IRREVERSIBLE THERMODYNAMICS*

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The macroscopic approach to irreversible thermodynamics originally proposed by Sliepcevich and Finn in 1963 is amplified to demonstrate that, of the four possible alternatives for obtaining the reciprocal relations, fluxes and forces for systems under the simultaneous influence of two potential differences, one alternative is identical to the results obtained by Onsager.

IN A PREVIOUS PAPER by Sliepcevich and Finn[9] a macroscopic approach for deriving the linear laws, which relate the fluxes to the forces for irreversible processes under the simultaneous influence of two potential differences, was proposed. Subsequent to this publication a number of readers raised questions regarding the validity of this derivation and whether the fluxes and forces so derived had any physical significance. More recently Andrews[1] has published a negation of the macroscopic derivation as extended by Sliepcevich and Hashemi[11]; however his paraphrasing of the macroscopic approach does not appear to be tenable.

In an attempt to amplify the macroscopic derivation, a simple example of a one-dimensional, one-component system under the influence of two potential differences will be used. Multicomponent systems will not be considered since in these cases the definition of heat is at best ambiguous[2, 5] and therefore, it is meaningless to relate the fluxes to physically significant quantities. Furthermore, systems under the influence of viscous dissipation forces or external fields (e.g., magnetic) pose some unresolved problems on their inclusion in the energy balance equations. An analysis of the complications introduced by the presence of electrical and magnetic fields has been presented by Martin[6].

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IN GENERAL, the literature of irreversible thermodynamics raises some profound questions as to its range of practical usefulness; an excellent review has been published by Wei[12]. In order to circumvent definitional dilemmas associated with more complex systems—which would serve no purpose other than to detract from the principal focus of this paper—attention will be given only to a simple process familiar to chemical engineers. Until agreement can be reached on the validity of the derivation for the simplified system treated herein, it would be folly to attempt to cover the more complex cases.

The system to be analyzed in this paper is a one-dimensional, one-component system in which the properties such as temperature T, pressure P, and chemical potential μ are assumed to be uniform throughout. Likewise, the properties of this same component which composes the surroundings are assumed to be uniform throughout and are denoted by the subscript i, viz. T_i, P_i, μ_i, which in general are different from the properties of the system. Obviously, then, discontinuities in the properties exist at the boundaries, and for this reason it has been called a discontinuous system[4]. Neglecting kinetic and potential energy effects (without loss in generality) the following equations apply when a quantity of mass δM_i, having a specific enthalpy, h_i, and a quantity of heat δQ, are transferred simultaneously and irreversibly across the boundary of the system at T_i such that no work is done.

$$\text{Energy balance: } -h_i\, \delta M_i + \delta(uM) = \delta Q \quad (a)$$

$$\text{Entropy balance: } \delta(sM) = \delta\left(\frac{Q}{T_i}\right) +$$

$$s_i \delta M_i + \frac{\delta l w}{T} \quad (b)$$

$$\text{Mass balance: } \delta M = \delta M_i \quad (c)$$

$$\text{Gibbs equation: } \delta u = T \delta s - P \delta v \quad (d)$$

Defining equation: $\mu = h - Ts = u + Pv - Ts$ (e)

where u, s, v are the specific internal energy, entropy and volume, respectively, μ is the chemical potential, and lw is the lost work as defined in Equation (b) so that $\dfrac{\delta lw}{T} = S_p$ = total entropy production. Combining these equations yields

$$\delta lw = [\delta\left(\frac{Q}{T_i}\right) + s_i\delta M]\,(T_i - T) + \delta M(\mu_i - \mu) \qquad (f)$$

Replacing the potential differences by Δ's, noting that $\Delta\mu_T = s_i\Delta T + \Delta\mu$ and converting to the differential form Equation (f) becomes

$$dlw = (\Delta T)\, d\frac{Q}{T_i} + (\Delta\mu_T)\, dM \qquad (1)*$$

Equation 1 is valid to the extent that Equations (a) through (e) hold, and no other restrictions are required. Although Equation 1 was derived for the discontinuous system the same form of the equation holds for steady state systems. However, in the latter case it is customary to replace the Δ's in Equation 1 by the gradients, namely —grad T and —grad μ.

Another aspect of Equation 1, which is commonly overlooked, is that it is perfectly valid—subject to the aforementioned restrictions—irrespective of whether dlw is path dependent or path independent. In general, dlw for closed systems is regarded as path dependent because heat Q and work W are path dependent. However, if either Q or W is zero, then the non-zero quantity becomes path independent, as required by the first law energy balance, and in this case dlw becomes path independent. For open systems in which a transfer of mass occurs across the boundaries as well as a transfer of heat and work, then it is conceivable that the energy term associated with mass transfer is path dependent if the properties of the mass being transferred vary with the amount of mass transported. However, for discontinuous or steady state systems, the properties are invariant at the boundary so

*Since $\dfrac{\partial\mu}{\partial T} = -s$, then it follows that $s_i\,(T_i - T) +$

$(\mu_i - \mu) = (\mu_i)_{P_i,T} - (\mu_i)_{P_i,T} + (\mu_i)_{P_i,T_i} - (\mu)_{P,T}$

$= (\mu_i)_{P_i,T} - (\mu)_{P,T} \equiv \Delta\mu_T$

that the energy term associated with mass transfer is path independent. Therefore for the case of either discontinuous or steady state, open systems in which no work is done, dlw is an exact differential.**

In reality it is not essential to the objectives of this paper to argue further regarding the necessity and sufficiency of the conditions for which dlw can be treated as path independent or an exact differential. As will be seen in the following development, the subsequent restrictions to systems under the influence of very small potential differences or gradients (or fluxes) is equivalent to considering only those processes for which dlw is an exact differential; in other words the linear laws and the bilinear form of the entropy production or lost work equation are tantamount to the assumption that dlw is an exact differential. Therefore, it is permissible to express Equation 1 as

$$dlw = (\Delta T)\, d\frac{Q}{T_i} + (\Delta\mu_T)\, dM \equiv$$
$$\left(\frac{\partial lw}{\partial \frac{Q}{T_i}}\right)_M d\frac{Q}{T_i} + \left(\frac{\partial lw}{\partial M}\right)_{\frac{Q}{T_i}} dM \qquad (2)$$

Once the conditions of exactness implied by Equation 2 are recognized, the remainder of the macroscopic derivation of the reciprocal relations is almost trivial.

FLUXES AS INDEPENDENT VARIABLES

EQUATION 1 CAN BE expressed in rate form:

$$\dot{lw} = \frac{\dot{Q}}{T_i}(\Delta T) + \dot{M}(\Delta\mu_T) \qquad (3)$$

where the dot above the symbol denotes the time (θ) derivative.

From Equation 3 and well-established thermodynamic concepts, four postulates can be inferred:[9]

I. $\dot{lw} = \dot{lw}\left(\frac{\dot{Q}}{T_i}, \dot{M}\right)$. Since both $\frac{\dot{Q}}{T_i}$ and $\dot{M}$ are continuous functions of ΔT and $\Delta\mu_T$,

**It is interesting to note that the form of Equation 1 is similar to the decrease in availability or maximum work which is an exact differential.[8] Likewise, dlw is path independent for a process between two prescribed states in which no work is transferred. In other words the lost work, lw, can be no greater, nor less, than the maximum work that could have been transferred if each step of the process was carried out reversibly.

$l\dot{w}$ can be expressed as a function of two independent variables, namely $\left(\dfrac{\dot{Q}}{T_i}, \dot{M}\right)$, $(\Delta T,$ $\Delta\mu_T)$, $\left(\dfrac{\dot{Q}}{T_i}, \Delta\mu_T\right)$ or $(\dot{M}, \Delta T)$.

II. $l\dot{w}(0,0) = 0$. If $\dfrac{\dot{Q}}{T_i}$ and $\dot{M}$ are each equal to zero, so is $l\dot{w}$.

III. $\dfrac{\partial l\dot{w}}{\partial \dfrac{\dot{Q}}{T_i}}(0,0) = 0$ and $\dfrac{\partial l\dot{w}}{\partial \dot{M}}(0,0) = 0$.

Since $l\dot{w}$ is always positive and is a continuous, even function, with continuous derivatives,

$$l\dot{w}\left(\frac{\dot{Q}}{T_i}\right) = l\dot{w}\left(-\frac{\dot{Q}}{T_i}\right) \text{ and } l\dot{w}(\dot{M}) = l\dot{w}(-\dot{M}).$$

IV. $\dfrac{\partial^2 l\dot{w}}{\partial \dfrac{\dot{Q}}{T_i} \partial \dot{M}} = \dfrac{\partial^2 l\dot{w}}{\partial\dot{M}\partial \dfrac{\dot{Q}}{T_i}}$. The equivalence

of the cross partials follows immediately from the first postulate.

Referring to Equation 3 and recalling that according to Fourier's law, $Q \frown \Delta T$, and according to Fick's law, $\dot{M} \frown \Delta\mu_T$, it is postulated that $l\dot{w}$ is a homogeneous function of the second degree in

$\dfrac{\dot{Q}}{T_i}$ and $\dot{M}$ (or in ΔT and $\Delta\mu_T$) at least to a first

approximation for small fluxes or forces. Thus Equation 3 can be expressed in general functional form for the case in which $l\dot{w}$ is time independent, such as for discontinuous or steady state systems,[10]

$$l\dot{w} = l\dot{w}\left(\frac{\dot{Q}}{T_i}, \dot{M}\right) \tag{4}$$

It is to be noted that Equation 4 implies that

$dl\dot{w}$ is an exact differential in $\dfrac{\dot{Q}}{T_i}$ and $\dot{M}$.

Applying Euler's theorem for homogeneous functions of the second degree to Equation 4:

$$l\dot{w} = \frac{1}{2}\left(\frac{\partial l\dot{w}}{\partial \dfrac{\dot{Q}}{T_i}}\right)_{\dot{M}}\frac{\dot{Q}}{T_i} + \frac{1}{2}\left(\frac{\partial l\dot{w}}{\partial \dot{M}}\right)_{\dfrac{\dot{Q}}{T_i}}\dot{M} \tag{5}$$

Recalling the definition of the time derivative $d(z)/d\theta = \dot{z}$ so that $dz = \dot{z}d\theta$, Equation 5 becomes, after multiplying through by $d\theta$

$$dl\dot{w} = \frac{1}{2}\left(\frac{\partial l\dot{w}}{\partial \dfrac{\dot{Q}}{T_i}}\right)_{\dot{M}} d\frac{\dot{Q}}{T_i} + \frac{1}{2}\left(\frac{\partial l\dot{w}}{\partial \dot{M}}\right)_{\dfrac{\dot{Q}}{T_i}}dM \tag{6}$$

Since $dl\dot{w}$ is exact, the coefficients of the dif-

ferentials of $\dfrac{\dot{Q}}{T_i}$ and $\dot{M}$ in Equations 2 and 6

can be equated. Thus,

$$\Delta T = \left(\frac{\partial l\dot{w}}{\partial \dfrac{\dot{Q}}{T_i}}\right)_M = \frac{1}{2}\left(\frac{\partial l\dot{w}}{\partial \dfrac{\dot{Q}}{T_i}}\right)_{\dot{M}} \tag{7}$$

$$\Delta\mu_T = \left(\frac{\partial l\dot{w}}{\partial \dot{M}}\right)_{\dfrac{\dot{Q}}{T_i}} = \frac{1}{2}\left(\frac{\partial l\dot{w}}{\partial \dot{M}}\right)_{\dfrac{\dot{Q}}{T_i}} \tag{8}$$

The right-hand partial differentials of Equations 7 and 8 can be expanded in a MacLaurin series neglecting terms higher than second order.

$$\Delta T = \frac{1}{2}\left(\frac{\partial l\dot{w}}{\partial \dfrac{\dot{Q}}{T_i}}\right)_{\dot{M}} = \frac{1}{2}\left(\frac{\partial^2 l\dot{w}}{\partial \dfrac{\dot{Q}}{T_i}^2}\right)_{0,0}\frac{\dot{Q}}{T_i}$$

$$+ \frac{1}{2}\left(\frac{\partial^2 l\dot{w}}{\partial\dot{M}\partial \dfrac{\dot{Q}}{T_i}}\right)_{0,0}\dot{M} \tag{9a}$$

$$\Delta T = L_{11}\frac{\dot{Q}}{T_i} + L_{21}\dot{M} \tag{9b}$$

$$\Delta\mu_T = \frac{1}{2}\left(\frac{\partial l\dot{w}}{\partial\dot{M}}\right)_{\dfrac{\dot{Q}}{T_i}} = \frac{1}{2}\left(\frac{\partial^2 l\dot{w}}{\partial \dfrac{\dot{Q}}{T_i}\partial\dot{M}}\right)_{0,0}\frac{\dot{Q}}{T_i}$$

$$+ \frac{1}{2}\left(\frac{\partial^2 l\dot{w}}{\delta\dot{M}^2}\right)_{0,0}\dot{M} \tag{10a}$$

$$\Delta\mu_T = L_{21}\frac{\dot{Q}}{T_i} + L_{22}\dot{M} \qquad (10b)$$

where the L's are substituted for the second order, partial differential, constant coefficients. Note particularly that since the second order cross partials are equal, then $L_{12} = L_{21}$. Equations 9b and 10b can be solved for $\frac{\dot{Q}}{T_i}$ and $\dot{M}$ without destroying the symmetry (equivalence of cross partials) to obtain

$$-\frac{\dot{Q}}{T_i} = \mathbf{L}_{11}\,\Delta T + \mathbf{L}_{12}\,\Delta\mu_T \qquad (11)$$

$$\dot{M} = \mathbf{L}_{21}\,\Delta T + \mathbf{L}_{22}\,\Delta\mu_T \qquad (12)$$

where the $\mathbf{L}$'s denote the terms containing the L's. It can be shown easily that $\mathbf{L}_{12} = \mathbf{L}_{21}$, since $L_{12} = L_{21}$.

The forces as defined by Equations 7 and 8 and the fluxes as given by Equations 11 and 12 are identical to those of Onsager.[3,7]

SELECTION OF OTHER INDEPENDENT VARIABLES

AS NOTED in Postulate I above, $l\dot{w}$ could just as well have been expressed in terms of other independent variables. For example, instead of Equation 4, one could have started with

$$l\dot{w} = l\dot{w}(\Delta T, \Delta\mu_T) \qquad (13)$$

By utilizing the same procedures as above, it can be shown that Equations 11 and 12 will result. In this case the fluxes and forces are defined as

$$\text{Flux} = -\frac{\dot{Q}}{T_i} = \tfrac{1}{2}\left(\frac{\partial l\dot{w}}{\partial \Delta T}\right)_{\dot{M}} \text{ and Force} = \Delta T \quad (14)$$

$$\text{Flux} = \dot{M} = \tfrac{1}{2}\left(\frac{\partial l\dot{w}}{\partial \Delta\mu_T}\right)_{\frac{\dot{Q}}{T_i}} \text{ and Force} = \Delta\mu_T \quad (15)$$

In the paper by Sliepcevich and Finn[9] the fluxes and forces were defined in the above manner. It can also be shown that these definitions are equivalent to those of Onsager.***

Similarly, Equations 16 and 17 could have been used as starting points.

***In reality, the definitions of the fluxes and forces as given by Equations 14 and 15 are more consistent with the treatment of the Onsager coordinates in the bilinear form of the entropy equation as intensive, rather than extensive, variables.

$$l\dot{w} = l\dot{w}\left(-\frac{\dot{Q}}{T_i}, \Delta\mu_T\right) \qquad (16)$$

$$\text{or} \qquad l\dot{w} = l\dot{w}(\Delta T, \dot{M}) \qquad (17)$$

to obtain Equations 11 and 12.

Of the four possibilities, Equations 4, 13, 16 and 17, Equation 17 would represent the most logical choice since ΔT and $\dot{M}$ are the quantities that can be measured directly.

CONCLUSION

IT IS SUBMITTED that the foregoing macroscopic approach constitutes a valid derivation of the Onsager reciprocal relations without recourse to the theorem of microscopic reversibility. Recent experimental evidence has caused some physicists to question the validity of the time reversal invariance principle on which the theorem of microscopic reversibility is based. Notwithstanding, the assumptions and postulates for the macroscopic derivation presented herein are
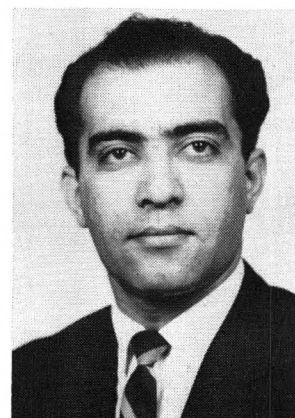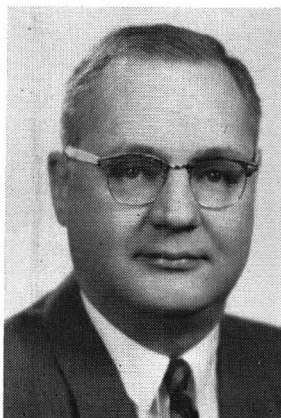
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equally tenable to those involved in the microscopic derivation since both are consistent with empirical observations on related physical phenomena.

The principal result of the Onsager development is that the reciprocal relations, derived by application of the theorem of microscopic reversibility, permit a direct comparison of fluxes and forces with physically, identifiable quantities. On the other hand, the macroscopic derivation presented herein achieves the same result by virtue of the fact that $d_l w$ and $d_l \dot{w}$ can be treated as exact differentials for the conditions under which the equations of irreversible thermodynamics hold and to the extent that the fundamental laws of classical macroscopic thermodynamics are valid. In other words, since the lost work is already known a priori to be path independent (when no work is done at any stage of the process) no new information is gained by resorting to the theorem of microscopic reversibility.

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APPROACHES TO

STATISTICAL

THERMODYNAMICS*

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Statistical thermodynamics connects classical thermodynamics which describes the energetic interactions of macroscopic systems with the properties of the microscopic or molecular constituents of a system. The connection expands the application of thermodynamics to extreme temperature, solid state, thermo-electric, and other phenomena. It permits derivation of equations of state, and calculation of thermodynamic properties from spectroscopic data. It provides insights to many thermodynamic properties, particularly the entropy. Like many other worthwhile goals, statistical thermodynamics may be approached in a number of ways. The various approaches each have their strong proponents and detractors and the selection of an approach is often a subjective decision reflecting the user's mathematical sophistication, epistemological philosophy and teacher's prejudice.

My purpose here is to outline the more common approaches to statistical thermodynamics, necessarily in qualitative terms and with more emphasis on the similarities than the differences. My point of view is summarized by the mountainscape sketched in Fig. 1. In the brief time available I will run you over the various trails, passes and pathways which have been used to connect microscopic to macroscopic thermodynamic behavior.