilibrium conditions any molecular process and the reverse of that process will be taking place on the average at the same rate . . . ."

This principle places a restriction on physical as well as chemical processes when there is coupling or interaction

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*See reference (*6*) for a more extended discussion of Thomson's hypothesis in relation to Onsager's theory.

†Admittedly the detailed balancing at equilibrium of reactions which are not coupled is provided for by the second law. However when there is coupling, relationships such as $K = k_1/k_2$ cannot be deduced from this law; the principle of microscopic reversibility must be used instead.

between them. But for its operation, equilibrium could be maintained by a cyclic process.

It will be noticed that frequent mention has been made of *equilibrium,* for example in Tolman's enunciation of the principle. It may be asked, how does it help in the development of a nonequilibrium thermodynamics? An extra assumption is needed, namely that the linear equations connecting forces and flows (as described in the next section) apply also to the natural fluctuations about the equilibrium state. These fluctuations are regarded as transient flows of heat, matter, etc., and the symmetric relationship between them, brought to light by microscopic reversibility, is regarded as being equally applicable to the large-scale flows which are the irreversible processes. This will be discussed in more detail later.

LINEAR EQUATIONS

To a usually satisfactory degree of approximation the rates of the transport processes are known to be proportional to the gradients of suitable potential functions. For example the flow of heat or electricity or the diffusion of a chemical substance is known to be proportional to the gradients of temperature, electric potential, and concentration* respectively, as expressed in Fourier's, Ohm's, and Fick's laws. Thus if J is the flow and X is the generalized force,

$$J = LX$$

When a type of system is considered in which two such processes take place simultaneously, their rates are J_1 and J_2 and the conjugate forces X_1 and X_2 respectively. Rather than to suppose that J_1 is uniquely and linearly determined by X_1 and J_2 by X_2, a more general assumption is that each flow is a linear function of both forces. Thus

$$\left.\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 \\ J_2 &= L_{21}X_1 + L_{22}X_2 \end{aligned}\right\} \qquad (1)$$

Such an assumption is necessary to give expression to the reality of the interaction if it exists in the particular system. The thermoelectric effect, for example, is due to the coupling between a flow of current and a flow of heat. When electrons flow through a wire, they carry with them not only their charge but also their kinetic energy. Their motion as current I thus creates a contribution to the over-all heat flow q. If $\Delta\phi$ and ΔT are differences of electric potential and of temperature, then in accordance with Equations (1) one writes

$$I = \text{const.}\ \Delta\phi + \text{const.}\ \Delta T$$

$$q = \text{const.}\ \Delta\phi + \text{const.}\ \Delta T$$

The first and fourth constants are related to the electric and thermal conductivities respectively. The second constant represents the effect of the temperature difference on the current, and the third shows the effect of the electromotive force on the flow of heat. The function of the Onsager theory in this particular example is to show the relationship which exists between these two coupling coefficients and thereby to derive the same equation relating the Peltier heat to $d\phi/dT$ as had been previously obtained by Thomson by use of his *ad hoc* hypothesis.

ENTROPY PRODUCTION

So far the forces, X, have not been closely defined and there is certainly a good deal of latitude in their choice. One should consider for example a region in a body where there is a local temperature T and a temperature difference dT over a distance dx. According to Fourier's law the component of heat flow in this direction is proportional to dT. However the thermal force could equally well be taken as dT itself, or as $d(1/T)$, etc. These changes merely alter the meaning of the scalar coefficient L and its relationship to the thermal conductivity, as conventionally defined. (Thus in the instance quoted the value of L is changed by a factor $-1/T^2$.)

A more restricted choice of the forces may be made on the basis of the entropy production in the system. In any irreversible process entropy is "created," and to an extent which depends on the magnitude of the flows J_i and the forces X_i. For example in a simple process of heat conduction the entropy creation (or energy dissipation) is proportional to the product $q\Delta T$, where q is the amount of heat which has been transmitted and ΔT is the temperature difference over which this amount of energy has been degraded.

The rate of entropy creation due to a number of processes taking place at rates J_1, J_2, etc., is dS/dt. It will be shown by use of an example that the entropy creation can be expressed as a sum of products. Thus

$$\frac{dS}{dt} = J_1X_1 + J_2X_2 + \cdots \qquad (2)$$

where the quantities X_1, X_2, etc., are proportional to the same forces which are used in the expression of Fourier's law, Ohm's law, etc.; that is to say, the forces which have been introduced into the linear equations (1) can always be chosen in such a way that they also satisfy Equation (2). When this has been done, the essential content of Onsager's theory is to show that the coupling coefficients L_{12} and L_{21} are equal:

$$L_{12} = L_{21} \qquad (3)$$

In more general terms the procedure in applying the thermodynamics of irreversible processes is as follows:

1. Determines the form of the quantities X_i which satisfy the relation

$$\frac{dS}{dt} = \sum J_iX_i \qquad (4)$$

2. Assume that the flows J_i can be expressed with sufficient accuracy in the particular system as linear functions of the X_i:

$$J_i = \sum_{k=1}^{n} L_{ik}X_k \ (i = 1, 2, \cdots n) \qquad (5)$$

3. Use Onsager's reciprocal relation

$$L_{ik} = L_{ki} \qquad (6)$$

to eliminate some of the coefficients from (5) and thus obtain physical relations which can be tested by experiment. (It may be noted that the trivial case $L_{ik} = L_{ki} = 0$ corresponds to the absence of coupling.)

The basic theory will be discussed later.

EXAMPLE OF THE THERMOMOLECULAR PRESSURE DIFFERENCE

The application of *nonequilibrium thermodynamics* could be illustrated by reference to a variety of phenomena in which there is coupling. Two of the simplest of these are the thermoelectric effect and the thermomechanical pressure difference. The latter is probably of greater interest and will be chosen for illustration.

Thermomolecular pressure difference is a generic term which includes at least three effects, quite distinct from each other at the molecular level but the same in regard to their macroscopic description. These are as follows: (1) The Knudsen effect in a gas; a stationary pressure difference develops between two vessels communicating with each other through holes small compared with the mean free path, as the result of a temperature difference. (2) Thermoosmosis; here again there is a stationary pressure difference as the result of a temperature difference, but the two vessels are separated from each other by a membrane in which the fluid (which may be a liquid) is slightly soluble. Pores are not involved. (3) The fountain effect in liquid helium 2; the liquid flows spontaneously through a capillary connecting two vessels at different temperatures and builds up a stationary difference of hydrostatic head.

In each of these systems the flow of energy between the two vessels is coupled to the flow of matter. For apart from the normal conduction of heat through the substance of the barrier (that is, the membrane, capillary, etc.) there is also a transport of energy which is carried by the molecules of the fluid. It will be shown that a stationary pressure dif-

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*In the case of diffusion the chemical potential should preferably be used in place of concentration in the expression of Fick's law.

ference will arise, as the result of the temperature difference, whenever the mean energy of the molecules passing across the barrier is not equal to the enthalpy of the bulk fluid on either side.

On the basis of these preliminaries, the problem is formally treated by use of the theory as described in the previous section. The two vessels, 1 and 2, communicating with each other through a small hole, capillary, or membrane, will each be taken to be of constant volume. The fluid in vessel 1 is at a uniform temperature T and pressure P, and the fluid in vessel 2 at a uniform temperature $T + dT$ and a pressure $P + dP$. The two vessels together form an isolated system (but they may be thought of as having been brought to their particular temperatures by recent contact with two heat reservoirs). The problem is to determine whether or not dP is zero when any flow of the fluid comes to an end; more particularly the problem is to obtain an expression for dP/dT.

It is an implicit assumption of the nonequilibrium thermodynamics that the Gibbs equation

$$dU = T\,dS - P\,dV + \sum \mu_i\,dn_i \qquad (7)$$

may be used, even though there is an absence of equilibrium. This will be discussed at a later stage. Bearing in mind the constancy of volumes and the fact that there is a single component fluid, one may write the Gibbs equation for the two vessels as

$$dU_1 = T\,dS_1 + \mu\,dn_1 \qquad (8)$$

$$\begin{aligned} dU_2 = {} & (T + dT)\,dS_2 \\ & + (\mu + d\mu)\,dn_2 \end{aligned} \qquad (9)$$

The entropy created in the process is

$$dS = dS_1 + dS_2 \qquad (10)$$

Using Equations (8) and (9), and noting that $dn_2 = -dn_1$ and $dU_2 = -dU_1$ (since one is concerned with an isolated system) one obtains

$$dS = -dU_2 \cdot \frac{dT}{T^2} - dn_2 \cdot d(\mu/T) \qquad (11)$$

It will be noted that these equations allow for the passage of heat between the two vessels, due to normal heat conduction across the barrier, as well as for the energy associated with the transport of matter.

If the process takes place in a time dt, one obtains for the rate of entropy creation

$$\frac{dS}{dT} = -\frac{dU_2}{dt} \cdot \frac{dT}{T^2} - \frac{dn_2}{dt} \cdot d\left(\frac{\mu}{T}\right) \qquad (12)$$

Since $dU_2 = -dU_1$, the quantity dU_2/dt is the rate J_u of passage of energy from vessel 1 to vessel 2. Similarly dn_2/dt is the rate J_m of flow of matter. The last equation may therefore be written

$$\begin{aligned} \frac{dS}{dt} &= -J_u \frac{dT}{T^2} - J_m\, d\left(\frac{\mu}{T}\right) \\ &= J_u\, d\left(\frac{1}{T}\right) - J_m\, d\left(\frac{\mu}{T}\right) \end{aligned} \qquad (13)$$

The forces X_u and X_m to be associated with the flow of energy and matter are therefore $d(1/T)$ and $-d(\mu/T)$ respectively.

One assumes the linear relations

$$J_m = -L_{11}\, d\left(\frac{\mu}{T}\right) - L_{12} \frac{dT}{T^2} \qquad (14)$$

$$J_u = -L_{21}\, d\left(\frac{\mu}{T}\right) - L_{22} \frac{dT}{T^2} \qquad (15)$$

Because of Onsager's relation, equation (3), the first of these equations may be written

$$J_m = -L_{11}\left\{d\left(\frac{\mu}{T}\right) + \frac{L_{21}}{L_{11}} \frac{dT}{T^2}\right\} \qquad (16)$$

By dividing (15) by (14) for the special case $dT = 0$ one obtains

$$\frac{L_{21}}{L_{11}} = \left(\frac{J_u}{J_m}\right)_{dT=0} \equiv Q \qquad (17)$$

The ratio L_{21}/L_{11} is therefore the energy flow per unit matter flow under isothermal conditions where there will be no heat conduction. The quantity Q as defined by Equation (17) will be called the *energy of transport.* Thus from (16) and (17)

$$J_m = -L_{11}\left\{d\left(\frac{\mu}{T}\right) + Q \frac{dT}{T^2}\right\} \qquad (18)$$

and at the stationary state where all transfer of matter has come to an end

$$d\left(\frac{\mu}{T}\right) = -Q \frac{dT}{T^2} \qquad (19)$$

From the classical thermodynamics of a single component system*

$$\begin{aligned} d\left(\frac{\mu}{T}\right) &= \frac{\partial(\mu/T)}{\partial T}\,dT + \frac{\partial(\mu/T)}{\partial P}\,dP \\ &= \frac{-h}{T^2}\,dT + \frac{v\,dP}{T} \end{aligned} \qquad (20)$$

Combining (19) and (20) one finally obtains

$$\frac{dP}{dT} = -\frac{(Q - h)}{vT} \qquad (21)$$

The thermomechanical pressure difference is thus proportional to the difference between the energy of transport and the enthalpy of the fluid in bulk. Before the significance of this equation is commented upon, an alternative treatment of the problem will be discussed.

ALTERNATIVE CHOICE OF THE FLOWS AND FORCES

As remarked previously, for the purpose of applying Onsager's relation the conjugate flows and forces must always be chosen to satisfy Equation (4). However this still leaves a good deal of latitude. For example, by combining Equations (13) and (20) one obtains

$$\begin{aligned} \frac{dS}{dt} &= -J_u \frac{dT}{T^2} - J_m\left(\frac{-h}{T^2}\,dT + \frac{v\,dP}{T}\right) \\ &= -(J_u - J_m h)\frac{dT}{T^2} - J_m \frac{v\,dP}{T} \end{aligned} \qquad (22)$$

The flow J_q is defined by

$$J_q \equiv J_u - J_m h \qquad (23)$$

and its physical significance will be discussed below. Then (23) may be written

$$\frac{dS}{dT} = -J_q \frac{dT}{T^2} - J_m \frac{v\,dP}{T} \qquad (24)$$

which represents a different choice of the conjugate flows and forces as compared with Equation (13). In particular, the force conjugate to the flow of matter is now proportional to the pressure difference. This is perhaps a more intuitive choice than the quantity $d(\mu/T)$ of Equation (13).

Since there is nothing in the Onsager theory to make one choice of flows and forces preferable to any other, provided they satisfy Equation (4), a new set of linear equations can be written in the form

$$J_m = -L_{11}' \frac{v\,dP}{T} - L_{12}' \frac{dT}{T^2} \qquad (25)$$

$$J_q = -L_{21}' \frac{v\,dP}{T} - L_{22}' \frac{dT}{T^2} \qquad (26)$$

together with $L_{12}' = L_{21}'$. Hence

$$J_m = -L_{11}'\left(\frac{v\,dP}{T} + \frac{L_{21}'}{L_{11}'} \frac{dT}{T^2}\right) \qquad (27)$$

Dividing (26) by (25) for $dT = 0$ one obtains

$$\frac{L_{21}'}{L_{11}'} = \left(\frac{J_q}{J_m}\right)_{dT=0} \equiv Q^* \qquad (28)$$

where Q^* is called the *heat of transfer.* Combining (27) and (28) one obtains

$$J_m = -L_{11}'\left(\frac{v\,dP}{T} + Q^* \frac{dT}{T^2}\right) \qquad (29)$$

Therefore at the stationary state, $J_m = 0$,

$$\frac{dP}{dT} = \frac{-Q^*}{vT} \qquad (30)$$

This equation is the same as (21), since Q^* is equal to $Q - h$. Thus from the definitions (28), (23), and (17)

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*See for example page 101 of reference 4.

$$Q^* = \left(\frac{J_q}{J_m}\right)_{dT=0} = \left(\frac{J_u}{J_m}\right)_{dT=0} - h \qquad (31)$$
$$= Q - h$$

It will now be shown that Q^* has a direct physical significance and is measurable, at least in principle.

The discussion in the previous section, leading to Equations (11) and (13), was based for convenience on an isolated system, recently separated from suitable heat reservoirs at temperatures T and $T + dT$. The energy of transport was defined by Equation (17):

$$Q \equiv \left(\frac{J_u}{J_m}\right)_{dT=0} = \left(\frac{dU_1}{dn_1}\right)_{dT=0}$$

Therefore Qdn_1 is the change of energy of vessel 1 when dn_1 moles pass through the barrier, under conditions of equal temperatures. This energy change may be expected to cause a change in the intensive variables in vessel 1 unless steps are taken to prevent this. To maintain constancy of the temperature and the pressure it will be necessary to restore contact with the heat reservoir, taking in heat dq, and also to use a piston and cylinder to adjust the pressure, with a work effect dw. At the end of this process—the loss of dn moles and the restoration of the original temperature and pressure—the energy change of vessel 1 is $-Qdn + dq - dw$. This is equal to $-udn$, since the temperature and pressure are constant over the process. Similarly $dw = -Pvdn$. Hence

$$-u\,dn = -Q\,dn + dq + Pv\,dn \qquad (32)$$

or

$$dq = (Q - h)\,dn = Q^*\,dn \qquad (33)$$

The heat of transport is therefore equal to the heat which must be supplied from a heat reservoir to maintain conditions of constant temperature and pressure in vessel 1, when 1 mole of the fluid passes from 1 to 2 when their temperatures are equal ($dT = 0$). The corresponding quantity J_q, defined in Equation (23), is the rate of heat flow from the reservoir. In fact the whole of this analysis, instead of being based on an isolated system, could equally well have been based on a system in which the two vessels were continuously in contact with the reservoirs (*10*). This would have resulted in Equation (24) as the immediate result, and Equation (13) could then have been obtained by the same transformation in reverse.

PHYSICAL SIGNIFICANCE OF THE EQUATIONS

Equation (21) and (30) were first obtained by use of the reciprocal relation (6) by Deryagin and Sidorenkov (*8*) but previously by Eastman (*9*) by adopting Thomson's hypothesis.

The simplest application of these equations is to the Knudsen effusion effect for which the energy and heat of transport are calculable from kinetic theory. By integration of Maxwell's equation it is readily shown that the mean kinetic energy of the molecules passing through a small hole is 2 RT/mole, whereas their mean kinetic energy in the bulk of the gas in $\frac{3}{2}$ RT/mole (*18*). This difference arises from the fact that relatively more fast-moving molecules pass through in unit time than slow-moving ones. Thus the energy of transport is given by

$$Q = 2RT + E \qquad (34)$$

The enphalpy h of the gas is

$$h = \frac{3}{2}RT + E + Pv$$
$$= \frac{5}{2}RT + E \qquad (35)$$

Hence the heat of transport is

$$Q^* = Q - h$$
$$= -RT/2 = -Pv/2 \qquad (36)$$

Substituting in (30) and integrating over a finite difference of temperatures between the two vessels, one obtains

$$\frac{P_2}{P_1} = \sqrt{\frac{T_2}{T_1}} \qquad (37)$$

This equation, which is also directly deducible from kinetic theory, has been amply confirmed by experiment by Knudsen and others. The heat effect corresponding to Q^* had also been detected experimentally by Dufour as early as 1872 and confirmed by Knudsen (*18*).

Thermoosmosis, which is the second example of the thermomolecular pressure difference, is quite different in its molecular mechanism. Here the two vessels are separated by a membrane in which the fluid is slightly soluble. To pass from one vessel to the other the fluid must undergo a process of solution at the one membrane surface and a process of evolution at the other. Within the membrane there is a concentration of dissolved fluid, this concentration varying across the thickness owing to a thermal diffusion process.

The effect has been investigated theoretically and experimentally by Denbigh and Raumann (*7*), Bearman and Koenig (*1*), and Crowe (*2*). Whereas in the Knudsen effect the higher pressure always develops on the warmer side, this is by no means necessarily the case in thermoosmosis which depends on a specific interaction between the fluid and the membrane. Hydrogen for example builds up the higher pressure on the cold side of a rubber membrane and has a heat of transport of 100 cal./mole, as determined by use of Equation (30). Carbon dioxide tends to pass through the same membrane in the reverse direction and has a heat of transport of −1,800 cal./mole.

In these experiments it was not possible to determine the value of Q^* other than by use of Equation (30) itself, and in this respect the theory has not been completely verified. However it will be seen that Equation (29) reduces to

$$J_m = \frac{-L_{11}'v\,dP}{T} \qquad (38)$$

in the absence of a temperature difference. The coefficient L_{11}' is thus related to the permeability of the membrane as measured under ordinary isothermal conditions. It was a satisfactory feature of the experiments that the approach to the stationary state under the nonisothermal conditions of the thermoosmosis system, could be used to obtain values of the membrane permeability, by use of Equation (29), in good agreement with values determined isothermally. This gives support to the assumptions underlying this equation, that is the supposition that the flow through the membrane depends linearly on the temperature difference dT as well as on the pressure difference dP.

The third example of the thermomolecular pressure difference is the fountain effect in liquid helium 2. The phenomenon seems to be due to a quantum effect which give rise to a large value of Q^* in the particular system. The experimental results of Mayer and Mellink and of Kapitza are stated to be in good agreement with Equation (30).

REVIEW OF THE THEORY

The discussion of the thermomolecular pressure difference was introduced to give some idea of nonequilibrium thermodynamics in action. Some other fields of application will be described more briefly later. At the present stage it is convenient to go back to the theory as outlined under Linear Equations and Entropy Production.

Two important assumptions have been used so far. The first of these is that the rates of the processes can be expressed in the form of Equation (5), that is as linear functions of certain thermodynamic forces which must be chosen so as to satisfy Equation (4). The experimental evidence shows that this is indeed the case with transport processes, their rates being proportional to gradients of temperature, electric potential, etc. Chemical reactions however are an exception. For a reaction $A \rightleftarrows B$ the rate of entropy production is proportional to the product of the reaction rate and the difference $\mu_A - \mu_B$ of chemical potentials. The latter is therefore the appropriate force, but it is not a quantity to which the reaction rate is linearly related, except when the reaction is close to equilibrium (*5*). For this reason alone the application of nonequilibrium thermodynamics to chemical reactions is somewhat limited.

The second important assumption is that the Gibbs equation $dU = TdS - PdV + \sum \mu_i dn_i$ can be used, despite the absence of equilibrium. In more general terms, what is assumed is that the entropy of a system, during an irreversible process, is completely determined by the energy, volume, and composition and does not depend on the gradients within the system.

By use of the kinetic theory of gases, or statistical mechanics, it can be shown that the extent to which this assumption holds depends on the smallness of the deviation from the equilibrium Maxwellian distribution of velocities, etc., during the course of the irreversible process. This has been done by Meixner (*13*) and Prigogine (*16*), who came to the conclusion that the Gibbs equation is applicable to a satisfactory degree of approximation in the typical field of the application of nonequilibrium thermodynamics, that is the transport processes. It would break down if for example the change in temperature over the distance of a mean free path was comparable in magnitude to the temperature itself, but this is not likely to be the case, except under extreme conditions.

There is however another important assumption which occurs in the deduction of the reciprocal relation $L_{ik} = L_{ki}$. A detailed derivation of this equation is much beyond the scope of the present paper, but a brief outline follows.

The proof of the relation is based not on the macroscopic deviations from equilibrium, such as one is concerned with when there are irreversible processes, but with the fluctuations which take place within a molecular system at equilibrium. Even at equilibrium of course the entropy does not always remain at its absolute maximum value, but oscillates irregularly over a minute range, corresponding to the fluctuating deviations from the smoothness of the energy and matter distribution within the system.

The principle of microscopic reversibility places a certain limitation on these fluctuations. For the sake of a concrete illustration one considers once again the distribution of matter and energy between two vessels, as described. However as an "aged system" is being discussed, there is a state of equilibrium. The quantities dU_2 and dn_2 in Equation (11) therefore now refer to fluctuations of energy and matter about the equilibrium state rather than to infinitesimal parts of finite changes. One supposes that at a given instant $dn_2 = -dn_1 = 10^{-22}$ moles (owing to a fluctuation of matter between the two vessels) and that τ seconds later $dU_2 = -dU_1 = 10^{-12}$ ergs (owing to a fluctuation of energy between the vessels). According to the principle of microscopic reversibility, this compound event is just as likely to occur on the average as the converse situation in which a disparity 10^{-12} ergs in the energy is followed τ sec. later by a disparity 10^{-22} moles in the amount of matter.

In more general terms, α and β are the amounts by which two variables deviate from their equilibrium values owing to the fluctuations. $\alpha(t)$ is the value of α at time t and $\beta(t + \tau)$ the value of β, τ sec. later. The mean value of the product $\alpha(t)\beta(t + \tau)$ is taken over a long duration (but the β value is always taken at τ sec. after the α value). According to microscopic reversibility the same mean value for the product $\alpha(t + \tau)\beta(t)$ will be obtained, in which it is now the α variable which is to be taken τ sec. later. Thus

$$\overline{\alpha(t)\beta(t + \tau)} = \overline{\alpha(t + \tau)\beta(t)} \tag{39}$$

Substracting $\overline{\alpha(t)\beta(t)}$ from both sides of (39) and dividing by τ one obtains

$$\begin{aligned}&\overline{\alpha(t)\left\{\frac{\beta(t + \tau) - \beta(t)}{\tau}\right\}}\\ &\qquad = \overline{\beta(t)\left\{\frac{\alpha(t + \tau) - \alpha(t)}{\tau}\right\}}\end{aligned} \tag{40}$$

The quantities in brackets are the changes in the variables β and α respectively divided by the time τ. It will be assumed—and this is the important assumption that has to be made—that the rate of changes of these fluctuating variables follows the ordinary linear macroscopic laws. That is to say, one assumes

$$\begin{aligned}&\left\{\frac{\alpha(t + \tau) - \alpha(t)}{\tau}\right\}\\ &\qquad = L_{11}X_\alpha + L_{12}X_\beta\end{aligned} \tag{41}$$

and

$$\begin{aligned}&\left\{\frac{\beta(t + \tau) - \beta(t)}{\tau}\right\}\\ &\qquad = L_{21}X_\alpha + L_{22}X_\beta\end{aligned} \tag{42}$$

where X_α and X_β are suitably defined forces. The time derivatives of the fluctuations are thus regarded as transient flows of energy and matter, obeying relations such as (14) and (15)*.

Substituting (41) and (42) in (40) one obtains

$$\begin{aligned}&\overline{\alpha(L_{21}X_\alpha + L_{22}X_\beta)}\\ &\qquad = \overline{\beta(L_{11}X_\alpha + L_{12}X_\beta)}\end{aligned} \tag{43}$$

ΔS is the entropy deviation from its maximum owing to the fluctuations. According to Einstein's fluctuation theory the probability that the one variable lies in the range α to $\alpha + d\alpha$ and the other variable lies in the range β to $\beta + d\beta$ is proportional to

$$e^{\Delta S/k}\, d\alpha\, d\beta$$

By use of this distribution function it is possible to work out mean values such those occurring in Equation (43). For example

$$\overline{\alpha X_\alpha} = \frac{\iint \alpha X_\alpha e^{\Delta S/k}\, d\alpha\, d\beta}{\iint e^{\Delta S/k}\, d\alpha\, d\beta} \tag{44}$$

(where the denominator normalizes the probabilities to unity)

Provided that the forces X_α and X_β which are suitable for use in (41) and (42) will also satisfy

$$\begin{aligned}\left(\frac{\partial\, \Delta S}{\partial \alpha}\right)_\beta &= X_\alpha;\\ \left(\frac{\partial\, \Delta S}{\partial \beta}\right)_\alpha &= X_\beta\end{aligned} \tag{45}$$

the mean values, as given by integrals such as (44), can be evaluated*. The result is

$$\overline{\alpha X_\alpha} = \overline{\beta X_\beta} = -k \tag{46}$$

$$\overline{\alpha X_\beta} = \overline{\beta X_\alpha} = 0 \tag{47}$$

Substituting these mean values in (43) one obtains

$$L_{12} = L_{21}$$

and similarly $L_{ik} = L_{ki}$ in the general case where there are more than two fluctuating variables.

Thus an important feature of the theory is the supposition that the linear equations apply equally to the fluctuations and to the macroscopic deviations from equilibrium which are observable in the form of the irreversible processes. The linear equations stretch outward from the equilibrium state, and the property $L_{ik} = L_{ki}$, which is provable for the fluctuations, must apply also to the irreversible processes themselves, provided that these processes actually obey linear equations, for example that the coefficients L_{ik} are independent of the magnitude of the gradients.

FIELD OF APPLICATION OF THE THEORY

Nonequilibrium thermodynamics does not have any very substantial applications to chemical reactions. Indeed the condition of microscopic reversibility has already been applied by the chemist, in an implicit form, whenever he uses the idea of detailed balancing to obtain a relationship between the velocity constants. Also, as previously mentioned, the rate of a reaction is not linearly related to the appropriate thermodynamic force, except when reaction is close to equilibrium. Even if this were

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*For further discussion see de Groot (*3*).

*See for example Prigogins (*17*), page 49.

not the case, the field of application would still be very limited, because reaction rate is a scalar quantity and cannot be coupled with the vector transport processes (Curie's symmetry principle). Nevertheless Prigogine (*17*) has made a number of interesting and tentative applications to biological systems in which there may be two or more reactions coupled among themselves.

The most important field of application is undoubtedly the transport processes, whose interaction at the molecular level leads to very interesting phenomena. Of course the new thermodynamics is unable to predict the magnitude of the coupling, but whenever it is nonzero the coupling coefficients $L_{ik}(i \neq k)$ are also nonzero, and in this situation the application of the reciprocal relation leads to physical relations which can be verified by experiment.

Examples already mentioned are the thermoelectric effect and the thermomolecular pressure difference. The coupling in the former case is due to the fact that the passage of electrons is simultaneously both an electric current and a flow of thermal energy; similarly, in the latter case a flow of matter carries with it an associated heat of transport under certain special conditions.

In multicomponent systems in which there is a temperature gradient the phenomenon of thermal diffusion can occur. Here again there is a fruitful field of application, and it can be shown that the separation achievable in thermal diffusion depends on the difference in the heats of transport of the individual components. The measurement of these quantities, and the attempt to interpret them in molecular terms, is an attractive line of enquiry in the theory of liquids.

Strictly speaking the chemical engineer should apply nonequilibrium thermodynamics whenever he is concerned with simultaneous heat and mass transfer. However the coupling is rather small, and the traditional methods, which assume these processes to be independent, are not likely to be much in error. The coupling is important only when one sets up a special type of apparatus which brings it into prominence, for example the thermogravitational system (Clusius-Dickel) which is used to magnify the separation achievable by thermal diffusion.

Simultaneous flows of energy and electricity and of energy and matter have been discussed so far. Coupling can also take place between the flows of electricity and of matter, in an isothermal system. This occurs for example when there is a diffusion of an electrolyte and a simultaneous flow of current, as in the concentration cell with transport. Here the coupling is due quite simply to the fact that the ions are charged; unequal diffusion of the ions implies a flow of current and vice versa. For this reason the rate of diffusion depends not only on the gradient of chemical potential or concentration but also on the gradient of electric potential. By application of the Onsager relation the well-known equation giving the diffusion potential in terms of the transport numbers of the ions can be readily derived. This had been obtained much earlier by Nernst, using a method similar to Thomson's.

Closely similar are the relationships which can be established between the various electrokinetic effects, for example the relation between the streaming potential and electroosmosis or between the electroosmotic pressure and the streaming current. There is also the possibility of the coupling of individual diffusion processes in a multicomponent system, as occurs (although only to a small extent) in solutions of electrolytes. Still another interesting application is heat conduction in anisotropic materials; also a number of interesting effects take place when an externally applied magnetic field interferes with the flow of heat and electricity. For further details of these phenomena and also for a much fuller account of the general theory, the reader is referred to monographs *3*, *6*, and *17*.

While the field of application of nonequilibrium thermodynamics may thus appear to be rather extensive, it should also be emphasized that it is strictly limited. The useful applications are to systems in which there are two or more processes between which there exists some mechanism of coupling. (And even in these systems the coupling is not often of a large order of magnitude.) What is not sufficiently realized is that the new branch of thermodynamics has nothing useful to say about irreversibility in general. Thus it offers no information whatever on such problems as the speed of chemical reaction, the rate of mass transfer, or the magnitude of fluid friction. And even in a system in which these processes take place simultaneously they are not of a kind between which coupling takes place. With these remarks in mind the chemical engineer will not be inclined to overexaggerate the practical uses of the new branch of thermodynamics but instead may hold it of value for its own intrinsic interest.

NOTATION

E = any additional energy associated with internal degrees of freedom of molecule (vibration, rotation)
h = molar enthalpy of fluid (at T, P)
I = current
k = Boltzman's constant
J_i = a generalized flow
J_m = flow of matter
J_u = flow of energy
L = scalar coefficient of nature of conductance or diffusion coefficient
L_{12} = coupling coefficient
L_{21} = coupling coefficient
L_{ik} = coefficient relating J_i to X_k
n_i = number of moles of species i
P = pressure
Q = energy of transport
Q^* = heat of transport
R = gas constant
S = entropy
t = time
T = absolute temperature
u = internal energy per mole
U = internal energy
v = molar volume of fluid (at T, P)
V = volume
X_i = force conjugate to the flow J_i

Greek Letters

α, β = values of fluctuating variables
μ_i = chemical potential of species i

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