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DEVELOPMENT OF CONSISTENT FORMS FOR THE GIBBS EQUATION AND THE ENTROPY BALANCE

ABSTRACT

The principles of conservation of matter and energy are readily quantified in the mass and energy balances of the First Low of Thermodynamics. On the other hand formulation of a comparable balance equation for the Second Law tends to be more abstruse in traditional expositions.

The objective herein is to demonstrate the basic Second Law equations--the Gibbs (or combined law) equation and the generalized entropy balance--can be obtained as a simultaneous result of combining the First Law mass and energy balances with corresponding energy transport of degradation functions. In this manner, consistency or reciprocity between the Gibbs equation and the entropy balance is assured. Another dividend from this approach is that it facilitates a more pragmatic interpretation of these relations.

RESUMEN

Los principios de conservación de materia y energía son rápidamente cuantificados en los balances de masa y energía en la lera. Ley de la Termodinámica. Por otra parte, la formulación de una ecuación de balance comparable para la 2da. Ley tiende a ser difícil de comprender en exposiciones tradicionales.

El objetivo de este trabajo es demostrar que las ecuaciones básicas de la 2da. Ley (la ecuación de Gibbs (o ley combinada) y el balance de entropía generalizado) pueden ser obtenidas como un resultado simultáneo de combinar la lera. Ley de balances de masa y energía con el correspondiene transporte de energía o funciones de degradación. De esta manera, se asegura la consistencia o reciprocidad entre la ecuación de Gibbs y el balance de entropía. Otra ventaja de este enfoque es que facilita una interpretación más pragmática de estas relaciones.

INTRODUCTION

The methodology presented herein was originally developed for use in the classroom to add a measure of concreteness to the concept of entropy which, for many students, seems hopelessly embedded in abstractionism.

To this end gross simplifications, including absence of any mathematical sophistication--yet without compromising the generality of the results--will constitute the procedure. What it lacks in elegance, it compensates in realization, as perceived by more than four decades of experience with students. Forthwith, then, a one-dimensional system composed of a single, non-reacting substance which is free from any effects due to external conservative fields, bulk kinetic energy, viscous dissipation forces, memory and nuclear transformations will be the focus of attention. Accordingly the basic equations for the First Law are the

Mass balance: $\qquad dM = \delta M_i - \delta M_o \qquad$ (1)

and the

Energy balance: $\quad dU = \delta Q + \underline{H}_i \delta M_i - \underline{M}_o \delta M_o - \delta W \qquad$ (2)

The Second Law equations, as established by practice, are the

Gibbs equations: $\quad dU = Tds - PdV + \underline{G}dM \qquad$ (3)

and the

Entropy balance: $\quad dS = \delta\left[\dfrac{Q}{T_{bq}}\right] + \underline{S}_i \delta M_i - \underline{S}_o \delta M_o + \dfrac{\delta L_w}{T}$

$$\qquad (4)$$

where the symbols have the following identities: M (mass), U (internal energy), Q (heat), H (enthalpy), W (work), T (temperature), S (entropy), P (pressure), V (volume), $\underline{G}$ (chemical potential although Gibbs used the symbol μ) and LW (lost work).[1]

The subscripts "i" and "o" represent "in" and "out" and the subscript "bq" on temperature indicates the temperature at the boundary where the heat transfer takes place. The bars under the symbols (H and S) denote the property per unit mass. M in equation (1), U in equation (2), all of the terms in equation (3) and S in equation (4) refer to properties within the system as contrasted to properties at the boundary which are always subscripted with lower case letters.

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Equations (1) and (2) are simply expressions of the accountability principle: "Accumulation equals Input minus Output". Note in this instance that the algebraic sign convention for mass in and mass out is always positive, whereas Q is positive for heat absorbed by the system from the surroundings and W is positive for work done by the system on the surroundings.

Equation (3), as originally proposed by Gibbs, constituted an extension of his equation for a closed system undergoing a reversible change of state to an open system by simply adding the $\underline{G}dM$ term. [2]. In so doing Gibbs stated explicity that equation (3) served as the defining equation for the potential, G.

Gibbs did not utilize, however, an entropy balance comparable to equation (4) which is simply: "Accumulation equals Input minus Output plus Production." In fact, this general form [3] --or its equivalent-- really did not become "popular" until a half century after Gibbs. Note that equation (4) is "analogous in structure" to the energy balance, equation (2), at least to the extent that it contains explicit terms for heat and mass transfers. However, the entropy balance corresponding to equation (4) cannot be postulated simply by analogy to the First Law energy balance, equation (2), with an a priori assurance that it will be consistent with equation (3) as originally proposed by Gibbs. For this reason the customary approach <u>has been</u> to accept equation (3) as the "defining equation for entropy" (not strictly in accord with the original development by Gibbs, as noted in the previous paragraph, since he used this equation to define chemical potential after having accepted Clausius' definition of entropy). Then, by substituting this equation for dU in the energy balance, equation (2), and carrying out essential algebraic manipulations (similar to those employed later in this presentation) a relationship corresponding to the entropy balance in equation (4) can be obtained. In this presentation, however, the objective is to obtain the Gibbs equation and the entropy balance simultaneously such that a variety of reciprocal forms can be examined. In so doing the content of the entropy production concept is exposed.

SIMULATION OF IRREVERSIBLE PROCESSES

The energy balance of equation (2) requires that the boundary of a system be conceptualized as three discrete sections: (1) a rigid, diathermal, impermeable wall which only allows heat transfer; (2) an adiabatic, impermeable wall or linkage which only allows work transfer; and (3) an adiabatic and anergistic wall that is permeable only to mass but not to heat or work transfers. (Notwithstanding, ambiguities continue to arise at boundaries where mechanical work is dissipated as frictional heat or viscous dissipation and/or where simultaneous heat and mass are exchanged.)

For finite rates of heat, work, and mass transfers, gradients in the corresponding potentials (driving forces) or properties must exist, at least at the boundaries; such gradients are assumed to be continous. In order to apply the concepts of ·classical thermodynamics (often equated to thermostatics) specifically the Gibbs relation, equation (3), the initially, non-uniform system must be subdivided into small elements or subsystems such that the assignment of "average" uniform properties [4] to the material inside the boundaries of the system is representative. The properties at the boundary, however, retain their original values. The net result is an element or subsystem having uniform properties throughout with discontinuities (or "jumps") in the corresponding properties at the boundaries. Accordingly, the conventional methods of thermostatics for the analysis of "discontinuous systems" apply by treating the boundary as one part with uniform properties and the system as the other part with a different set of uniform properties. Note that the requirement of uniformity does not impose constancy with time; i.e. properties can be time vairant, but at every instant of time they must be uniform throughout the element; this condition must be fulfilled in order to apply the Gibbs relation, equation (3), which expresses dU in terms of properties of the system. On the other hand the energy balance, equation (2), expresses dU in terms of <u>transitory</u> quantities which are defined, and exist, only at the boundary during the actual transfer process.

Gibbs first "derived" the closed system form of equation (3)

$$dU = (TdS - PdV)_{rev} \qquad (5)$$

from the energy balance for a simple, closed system ($\delta M_i = 0 = \delta M_o$) by considering only a reversible process in which case all that was required was to substitute (TdS) and (PdV) for δQ and δW, respectively, in the closed system energy balance. In the present development, the open system form of the Gibbs relation, equation (3), and the entropy balance, equation (4), will be obtained simultaneously from the energy balance, equation (2), without imposing the restriction of a reversible process. To do so, will require the definition of an energy transport or degradation function which remains valid even for irreversible (real) processes.

Whenever a gradient of discontinuity (as explained above) in the potential or thermodynamic force exists--such as pressure, temperature, chemical potential or electromotive force --a transfer or displacement of a conjugate quantity-- such as volume, "entrops" (heat energy per unit of absolute temperature), mass, electric charge, etc.--<u>can</u> occur, subject of course to the conditions of constraint. The <u>net</u> energetic effect associated with each transfer can be expressed in general by

$$(\delta\lambda) \equiv (\psi_b - \psi)(\delta\Omega) \qquad (6)$$

where ($\delta\Omega$) designates the quantity transported or displaced at the boundary; ψ_b and ψ designate the

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thermodynamic potentials at the boundary and within the uniform system (or subsystem) respectively and $(\delta\lambda)$ designates the net or residual energy associated with the transfer. For the time being it is better to regard equation (6) as a mathematical definition; later its physical significance will become evident. Equation (6) can be specialized for heat, mass and work transfers as follows:

$$\delta\lambda_Q = (T_{bq} - T)\ \delta\left[\frac{Q}{T_{bq}}\right] \tag{7}$$

$$\delta\lambda_{M_1} = (\underline{H}_1 - \underline{H})\ (\delta M_1) \tag{8}$$

$$\delta\lambda_{M_o} = (\underline{H}_o - \underline{H})\ (\delta M_o) \tag{9}$$

$$\delta\lambda_W = (P_{bw} - P)\ (\delta V) \tag{10}$$

Note in equation (10) that only the pressure/volume transport will be considered here, for simplicity. [5] Introducing definitions (7) through (10) into the energy balance, equation (2), in accordance with the principle of equiponderation,

$$dU = \left[\ \delta Q - (T_{bq} - T)\ \delta\left[\frac{Q}{T_{bq}}\right] + \delta\lambda_Q\ \right] -$$

$$\left[\ \delta W - (P_{bw} - P)\ \delta V + \delta\lambda_W\ \right] +$$

$$\left[\ \underline{H}_1\delta M_1 - (\underline{H}_1 - \underline{H})\delta M_1 + \delta\lambda_{M_1}\ \right] -$$

$$\left[\ \underline{H}_o\delta M_o - (\underline{H}_o\delta M_o - (\underline{H}_o - \underline{H})\delta M_o + \delta\lambda_{M_o}\ \right] \tag{11}$$

Note that the second and third terms within each bracket are equivalents because of equations (7) through (10). Also, for this simple system,

$$\delta W = P_{bw}\ \delta V = P_{bw}\ dV \tag{12}$$

By combining equations (1), (11) and (12), simplifying and regrouping terms,

$$dU = T\left[\delta\left(\frac{Q}{T_{bq}}\right) + \frac{\delta\lambda_Q - \delta\lambda_W + \delta\lambda_{M_1} - \delta\lambda_{M_o}}{T}\right] - PdV + \underline{H}dM \tag{13}$$

Since U is a state function it is permissible to replace the bracketed term by the derivative of a state function; therefore, let

$$d\sigma \equiv \left[\delta\left(\frac{Q}{T_{bq}}\right) + \frac{\delta\lambda_Q - \delta\lambda_W + \delta\lambda_{M_1} - \delta\lambda_{M_o}}{T}\right] \tag{14}$$

equation (13) becomes

$$dU = T\delta\sigma - PdV + \underline{H}dM \tag{15}$$

Although equations (14) and (15) are "uncommon", they to consitute a compatible pair which could be used, presumably, in place of the conventional entropy balance, equation (4), and the conventional Gibbs relation, equation (3). It is also obvious in equation (14) that if all the potentials are balanced, i.e. all $\delta\lambda$'s are zero, the σ function is identical to the entropy function for a closed system. (In fact, it can be shown that $d\sigma + \underline{S}dM = dS$.)

CONVENTIONAL ENTROPY BALANCE

Since entropy is a function of state it can be considered to be a property of matter in the same sense as internal energy. Thus, it follows that in an exchange of mass between the system and surroundings, a corresponding quantity of entropy is transferred. Inspection of equation (15) indicates that since $(\underline{H}dM)$ is the only term explicit in (dM), it must account for all energetic effects associated with transfer of mass. Intuitively then, enthalpy (H) must contain implicitly and identifiable part related to entropy. Furthermore by analogy with the energy balance, equation (2), and in anticipation fo the desired form of the entropy balance as given by equation (4), it is evident that explicit terms for entropy flux associated with mass transfers will have to be introduced in equation (13). Accordingly $\underline{S}_1\delta M_1$ and $\underline{S}_o\delta M_o$ are added and subracted within the brackets of the right side of equation (13). Now, in keeping with the fact that all of the λ terms are expressed as differences in properties between the boundary and system, as shown in equation (11), $\underline{S}dM$ is subtracted and its equivalent $\underline{S}(\delta M_1 - \delta M_o)$ is added within the brackets. Collecting and grouping terms leads to

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$$dU = T\left[\delta\left(\frac{Q}{T_{bq}}\right) + \underline{S}_1\delta M_1 - \underline{S}_o\delta M_o + \frac{1}{T}\left\{\delta\lambda_Q - \delta\lambda_W + \delta\lambda_{M_1} - \right.\right.$$

$$\left.\left. T(\underline{S}_1-\underline{S})\delta\underline{M}_1 - \delta\lambda_{M_o} + T(\underline{S}_o-\underline{S})\delta M_o\right\}\right] - PdV + (\underline{H}-T\underline{S})dM \quad (16)$$

Defining and recalling equations (7) through (10)

$$dS \equiv \delta\left(\frac{Q}{T_{bq}}\right)\underline{S}_1\delta M_1 - \underline{S}_o\delta M_o + \frac{1}{T}\left\{(T_{bq}-T)\delta\left(\frac{Q}{T_{bq}}\right)-(P_{bw}-P)\delta V + \right.$$

$$\left. \left[(\underline{H}_1-\underline{H})-T(\underline{S}_1-\underline{S})\right]\delta M_1 - \left[(\underline{H}_o-\underline{H})- T(\underline{S}_o-\underline{S})\right]\delta M_o\right\} \quad (17)$$

Combining equations (16) and (17)

$$dU = Tds - PdV + \underline{G}dM \quad (3)$$

where $\underline{G} \equiv \underline{H} - T\underline{S}$ \quad (18)

Equation (18) can be used to eliminate H in equation (17) to obtain another version of the entropy balance,

$$dS = \delta\left(\frac{Q}{T_{bq}}\right) + \underline{S}_1\delta M_1 - \underline{S}_o\delta M_o + \frac{1}{T}\left\{(T_{bq}-T)\delta\left(\frac{Q}{T_{bq}}\right)\right.$$

$$\left. (P_{bw}-P)\delta V + \left[(\underline{G}_1-G) + S_1(T_1-T)\right]\delta M_1 - \right.$$

$$\left. - \left[(\underline{G}_o-\underline{G}) + \underline{S}_o(T_o-T)\right]\delta M_o\right\} \quad (19)$$

Each of the terms within the braces of equation (17) can now be identified with the Second Law Generalization

$$[\Delta S]_{univ} \equiv [\Delta S]_{sys} + [\Delta S]_{sur} \geq 0 \quad (20)$$

where subscipts "univ", "sys" and "sur" refer respectively to the universe, system and surroundings (same as boundary in the above). Applying equation (20) individually to the processes of heat, work and mass transfer:

$$\left[\Delta S_Q\right]_{univ} = \left[\delta\left(\frac{Q}{T}\right)\right]_{sys} - \left[\delta\left(\frac{Q}{T_{bq}}\right)\right]_{sur} =$$

$$\frac{(T_{bq}-T)\delta\left(\frac{Q}{T_{bq}}\right)}{T} \equiv \frac{\delta LW_Q}{T} \quad (21)$$

$$\left[\Delta S_W\right]_{univ} = \left[\frac{(P-P_{bw})dV}{T}\right]_{sys} + [0]_{sur} =$$

$$-\frac{(P_{bw}-P)dV}{T} \equiv \frac{\delta LW}{T} \quad (22)$$

$$\left[\Delta S_{M_1}\right]_{univ} = \left[\underline{S} + \frac{(\underline{H}_1-\underline{H})}{T}\right]_{sys}\delta M_1 - \left[\underline{S}_1\delta M_1\right]_{sur}$$

$$= \frac{[(\underline{H}_1-\underline{H})-T(\underline{S}_1-\underline{S})]\delta M_1}{T} \equiv \frac{\delta LW_{M_1}}{T} \quad (23)$$

$$\left[\Delta SM_o\right]_{univ} = -\frac{\left[(\underline{H}_o-\underline{H})-T(\underline{S}_o-\underline{S})\right]\delta M_o}{T} = \frac{\delta LW_{M_o}}{T} \quad (24)$$

Introducing equations (21) through (24) into equation (17),

$$dS = \delta\left(\frac{Q}{T_{bq}}\right) + \underline{S}_1\delta M_1 - \underline{S}_o\delta M_o +$$

$$\left[\frac{\delta LW_Q + \delta LW_W + \delta LW_{M_1} + \delta LM_{M_o}}{T}\right] \quad (25)$$

$$dS = \delta\left(\frac{Q}{T_{bq}}\right) + \underline{S}_1\delta M_1 - \underline{S}_o\delta M_o \pm \frac{\delta LW}{T} \quad (4)$$

Comparing equations (21) through (24) with (7) through (10),

$$\delta LW_Q = \delta\lambda_Q \quad (26)$$

$$\delta LW_w = -\delta\lambda_W \quad (27)$$

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$$\delta LW_{M_1} = \left[\delta\lambda_{M_1} - T(\underline{S}_1 - \underline{S})\delta M_1 \right] \qquad (28)$$

$$\delta LW_{M_o} = - \left[\delta\lambda_{M_o} - T(\underline{S}_o - \underline{S})\delta M_o \right] \qquad (29)$$

The physical significance of the energy transport function, $\delta\lambda$, should now be evident. (The difference in algebraic signs arises because λ was defined in a consistent manner whereas Q, W, δM_1 and δM_o are defined by convention.)

In view of equations (21) through (24) the entropy balance equation (17), (25) or (4) can also be written

$$dS = \left[\delta\left(\frac{Q}{T_{bq}}\right) + \underline{S}_1\delta M_1 - \underline{S}_o\delta M_o \right] + \left[\left(\Delta S_Q\right) + \left(\Delta S_W\right) + \left(\Delta S_{M_1}\right) + \left(\Delta S_{M_o}\right) \right]_{univ} \qquad (30)$$

which is essentially a statement that

increase in entropy of the system	-	decrease in entropy of the surroundings due to heat and mass transfer	+	increase in entropy of the system plus the surroundings due to heat, work and mass transfer

(31)

Clearly, equation (31) is--as pointed out earlier in footnote (3)--both conceptually and fundamentally different from Clausius' equation

$$dS = d_{ext}S + d_{int}S \qquad (32)$$

where $d_{ext}S$ is the entropy change of the system due to entropy transfers from the surroundings and $d_{int}S$ is due to entropy changes within the system. By this definition, equation (32) can now be expressed in terms of its implicit variables

$$d_{ext}S = \delta\left(\frac{Q}{T}\right) + \underline{S}dM \qquad (33)$$

Combining equations (32) and (33) and substituting the result into equation (17) and recalling equations (8), (9) and (10)

$$d_{int}S = + \left[\frac{-\delta\lambda_W + \delta\lambda_{M_1} - \delta\lambda_{M_o}}{T} \right] \qquad (34)$$

or with use of equations (27), (28) and (29)

$$d_{int}S = \frac{1}{T}\left[\delta LW_W + \delta W_{M_1} + T(\underline{S}_1 - \underline{S})\delta M_1 - \delta LW_{M_o} - T(\underline{S}_o - \underline{S})\delta M_o \right] \qquad (35)$$

Obiously, $d_{int}S$ of equation (32) is an incomplete statement of the entropy production concept [as in clearly evident by equations (34) and (35) since it does not take into account irreversibilities due to heat transfer and a portion of the irreversibilites due to mass transfer. Equation (32) can be written, by virtue of equation (8), (9) and (10) as

$$[dS] = \left[\delta\left(\frac{Q}{T}\right) + \underline{S}dM \right] + \left[\frac{(P-P_b)dV + (\underline{H}_1 - \underline{H})\delta M_1 - (\underline{H}_o - \underline{H})\delta M_o}{T} \right]$$

(36)

which is the equivalent of equation (32) and represents

increase in entropy of the system	=	increase in entropy of the system due to the "reversible" parts of heat and mass transfer	+	change in entropy of the system due to all of the irreversibilities arising from work transfer, a portion of the irreversibilities due to mass transfer but none of the irreversibilities due to heat transfer

(37)

The principal difference between the entropy balances, equations (31) and (37) is that the former focuses on changes in the entropy of the system and the surroundings whereas the latter is expressed entirely in terms of changes in the system. Although equation (25) or (4) is the common form for the entropy balance, the interpretation given in equation (31) is generally overlooked. The most significant difference between the entropy balances of equations (25) and (36) is that in the former the last term, LW, is always equal to or greater than zero because of equation (20) whereas in

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equation (36) the last bracketed term can be negative since there is not any thermodynamic requirement that the enthalpy difference terms contained therein be positive even though the $(P - P_b)\delta V$ term is always equal to or greater than zero. Nevertheless, the compatible form of the Gibbs equation that goes with equation (36) is still.

$$dU = TdS - PdV + \underline{G}dm \qquad (3)$$

Equation (4) or (25) has been the preferred form of the entropy balance in practice. Aside from conforming in structure to the energy balance, its other salient features include:

(1) It is a direct result of introducing energy transport or degradation functions (irreversible concepts) such as equations (7) through (10) into the energy balance.

(2) The heat transfer term, Q, in equation (4) is divided by the local temperature at the boundary where the heat transfer takes place, whereas the lost work term, LW, is divided by the uniform (representative average) temperature of the system which might be substantially different from the boundary temperature.

(3) The lost work term accounts for all of the consequences of irreversible transfers of heat, work and mass. Obviously for multicomponent systems undergoing chemical, electrical, magnetic, surface, etc. effects additional terms of the general form $(F_{bw} - F)\delta D$, similar to $(P_{bw} - P)\delta V$, will have to be included.

The Gibbs relation, equation (3), likewise has distintive features:

(1) It can only be applied to a system having uniform properties throughout at any particular instante of time; however the properties can vary with time.

(2) As is evident from the foregoing derivations, it is "applicable" to irreversible as well as reversible processes (frequently a point of confusion in the literature).

(3) Although the term $\underline{G}dM$ as discussed herein was restricted to mass transfer across the boundary, a similar, but additional, term which accounts for "internal transfers or exchanges" due to chemical or diffusional effects within the system would be needed. The fact that these two types of mass transfer (external and internal) are universally lumped within one $\underline{G}dM$ is a source of confusion. Notwithstanding, equation (3) can be generalized for systems undergoing electrical, magnetic, surface, etc. effects by adding appropriate "reversible work" terms similar to PdV.

(4) The only useful form of the Gibbs equation is the one written for a unit mass of material as explained in footnote (2).

In this case the $\underline{G}dM$ term due to mass transfer across the boundaries disappears, but the corresponding term due to "chemical work" would not.

OTHER FORMS

Many other "valid" forms of the entropy balance along with the corresponding reciprocal forms of the Gibbs equation can be obtained by the methods illustrated herein since all that is involved is selective transposition of terms constituting LW as identified by equations (26) through (29). For example:

$$dS = \delta\left(\frac{Q}{T}\right) + \underline{S}_1\delta M_1 - \underline{S}_o\delta\underline{M}_o \pm \left\{\frac{\delta LW_W + \delta LW_{M_1} + \delta LW_{M_o}}{T}\right\} \qquad (38)$$

$$dU = Tds - PdV + \underline{G}dM \qquad (39)$$

Note that the denominator for the first term on the right of equation (36) is T rather than T_{bq}; $\delta(Q/T)$ represents the entropy change of the system due to heat transfer. It is a result of combining $\delta(Q/T_{bg})$ with $\delta LW_Q/T$; consequently the LW group within the braces of equation (38) no longer includes a term for irreversible heat transfer. Nevertheless the Gibbs relation is identical to the conventional equation (3).

By similar extraction and transposition of the terms contained in the LW group, two more compatible sets are:

$$dS^* = \delta\left(\frac{Q}{T}\right) + \frac{\underline{H}_1\delta M_1 - \underline{H}_o\delta M_o}{T} + \frac{\delta LW_W}{T} \qquad (40)$$

$$dU = TdS^* - PdV \qquad (41)$$

and

$$dS^{**} = \delta\left(\frac{Q}{T_{bq}}\right) + \frac{\underline{H}_1\delta M_1 - \underline{H}_o\delta M_o}{T} + \left[\frac{\delta LW_Q + \delta LW_W}{T}\right] \qquad (42)$$

$$dU = TdS^{**} - PdV \qquad (43)$$

(The asterisks on S are used here simply to distinguish their definitions from equation (4) although numerically $dS = dS^* = dS^{**}$.) Note in equation (40) that any irreversibilities or lost work due to heat and mass transfer are "embedded" in the first two terms on the right; whereas in equation (42) only the lost work due to mass tansfer is embedded in the second term. Nevertheless, the Gibbs equation for both cases has the same form. The inference here is that the Gibbs equation of itself does not give a comprehensive definition for entropy except for reversible processes in closed system.

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CLOSURE

The methodology presented herein may appear on the surface to be hardly more than a tedious exercise in futility. In reality the techniques are as wholesome as the more conventional practice of forcing the "reversible" Gibbs equation into the energy balance, and again via the process of equiponderation, arriving at a preconceived form for the entropy balance. However, the procedure illustrated in this paper, wherein the Gibbs equation and entropy balance "fall out" simultaneously, unmasks potential pitfalls inherent in simply verbalizing the entropy balance. Whatever the final verdict, many students and teachers exposed to this treatment over the past four decades attest its virtue.

FOOTNOTES

1. The quantity $(\delta LW/T)$ is frequently designated by other symbols; for example, S_p = entropy production.

2. It is imperative to realize that Gibbs equation was originally restricted to a one component system of variable mass. Nevertheless, equation (3) as written is meaningless when applied to an open system undergoing a change in mass. In this event, the left hand side of the equation, upon integration becomes

$$(U_2 - U_1) = (M_2 \underline{U}_2 - M_1 \underline{U}_1) = M_1(\underline{U}_2 - \underline{U}_1) + (M_2 - M_1)\underline{U}_2$$

Clearly the magnitude of the difference in the total energy $(U_2 - U_1)$ is completely arbitrary and is dependent energy $(U_2 - U_1)$ is completely arbitrary and is dependent on the reference state selected because of the presence of the last term $(M_2 - M_1)\underline{U}_2$. (As Bridgman somewhat ironically commented: "It means nothing to ask what is the difference of the energy between one and two grams of iron.") The salvation is to restrict use of the Gibbs equation to systems of constant (preferably unit) mass:

$$d\underline{U} = Td\underline{S} - Pd\underline{V}$$

where $U = \underline{U}M$, $S = \underline{S}M$ and $V = \underline{V}M$

Combining these two equations for a system of variable mass leads immediately to

$$dU = TdS - PdV + (\underline{U} - T\underline{S} + P\underline{V})dM$$

Defining, $(\underline{U} - T\underline{S} + P\underline{V}) = \underline{G}$, results in equation (3).

3. As will be shown later this form of the entropy balance is both conceptually and fundamentally different from the Clausius equation

$$dS = d_{ext}S + d_{int}S$$

where the terms on the right discriminate between the entropy change of the system due to entropy transfers from the surroundings $(d_{ext}S)$ and to entropy generated within the system $(d_{int}S)$.

4. Average uniform properties should not be confused with the concept of "local equilibrium"; the latter is hardly more than an equivocal assertion. On the other hand, it should be understood that an obvious alternative to the non-uniformity complication is to integrate over the volume of the system and over the surface of the boundary. Although these integrals are copiously displayed in the literature, they are rarely--if ever--formally solved simply because the required functional relationships among the variables, particularly in multicomponent systems, are non-existent. Consequently, "engineering" approximations are the salvation. Furthermore, there seems to be a redeeming virtue in associating the entropy production concept with jump discontinuities in the properties.

5. Had it not been for all of the simplifications introduced at the onset, the more general expression for $\delta\lambda_w$ would have been

$$\delta\lambda_w \equiv - (F_{bw} - F)d\ell$$

where the right side of the equation is symbolic for other forms of work such as surface, chemical, electrical, magnetic and elastic strain.

6. Equation (19) clearly shows that ΔG is the "driving force" for mass transfer only when $\Delta T = 0$.

PREFACE

In the Fall of 1974 when I returned to the formal classroom to teach the required graduate course in chemical engineering thermodynamics, after an intermission of several years, I was fortunate to find a student of the caliber of Oladis Marici Troconis Rincón in my class. Her dedication and resolve were not surprising, however, because over the years my colleagues and I have observed that graduate students in chemical and petroleum engineering from Venezuela have a profound interest in thermodynamics. Accordingly, when Professor Rincón invited me to participate in this centennial publication, it seemed befitting for me to select a topic on thermodynamics.

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