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### The Symmetrical Fundamental Property Relation of Thermodynamics\*

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While the relation between thermodynamic properties of any uniform mass of material, first presented by Gibbs in the form  $dU = TdS - PdV + \sum \mu_i dn_i$  is well understood, its attempted extension to effects other than thermal, compression, and change in mass has caused some confusion. The above equation can be presented in a symmetrical form and, on going back to basic principles, it proves possible also to develop the complete symmetrical fundamental property relation including surface, tensile, gravitational, centrifugal, kinetic, electrical, and magnetic effects. Integration of the resulting differential equation yields the primitive or non-differential form. The complete sets of cross partial derivatives, which can be obtained from a generalized form of the fundamental equation, may be compared with the derivatives obtained by conventional methods. Selection of useful cross partials for practical situations is demonstrated.

#### Discussion of Problem and Difficulties of Present Treatment

Any change in the state of a finite collection of matter or substance results in a change in its thermodynamic properties. These property changes are not independent, but are inter-related by the most important equation in macroscopic thermodynamics, namely, the well-known property relation originally presented by Gibbs [5]<sup>1)</sup>,

$$dU = TdS - PdV + \sum_i \mu_i dm_i, \quad (1)$$

where the symbols are defined in the table of nomenclature. The extreme power and utility of this equation may be appreciated when it is realized that every other relation between thermodynamic properties is derivable from it or from its more general form. As it stands in its simplest form, Eqn. (1) considers only thermal, compres-

sion, and mass change effects in any substance whose temperature, pressure, and chemical potentials are uniform throughout. It is the extension to other effects that is the subject of this paper, for although Eqn. (1) is well understood, its inclusion of effects such as surface, tensile, gravitational, centrifugal, kinetic, electrical, and magnetic has caused some confusion.

If Eqn. (1) is divided by  $dm_i$  at constant  $S$ ,  $V$ , and  $m_j$  (where  $m_j$  refers to all but the  $i$ -th component), the result is the defining equation for the mass or chemical potential of the  $i$ -th component,

$$\mu_i = \left( \frac{\partial U}{\partial m_i} \right)_{S,V,m_j} \quad (2)$$

Its significance may be understood more easily by defining the Gibbs free energy,

$$G = U + PV - TS, \quad (3)$$

which may be differentiated and combined with Eqn. (1) to give

$$dG = -SdT + VdP + \sum_i \mu_i dm_i. \quad (4)$$

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1) Nomenclature see P. 256

Dividing through Eqn. (4) by  $dm_1$  at constant  $T$ ,  $P$ , and  $m_j$  shows that

$$\mu_1 = \left( \frac{\partial G}{\partial m_1} \right)_{T,P,m_j} \quad (5)$$

Since, for this case where only thermal, compression, and mass effects are considered, the derivative of an extensive property with respect to  $m_1$  at constant  $T$ ,  $P$ , and  $m_j$  is the partial extensive property, the chemical potential is the partial free energy,

$$\mu_1 = \bar{G}_1 \quad (6)$$

This may be inserted into Eqn. (1) to give

$$dU = TdS - PdV + \sum_i \bar{G}_i dm_i \quad (7)$$

Differentiation of Eqn. (3) with respect to  $m_1$  at constant  $T$ ,  $P$ , and  $m_j$  shows from the above definition of a partial extensive property that

$$\bar{G}_1 = \bar{U}_1 + P\bar{V}_1 - T\bar{S}_1 \quad (8)$$

which may be put into Eqn. (7) to yield

$$dU = TdS - PdV + \sum_i (\bar{U}_1 + P\bar{V}_1 - T\bar{S}_1) dm_i \quad (9)$$

Although Eqn. (7) appears frequently in the literature, it may also be displayed in a beautifully symmetric form as may be seen by rearranging Eqn. (9) to

$$dU - \sum_i \bar{U}_i dm_i = T(dS - \sum_i \bar{S}_i dm_i) - P(dV - \sum_i \bar{V}_i dm_i) \quad (10)$$

Since this equation does not involve free energy, one would expect that it can be derived from Eqn. (1) without having artificially to define free energy. Indeed, this is the case for one merely divides through Eqn. (1) by  $dm_1$  at constant  $T$ ,  $P$ , and  $m_j$  to obtain

$$\left( \frac{\partial U}{\partial m_1} \right)_{T,P,m_j} = T \left( \frac{\partial S}{\partial m_1} \right)_{T,P,m_j} - P \left( \frac{\partial V}{\partial m_1} \right)_{T,P,m_j} + \mu_1 \quad (11)$$

The derivatives are all partial extensive properties, so

$$\mu_1 = \bar{U}_1 + P\bar{V}_1 - T\bar{S}_1 \quad (12)$$

Although one may well ask why partial properties are defined by a differentiation at constant  $T$  and  $P$ , it is not difficult to see that insertion of Eqn. (12) into Eqn. (1) yields Eqn. (9) or (10) directly.

So far the development is conventional and little different from that presented in dozens of textbooks, except for Eqn. (10) which emphasizes the symmetrical character of the fundamental property relation. The extension to effects other than thermal, compression, or change of mass is not nearly so simple, as demonstrated by the difficulties encountered by many authors. Some of these authors say that the additional effects are handled simply by adding to Eqn. (1) terms of the form, (Intensive Property)(Extensive Property), since this is the form of the terms already appearing in the equation. Others add terms in a rather intuitive manner directly to Eqn. (4), implying there is a better or greater understanding of a quantity such as free energy that has been defined simply for convenience than there is of the basic quantity

energy. (It is not meant that energy itself is a simple concept, but it is certainly simpler than free energy.) Some authors find it desirable to employ new definitions of enthalpy or free energy by including terms that involve the additional effects, while others say that little is to be gained by use of the newly defined quantity. Because of the multiplicity of books on thermodynamics and because of the variation in treatment of the different energy effects, it is not feasible in this paper to analyze the problems of all of them. The difficulties of a few will be presented to show the confusion that exists and to give a framework of reference for the development of the complete fundamental property relation of thermodynamics.

Let us start by examining the treatment of the gravitational effect in the pioneering work of *Lewis* and *Randall* as revised by *Pitzer* and *Brewer* [14]. It is stated [17], more or less without proof, that the reversible lifting of a weight increases its free energy per molal mass  $M$  by an amount,

$$dG = gMdz \quad (13)$$

or

$$\left( \frac{\partial G}{\partial z} \right)_{P,T,\dots} = gM \quad (14)$$

Preceding this relation it is emphasized that although potential energy and internal energy may be separated, the energy-content function  $E$  is to include gravitational energy<sup>2)</sup>. From their previous definition [15] and from their later discussion [19] the Gibbs free energy is defined as

$$G = E + PV - TS \quad (15)$$

The free energy relation when gravity is not of importance is given [6] in essentially the same form as Eqn. (4). If any mass,  $m = nM$ , is lifted, Eqn. (14) may be written

$$\left( \frac{\partial G}{\partial z} \right)_{P,T,\dots} = gm \quad \text{or} \quad dG = gmdz \quad (16)$$

and this may be added to Eqn. (4) to give

$$dG = SdT + VdP + \sum_i \mu_i dm_i + gmdz \quad (17)$$

Now Eqn. (15) may be differentiated and combined with Eqn. (17) to yield

$$dE = TdS - PdV + \sum_i \mu_i dm_i + gmdz \quad (18)$$

In attempting to generalize on the terms in an equation such as Eqn. (18), the equation

$$dE = \sum_i X_i dx_i \quad (19)$$

is presented [18] where  $X_i$  is an intensive variable or force and  $x_i$  is an extensive variable. A table of  $X_i$ 's and  $x_i$ 's is given so that one may readily construct the relation comparable to Eqn. (18) as

2) This is the opposite approach from *Gibbs* [8] who wrote, "The energy of the mass will now consist of two parts, one of which depends upon its intrinsic nature and state, and the other upon its position in space". In this paper the method of *Gibbs* is followed with  $U$  denoting the internal or intrinsic energy and  $\Phi m$  or  $gmz$  denoting the potential energy in the gravitational field.

$$dE = TdS - PdV + \sum_i \mu_i dm_i + gzd m . \quad (20)^{3)}$$

It is obvious there is a contradiction between Eqn. (18) and (20), since the former equation indicates the proper term to account for the gravitational energy effect is  $gmdz$  while the latter equation says it is  $gzdm$ . As will be shown, Eqn. (18) requires a new chemical potential to be defined to include gravitational potential if it is to be correct. Also the last term is of the surprising form, (Extensive Property)  $d$  (Intensive Property), which seems inconsistent with respect to the other terms in the equation. The reason is, of course, that  $gmdz$  represents a change of external energy whereas the other terms contribute to the change of internal or intrinsic energy. Failure to distinguish between internal and external energy is a primary source of confusion here. Eqn. (20) is a specific case of change at constant gravitational energy and is not applicable to lifting a mass.

As a second example of difficulty, the text of *Aston and Fritz* [1] is considered. For a reversible process involving a closed system (italics due to the authors who are emphasizing this restriction) the generalized equation

$$dE = TdS - PdV - \sum_i X_i dx_i \quad (21)^{4)}$$

is given [2] with the  $X_i$ 's and  $x_i$ 's being respectively the intensive and extensive variables other than the usual ones due to thermal and compression effects. In considering the gravitational effect [3] the intensive variable is identified as

$$X_i = gz \quad (22)^{5)}$$

and the extensive variable as

$$x_i = m . \quad (23)$$

Consequently, Eqn. (21) becomes

$$dE = TdS - PdV - gzd m \quad (24)$$

which is obviously contradictory to the statement that the application is to a closed system where  $m$  cannot change. Furthermore, because of the minus sign, the equation says the energy<sup>4)</sup> decreases if the mass is increased in a potential field, a result which can be considered absurd if they mean total energy and incorrect if they mean internal energy which is independent of gravity. It is interesting here that the authors recognized

3) Following their text exactly [18], one would write the last term as  $g(z - z_0)dM$ . The reference point for gravitational energy, however, may be taken as  $z_0 = 0$ . Also the authors used the molal mass  $M$ , whereas here any mass,  $nM$  or  $m$ , is taken as the extensive property, since the molal mass is a constant.

4) It should be noted that *Aston and Fritz* use  $E$  as just energy and nowhere in their book do they say it is either internal or total energy, as emphasized by *Gibbs* [8]. They do, however, define enthalpy as  $H = E + PV + \sum X_i x_i$  which would become  $H = E + PV + mgz$  for this case. If their  $E$  does include potential energy as it appears in Eqn. (21), their enthalpy includes it twice!

5) The expression  $X_i = \int_{z_0}^z g dz$  is the one actually given. If  $z_0$  is taken as 0 and  $g$  is assumed constant for all practical purposes,  $X_i = gz$ , as above.

some inconsistency in their treatment, for they offered a rather incomprehensible explanatory footnote that "the potential energy is regarded somewhat artificially as being built up by introduction of small amounts of mass  $dm$  at the potential  $\Phi$ " ( $\Phi = gz$ ). This fails, however, to explain how the mass can change by  $dm$  in a closed system. The reason this discrepancy was not detected was that  $G$  was defined as  $E - TS + PV + X_i x_i$ . Upon differentiation and combining with Eqn. (21),

$$dG = -SdT + VdP + \sum_i x_i dX_i . \quad (25)$$

Without bothering to go back to Eqn. (21), they put (22) and (23) into (25) to get

$$dG = -SdT + VdP + gmdz . \quad (26)$$

This equation fortuitously solved problems of equilibrium in a gravitational field, so they erroneously considered their development satisfactory.

As a third and last example, we shall look at the well-known textbook by *Guggenheim* [10]. He considers [12] the work done in transferring  $dn_i$  moles of  $i$  from phase  $\alpha$  to phase  $\beta$ , each with its own gravitational potential,

$$W = (\Phi^\beta - \Phi^\alpha) M_i dn_i . \quad (27)$$

From this he deduces that terms of the form  $\sum_i \Phi^\alpha M_i dn_i^\alpha$  must be added to the property relation (1) in terms of moles for each phase  $\alpha$ , so that

$$dU^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_i (\mu_i^\alpha + M_i \Phi^\alpha) dn_i^\alpha , \quad (28)$$

It is not absolutely clear whether his  $U$  is internal energy alone or the sum of internal and gravitational potential energy, for he states [11] that " $U$ , which we call energy, is sometimes called total energy and sometimes internal energy, the name used by *Clausius*". Because his Eqn. (28) shows the energy as a function of the potential field and in view of his later [13] consideration of electrical effects, it will be assumed that he means all of the energy, which is the sum of the internal and potential energy. Consequently, in the nomenclature of this paper Eqn. (28) reads

$$dE^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_i (\mu_i^\alpha + M_i \Phi^\alpha) dn_i^\alpha . \quad (29)$$

Since the total energy is the internal energy plus the potential energy,

$$E = U + m\phi = U + \sum_i M_i n_i \Phi \quad (30)$$

and Eqn. (29) may be written

$$dE^\alpha = d(U^\alpha + \sum_i M_i n_i^\alpha \Phi^\alpha) = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_i (\mu_i^\alpha + M_i \Phi^\alpha) dn_i^\alpha . \quad (31)$$

Upon simplification this reduces to

$$dU^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_i \mu_i^\alpha dn_i^\alpha - \sum_i M_i n_i^\alpha d\Phi^\alpha . \quad (32)$$

Here is an equation, obtained by simply substituting the sum of internal and potential energy for the total energy, which cannot be correct, for it says that the internal energy of matter changes with the potential energy. A close inspection of the way *Guggenheim* applied Eqn.

(29) to problems in gravitation shows that the designation of a phase  $\alpha$  implies a point  $\alpha$  in space where the gravitational potential is assumed fixed<sup>6)</sup>. He has considered it impossible in the problem he treats for  $\Phi^\alpha$  to change, which means that in Eqn. (29) he has omitted a term involving  $d\Phi^\alpha$ . Thus, his equation cannot be applied to the simple lifting of a weight because position  $\alpha$  and thus  $\Phi^\alpha$  would change. His equation is, therefore, a specific limited case.

Comparison of Eqn. (18) of *Lewis, Randall, Pitzer, and Brewer* with Eqn. (29) of *Guggenheim* who follows the method of *Gibbs*, shows the chemical potentials to be different if the gravitational potential is included in Eqn. (18). This difference may lead to confusion which is unfortunate in view of the previous clarity of definition of the chemical potentials, for as *Gibbs* in his treatment of equilibrium under the influence of gravity [9] has so succinctly stated, "The expressions  $\mu_i$  denote quantities which we have called the potentials for the several components, and which are entirely determined at any point in a mass by the nature and state of the mass at that point. We may avoid all confusion between these quantities and the potential of the force of gravity, if we distinguish the former, when necessary, as *intrinsic potentials*". The italics are due to *Gibbs* himself who is emphasizing that the chemical potentials depend on the internal state of matter, as do internal energy and entropy.

In view of the difficulties demonstrated in three of the outstanding books in thermodynamics today, it is fair to say that misimpressions of the true situation are widely prevalent. Furthermore, it is interesting that some of these erroneous concepts were propagated many years ago and have long gone unchallenged. The unfortunate part of the whole picture is that *Gibbs* did not show in any way how the additional effects such as gravitation, for example, were to be included in the fundamental property relation. He treated the problem of equilibrium in a gravitational field by showing that the sum of the chemical potential and gravitational potential must be zero for each component, but he did not pursue the problem further. The second part of this paper will attempt to show the logical pursuit of the problem to its ultimate conclusion.

### Development of the Complete Symmetrical Fundamental Property Relation

Consider as a system a uniform collection of ponderable matter, where uniformity implies the same chemical composition and physical state throughout all regions.

6) Several years ago the author had the good fortune to meet Prof. *Guggenheim* and show him this development. He said the interpretation of the energy term was correct and he recognized the limitation of Eqn. (29). Because  $\alpha$  is taken as a fixed point in space, Prof. *Guggenheim* considered that  $d\Phi^\alpha$  could arise in gravitation only by having the earth somehow change its mass, or in a centrifugal field only by changing the angular velocity. As will be shown, if attention is focused on a quantity of matter which may exist at any point in space, the  $\alpha$  superscript may be dropped and a corrected form of Eqn. (29) applied to the change of potential energy due to a change in position.

Let the total energy (sum of intrinsic energy, potential energy due to position in any kind of force field, and energy due to its massive macroscopic movement such as kinetic) be denoted by  $E$ . This total energy may be changed in three ways:

- 1.) The mass of matter may transfer heat with its surrounding environment.
- 2.) It may transfer work with its surroundings.
- 3.) It may exchange matter with the surroundings and since the exchanged matter possesses energy, there will be an associated energy transfer<sup>7)</sup>.

The energy balance for these energy and mass transfers is

$$dE = \delta Q - \delta W + \sum_i \bar{E}_i dm_i \quad (33)$$

Here the heat and work are denoted by  $\delta Q$  and  $\delta W$  to distinguish them from properties of the system of matter. The energy of each component added per unit mass of that component is  $\bar{E}_i$  which will later be shown as the partial energy of the component. The accompanying entropy balance for the energy and mass transfer is:

$$dS = \frac{\delta Q}{T} + \frac{\delta LW}{T} + \sum_i \bar{S}_i dm_i \quad (34)$$

where  $\bar{S}_i$  is the entropy per unit mass of each component added. This equation simply means that the entropy change of the system of matter is the sum of the heat transfer divided by temperature, the lost work  $LW$  divided by temperature, and the entropy carried in with any entering matter.

Let us now make all the energy transfer processes occur in such a way that the properties of the system of matter are at all times uniform throughout and the properties of the entering matter are identical to those of the system under observation. This means that if the temperature is to rise, it rises uniformly throughout the whole mass of matter; or if a given component is added, it is at the same temperature, pressure, and chemical potential as in the system. Such a requirement makes the process reversible because at no point is there to be allowed a finite difference in any potential driving force, and for a reversible process there will be no lost work. Thus, Eqn. (2) may be written:

$$\delta Q = T dS - T \sum_i \bar{S}_i dm_i \quad (35)$$

Elimination of  $\delta Q$  between Eqn. (33) and (35) gives

$$dE = T dS - T \sum_i \bar{S}_i dm_i - \delta W + \sum_i \bar{E}_i dm_i \quad (36)$$

The total energy is taken to be the sum of the internal energy, the kinetic energy, and any potential energy due to position in force fields,

$$E = U + mu^2/2 + m\Phi - \epsilon\mathcal{P} - \mathcal{E}\mathcal{M} \quad (37)$$

7) Actually, there is also a transfer of mass associated with the work and heat transfer as determined by the Einstein relation between energy and mass,  $m = E/c^2$ . In the ordinary situation, however, the mass equivalent of energy is only minute and practically unmeasurable due to the vast magnitude of the square of the velocity of light,  $c^2$ . Consequently, at this point the mass and energy balances will be taken to hold independently.

Here  $\varepsilon$  is the electric potential or field and  $\mathfrak{P}$  is the electric polarization of the matter, while  $\mathfrak{H}$  is the magnetic field and  $\mathfrak{M}$  is the magnetic polarization. The negative signs on the electric and magnetic potential energy terms may be surprising but electromagnetic theory shows that the potential energy decreases if a polarizable material is moved to a position of greater field strength. If Eqn. (37) is differentiated with respect to the mass of one component at constant values of all the intensive properties that determine the state of matter, the partial energy per component is obtained as

$$\bar{E}_i = \bar{U}_i + u^2/2 + \Phi - \varepsilon \bar{\mathfrak{P}}_i - \mathfrak{H} \bar{\mathfrak{M}}_i . \quad (38)$$

For a single pure component this operation is identical to dividing through the total properties by the mass  $m$  to obtain the specific properties per unit mass.

The work transferred between the system of matter and the surroundings is the sum of all possible ways of doing work,

$$\delta W = P dV - P \sum_i \bar{V}_i d m_i - \gamma d\alpha + \gamma \sum_i \bar{\alpha}_i d m_i - F dl + F \sum_i \bar{l}_i d m_i - m d\Phi - m u du + \mathfrak{P} d\varepsilon + \mathfrak{M} d\mathfrak{H} . \quad (39)$$

The terms obviously require considerable explanation. The first term is simply the work done on the surroundings if the system expands. The second term is work done by the surroundings to force  $d m_i$  of matter into the system under the system pressure. It is nothing more than the familiar  $P \bar{V}$  flow energy or flow work term that appears in the usual flow energy balance equations. The  $\gamma d\alpha$  term gives the work to overcome surface tension to create new area, while the  $\gamma \sum_i \bar{\alpha}_i d m_i$  is the work necessary to force  $d m_i$  of matter into the system. Because the surface is under tension, it actually tends to open up a hole, so to speak, to encourage the matter to enter. Thus, work is delivered to the surroundings in this process. Except for sign this  $\gamma \bar{\alpha}$  work is similar to the  $P \bar{V}$  work. The  $F dl$  term is the work to elongate the material in tension, while the  $F \sum_i \bar{l}_i d m_i$  is the tensile work delivered to the surroundings when some mass  $d m_i$  is admitted to the system of matter. As with surface tension the material literally tends to pull apart to allow the matter to enter, which accounts for the positive sign just as with the surface term. Actually, this tensile term has been taken as a simple example of the strain produced by a stress in tension on matter which usually is solid, though it may be liquid in a few unusual situations. In the more general case one sets up a strain tensor that gives the change in dimensions of an elastic solid along all coordinates resulting from all components of the stress. Such a tensor would account for tension, compression or expansion, and the normal and shear components of each, and would give terms of the same general form as that for simple tension. The term  $m u du$  accounts for the work to increase the velocity or kinetic energy of the whole mass of matter, while  $m d\Phi$  is the work to move the mass in a gravitational or centrifugal field. If it is the earth's field,  $\Phi$  is  $gz$ , as given earlier, and if a centrifugal field,  $\Phi$  is  $-\omega^2 r^2/2$ , where  $\omega$  is the angular velocity and  $r$  the radius.

The last two terms deal with the work involved in moving polarizable matter in electric and magnetic fields. As an example, suppose a material of magnetic polarization  $\mathfrak{M}$  is moved through a change  $d\mathfrak{H}$  in the magnetic field. The work required is  $-\mathfrak{M} d\mathfrak{H}$  or the work delivered to the surroundings is  $\mathfrak{M} d\mathfrak{H}$  as shown in magnetic theory. This does not presuppose that the polarization  $\mathfrak{M}$  is a constant, for with para- and diamagnetic substances  $\mathfrak{M}$  is a function of the field  $\mathfrak{H}$ . The situation is similar to the usual simple work expression,  $\delta W = F dx$ , where  $F$  may vary with the displacement  $x$ .

It is to be noted and emphasized that the introduction of mass into the system of matter requires no work to overcome any kinetic, gravitational or centrifugal, electrical or magnetic force. The reason is simply that the material being introduced is at the same potential as the system to which it is being added and the potential energies associated with the material being introduced are already accounted for in the last four terms of Eqn. (38).

If the total derivative of Eqn. (37) along with (38) and (39) are inserted into Eqn. (36) the result is the complete fundamental property relation

$$dU = T dS - P dV + \gamma d\alpha + F dl + \varepsilon d\mathfrak{P} + \mathfrak{H} d\mathfrak{M} + \sum_i (\bar{U}_i - T \bar{S}_i + P \bar{V}_i - \gamma \bar{\alpha}_i - F \bar{l}_i - \varepsilon \bar{\mathfrak{P}}_i - \mathfrak{H} \bar{\mathfrak{M}}_i) d m_i \quad (40)$$

where use has been made of the fact that  $dm = \sum_i d m_i$ .

It is worth noting that the kinetic and gravitational or centrifugal potential terms vanish so that the internal energy is completely independent of these effects, as it should be. Although portions of Eqn. (40) have been presented previously, the equation has not been derived before in its entirety. In fact, it is the extension to the entire equation that has resulted in many contradictions in the literature.

If Gibbs free energy is defined as

$$G = U - TS + PV - \gamma\alpha - Fl - \varepsilon\mathfrak{P} - \mathfrak{H}\mathfrak{M} \quad (41)$$

it may be differentiated at constant,  $T$ ,  $P$ ,  $\gamma$ ,  $F$ ,  $\varepsilon$ ,  $\mathfrak{H}$ , and  $m_i$  to give the partial extensive quantities

$$\bar{G}_i = \bar{U}_i - T \bar{S}_i + P \bar{V}_i - \gamma \bar{\alpha}_i - F \bar{l}_i - \varepsilon \bar{\mathfrak{P}}_i - \mathfrak{H} \bar{\mathfrak{M}}_i . \quad (42)$$

Combining Eqn. (40) and (42) yields

$$dU = T dS - P dV + \gamma d\alpha + F dl + \varepsilon d\mathfrak{P} + \mathfrak{H} d\mathfrak{M} + \sum_i \bar{G}_i d m_i \quad (43)$$

where the partial free energy  $\bar{G}_i$  is the previously used chemical potential  $\mu_i$ . Since this equation is homogeneous in the mass (i. e., doubling the mass at constant state of fixed  $T$ ,  $P$ ,  $\gamma$ ,  $F$ ,  $\varepsilon$ ,  $\mathfrak{H}$ , and  $\bar{G}_i$  doubles  $U$ ,  $S$ ,  $V$ ,  $\alpha$ ,  $l$ ,  $\mathfrak{P}$ ,  $\mathfrak{M}$ , and  $m$ ) it may be integrated from zero to finite mass as

$$U = TS - PV + \gamma\alpha + Fl + \varepsilon\mathfrak{P} + \mathfrak{H}\mathfrak{M} + \sum_i \bar{G}_i m_i . \quad (44)$$

Comparing Eqn. (41) and (44) shows that

$$G = \sum_i \bar{G}_i m_i \quad (45)$$

which simply says that the total free energy is the sum of the individual masses times their respective free energies per unit mass (i. e., partial free energy).

If Eqn. (40) is rearranged, its symmetry may be readily seen, as it cannot in the form of Eqn. (43) or the short form presented by *Gibbs*,

$$\begin{aligned} dU - \sum_i \bar{U}_i dm_i &= T(dS - \sum_i \bar{S}_i dm_i) - P(dV - \\ &- \sum_i \bar{V}_i dm_i) + \gamma(d\alpha - \sum_i \bar{\alpha}_i dm_i) + F(dl - \\ &- \sum_i \bar{l}_i dm_i) + \varepsilon(d\mathfrak{P} - \sum_i \bar{\mathfrak{P}}_i dm_i) + \mathfrak{H}(d\mathfrak{M} - \\ &- \sum_i \bar{\mathfrak{M}}_i dm_i) \quad (46) \end{aligned}$$

This symmetry is only exhibited by the internal or intrinsic energy relation. The total energy relation is obtained by substituting Eqn. (37) and (39) into (36),

$$\begin{aligned} dE &= TdS - PdV + \gamma d\alpha + Fdl + mudu + \frac{u^2}{2} dm + \\ &+ md\Phi + \Phi dm - \mathfrak{P}d\varepsilon - \mathfrak{M}d\mathfrak{H} + \sum_i (\bar{U}_i - T\bar{S}_i + \\ &+ P\bar{V}_i - \gamma\bar{\alpha}_i - F\bar{l}_i - \varepsilon\bar{\mathfrak{P}}_i - \mathfrak{H}\bar{\mathfrak{M}}_i) dm_i \quad (47) \end{aligned}$$

or

$$\begin{aligned} dE &= TdS - PdV + \gamma d\alpha + Fdl + mudu + md\Phi - \\ &- \mathfrak{P}d\varepsilon - \mathfrak{M}d\mathfrak{H} + \sum_i \left( \bar{U}_i - T\bar{S}_i + P\bar{V}_i - \gamma\bar{\alpha}_i - \right. \\ &\left. - F\bar{l}_i - \varepsilon\bar{\mathfrak{P}}_i - \mathfrak{H}\bar{\mathfrak{M}}_i + \frac{u^2}{2} + \Phi \right) dm_i \quad (48) \end{aligned}$$

By comparison it is seen that the internal energy relation Eqn. (40) or (41) is composed on the right side of terms which are all of the form mentioned earlier, (Intensive Property)d(Extensive Property), while Eqn. (48) has some terms of the form (Extensive Property)d(Intensive Property). It is this difference and failure to define clearly the intrinsic properties of matter that has caused some of the errors in the treatments cited in Part I. For example, when treating a gravitational field alone, Eqn. (48) becomes

$$\begin{aligned} dE &= TdS - PdV + md\Phi + \sum_i (\bar{U}_i - T\bar{S}_i + \\ &+ P\bar{V}_i + \Phi) dm_i \quad (49) \end{aligned}$$

Noting that  $\Phi = gz$  for the earth's gravity and  $d\Phi = g dz$ , this may be written as

$$\begin{aligned} dE &= TdS - PdV + gmdz + \sum_i (\bar{U}_i - T\bar{S}_i + \\ &+ P\bar{V}_i + gz) dm_i \quad (50) \end{aligned}$$

Now define free energy in terms of total energy which is  $U + gzm$  or  $U + gz \sum m_i$ ,

$$G = E - TS + PV = U + gz \sum_i m_i - TS + PV \quad (51)$$

so that by differentiation,

$$\left( \frac{\partial G}{\partial m_i} \right)_{T,P,z,m_j} = \bar{G}_i = \bar{U}_i - T\bar{S}_i + P\bar{V}_i + gz \quad (52)$$

Thus, Eqn. (40) is

$$dE = TdS - PdV + gmdz + \sum_i \bar{G}_i dm_i \quad (53)$$

This may be compared with Eqn. (40) and the two considered the same if the chemical potential,  $\mu_i$ , includes gravitational potential, a condition not given by the

authors [18]. Eqn. (52), however, cannot be made correct by this interpretation. Even if free energy is defined in terms of internal energy rather than total energy, as in Eqn. (41), it will not make Eqn. (52) right, because there is a missing  $dz$  term.

It would be expected that if any new energy effects on matter are discovered in the future, terms would be added to Eqn. (40) of the form  $X_i dx_i$  as earlier defined, but that this generalization would not apply to Eqn. (48), since terms of the form,  $x_i dX_i$ , may arise in this equation.

As stated, Eqn. (8) is the basis of all other macroscopic thermodynamic property relations of matter. As pointed out by *Gibbs* [6], other fundamental equations may be derived by defining new variables such as  $G$  which leads to

$$\begin{aligned} dG &= -SdT + VdP - \alpha d\gamma - ldF - \mathfrak{P}d\varepsilon - \\ &- \mathfrak{M}d\mathfrak{H} + \sum_i \bar{G}_i dm_i \quad (54) \end{aligned}$$

Such new variables are defined only for convenience, however, and since Eqn. (40) is the equation which is logically developed from the basic energy and entropy balances, it is the fundamental equation. This, furthermore, implies the *fundamental intrinsic thermodynamic properties* of matter are those which occur in Eqn. (40), such as  $U, T, S, P, V, \gamma, \alpha, F, l, \varepsilon, \mathfrak{P}, \mathfrak{H}, \mathfrak{M}$ , and  $m$ . This list is complete at present except for the sets of stress-strain tensor relations in elastic solids, of which  $F$  and  $l$  are simple examples, and for certain alternate electromagnetic properties that may be used in place of  $\mathfrak{P}$  and  $\mathfrak{M}$ . Also it is to be understood that mass may be alternately measured in terms of moles of chemical species (since  $m = \sum_i M_i n_i$ ) so that Eqn. (40) may be written

$$\begin{aligned} dU &= TdS - PdV + \gamma d\alpha + Fdl + \varepsilon d\mathfrak{P} + \mathfrak{H}d\mathfrak{M} + \\ &+ \sum_i (\bar{U}_i - T\bar{S}_i + P\bar{V}_i - \gamma\bar{\alpha}_i - F\bar{l}_i - \varepsilon\bar{\mathfrak{P}}_i - \\ &- \mathfrak{H}\bar{\mathfrak{M}}_i) dn_i = TdS - PdV + \gamma d\alpha + Fdl + \\ &+ \varepsilon d\mathfrak{P} + \mathfrak{H}d\mathfrak{M} + \sum_i \bar{G}_i dn_i \quad (55) \end{aligned}$$

with the partial quantities now specifically being partial molal quantities.

To complete this discussion, a few examples of the development of other property relations will be given. If Eqn. (44) is differentiated and compared with Eqn. (43), it is seen that

$$\begin{aligned} SdT - VdP + \alpha d\gamma + ldF + \mathfrak{P}d\varepsilon + \mathfrak{M}d\mathfrak{H} + \\ + \sum_i m_i d\bar{G}_i = 0 \quad (56) \end{aligned}$$

which is the extended version of the well-known Gibbs-Duhem equation in which the independent variables are now the intensive properties of Eqn. (43).

The cross partial derivative relationships of Eqn. (40) are of great utility. They may be developed by the use of Jacobians, though the procedure that follows is more instructive. *Gibbs* [7] arrived at them by considering the definition of the subsidiary convenience properties,  $H, A$ , and  $G$ , and by showing that the equations for  $dH, dA$ , and  $dG$  (Eqn. (54) is an example) can be taken as funda-

mental equations as well as Eqn. (40). This procedure may be misleading, however, for it tends to create the impression that the cross derivatives somehow depend upon these defined functions. This is definitely not the case, as all that is needed is built into Eqn. (40). This equation may be written in the generalized form (as done in Part I)

$$dU = X_1 dx_1 + X_2 dx_2 + \dots X_m dx_m + X_n dx_n + \dots \quad (57)$$

This may be divided by  $dx_m$  at constant  $x_n$  and  $x_j$ , where  $x_j$  refers to all  $x$ 's except  $x_m$  and  $x_n$ , to give

$$\left(\frac{\partial U}{\partial x_m}\right)_{x_n, x_j} = X_m \quad (58)$$

Now differentiate partially with respect to  $x_n$ ,

$$\left(\frac{\partial^2 U}{\partial x_m \partial x_n}\right)_{x_j} = \left(\frac{\partial X_m}{\partial x_n}\right)_{x_m, x_j} \quad (59)$$

Reversing the order followed in Eqn. (38) and (39) by dividing by  $dx_n$  first yields

$$\left(\frac{\partial^2 U}{\partial x_n \partial x_m}\right)_{x_j} = \left(\frac{\partial X_n}{\partial x_m}\right)_{x_n, x_j} \quad (60)$$

Noting that the second derivatives are equal because they are independent of the order of differentiation for continuous functions, one obtains the Maxwell relation for the independent variables,  $x_m$  and  $x_n$ ,

$$\left(\frac{\partial X_m}{\partial x_n}\right)_{x_m, x_j} = \left(\frac{\partial X_n}{\partial x_m}\right)_{x_n, x_j} \quad (61)$$

This is familiar to every student of thermodynamics, but it is the next several cross-partials that need explanation.

Suppose that in Eqn. (58) one wishes to hold the other  $X$ 's constant instead of the  $x$ 's. Using  $X_j$  to represent all  $X$ 's except  $X_m$  and  $X_n$ , one may write

$$\left(\frac{\partial U}{\partial x_m}\right)_{x_n, X_j} = X_1 \left(\frac{\partial x_1}{\partial x_m}\right)_{x_n, X_j} + \dots + X_m \quad (62)$$

This may be differentiated partially with respect to  $x_n$  to give

$$\left(\frac{\partial^2 U}{\partial x_m \partial x_n}\right)_{X_j} = X_1 \left(\frac{\partial^2 x_1}{\partial x_m \partial x_n}\right)_{X_j} + \dots + \left(\frac{\partial X_m}{\partial x_n}\right)_{x_m, X_j} \quad (63)$$

Reversing the order of differentiation as conducted in Eqn. (62) and (63) gives

$$\left(\frac{\partial^2 U}{\partial x_n \partial x_m}\right)_{X_j} = X_1 \left(\frac{\partial^2 x_1}{\partial x_n \partial x_m}\right)_{X_j} + \dots + \left(\frac{\partial X_n}{\partial x_m}\right)_{x_n, X_j} \quad (64)$$

Comparing Eqn. (64) and (65) and utilizing the independency of the order of differentiation,

$$\left(\frac{\partial X_m}{\partial x_n}\right)_{x_n, X_j} = \left(\frac{\partial X_n}{\partial x_m}\right)_{x_n, X_j} \quad (65)$$

Since the procedures leading to Eqn. (61) and (65) would not be changed by mixing up to the choices of any given  $X_i$  or  $x_i$  to be held constant, one may write

$$\left(\frac{\partial X_m}{\partial x_n}\right)_{x_m, X_1 \text{ or } x_1, X_2 \text{ or } x_2, \dots} = \left(\frac{\partial X_n}{\partial x_m}\right)_{x_n, X_1 \text{ or } x_1, X_2 \text{ or } x_2, \dots} \quad (66)$$

One may, therefore, select two independent variables for the cross derivatives and hold either the intensive or extensive variables fixed in all the other terms of Eqn. (25).

Sets of independent variables other than  $x_m$  and  $x_n$  are often desired. The possible choices from  $X_m$ ,  $x_m$ ,  $X_n$ , and  $x_n$  are  $x_m$  and  $x_n$ ,  $X_m$  and  $X_n$ ,  $x_m$  and  $X_n$ , and  $X_m$  and  $x_n$ . Selecting sets that involve  $X_m$  and  $x_m$ , say, is possible, but of no value in thermodynamics. Since  $x_m$  and  $x_n$  were treated in Eqn. (66), consider the variables  $X_m$  and  $X_n$ , by dividing through Eqn. (57) by  $dX_m$  to get the partial derivative,

$$\left(\frac{\partial U}{\partial X_m}\right)_{X_n, x_j} = X_m \left(\frac{\partial x_m}{\partial X_m}\right)_{X_n, x_j} + X_n \left(\frac{\partial x_n}{\partial X_m}\right)_{X_n, x_j} \quad (67)$$

Now differentiate partially with respect to  $X_n$ ,

$$\left(\frac{\partial^2 U}{\partial X_m \partial X_n}\right)_{x_j} = X_m \left(\frac{\partial^2 x_m}{\partial X_m \partial X_n}\right)_{x_j} + X_n \left(\frac{\partial^2 x_n}{\partial X_m \partial X_n}\right)_{x_j} + \left(\frac{\partial x_n}{\partial X_m}\right)_{X_n, x_j} \quad (68)$$

Reversing the order followed in Eqn. (62) and (63) gives

$$\left(\frac{\partial^2 U}{\partial X_n \partial X_m}\right)_{x_j} = X_m \left(\frac{\partial^2 x_m}{\partial X_n \partial X_m}\right)_{x_j} + \left(\frac{\partial x_m}{\partial X_n}\right)_{X_m, x_j} + X_n \left(\frac{\partial^2 x_n}{\partial X_n \partial X_m}\right)_{x_j} \quad (69)$$

Comparison of Eqn. (68) and (69) shows that

$$\left(\frac{\partial x_n}{\partial X_m}\right)_{X_n, x_j} = \left(\frac{\partial x_m}{\partial X_n}\right)_{X_m, x_j} \quad (70)$$

If the  $X_j$  are held constant during the differentiation, one may write

$$\left(\frac{\partial U}{\partial X_m}\right)_{X_n, X_j} = X_1 \left(\frac{\partial x_1}{\partial X_m}\right)_{X_n, X_j} + \dots X_m \left(\frac{\partial x_m}{\partial X_m}\right)_{X_n, X_j} + X_n \left(\frac{\partial x_n}{\partial X_m}\right)_{X_n, X_j} \quad (71)$$

This may be differentiated partially with respect to  $X_n$  to obtain

$$\left(\frac{\partial^2 U}{\partial X_m \partial X_n}\right)_{X_j} = X_1 \left(\frac{\partial^2 x_1}{\partial X_m \partial X_n}\right)_{X_j} + \dots X_m \left(\frac{\partial^2 x_m}{\partial X_m \partial X_n}\right)_{X_j} + X_n \left(\frac{\partial^2 x_n}{\partial X_m \partial X_n}\right)_{X_j} + \left(\frac{\partial x_n}{\partial X_m}\right)_{X_n, X_j} \quad (72)$$

Reversing the order of differentiation followed in Eqn. (71) and (72) gives

$$\left(\frac{\partial^2 U}{\partial X_n \partial X_m}\right)_{X_j} = X_1 \left(\frac{\partial^2 x_1}{\partial X_n \partial X_m}\right)_{X_j} + \dots X_m \left(\frac{\partial^2 x_m}{\partial X_n \partial X_m}\right)_{X_j} + \left(\frac{\partial x_m}{\partial X_n}\right)_{X_m, X_j} + X_n \left(\frac{\partial^2 x_n}{\partial X_n \partial X_m}\right)_{X_j} \quad (73)$$

Comparing Eqn. (72) and (73) shows that

$$\left(\frac{\partial x_n}{\partial X_m}\right)_{X_n, X_j} = \left(\frac{\partial x_m}{\partial X_n}\right)_{X_m, X_j} \quad (74)$$

As with Eqn. (66) it follows that one may select any of the  $x_j$  or  $X_j$  to be held constant so that Eqn. (70) and (74) become

$$\left(\frac{\partial x_n}{\partial X_m}\right)_{X_n, X_1 \text{ or } x_1, X_2 \text{ or } x_2} = \left(\frac{\partial x_m}{\partial X_n}\right)_{X_m, X_1 \text{ or } x_1, X_2 \text{ or } x_2} \quad (75)$$

Following the same procedure with the independent variables,  $x_m$  and  $X_n$ , and  $X_m$  and  $x_n$ , shows that

$$\left(\frac{\partial x_n}{\partial x_m}\right)_{X_n, X_1 \text{ or } x_1, X_2 \text{ or } x_2, \dots} = -\left(\frac{\partial X_m}{\partial X_n}\right)_{x_m, X_1 \text{ or } x_1, X_2 \text{ or } x_2, \dots} \quad (76)$$

and

$$\left(\frac{\partial X_n}{\partial X_m}\right)_{x_n, X_1 \text{ or } x_1, X_2 \text{ or } x_2, \dots} = - \left(\frac{\partial x_m}{\partial x_n}\right)_{x_m, X_1 \text{ or } x_1, X_2 \text{ or } x_2, \dots} \quad (77)$$

To show how the preceding partial derivative relations are actually used, consider the interaction of the tension and electrical effects. Four relations follow directly from Eqn. (66), (75), (76), and (77), respectively, as applied to Eqn. (43).

$$\left(\frac{\partial F}{\partial \mathfrak{P}}\right)_1 = \left(\frac{\partial \varepsilon}{\partial l}\right)_{\mathfrak{P}} \quad (78)$$

$$\left(\frac{\partial \mathfrak{P}}{\partial F}\right)_{\varepsilon} = \left(\frac{\partial l}{\partial \varepsilon}\right)_F \quad (79)$$

$$\left(\frac{\partial l}{\partial \mathfrak{P}}\right)_F = \left(\frac{\partial \varepsilon}{\partial F}\right)_{\mathfrak{P}} \quad (80)$$

$$\left(\frac{\partial F}{\partial \varepsilon}\right)_1 = - \left(\frac{\partial \mathfrak{P}}{\partial l}\right)_{\varepsilon} \quad (81)$$

This list, which actually covers 128 possibilities, is exhaustive and no additional cross partials of use in thermodynamics can be obtained by defining any new functions in terms of the fundamental properties. Just which cross partials are useful in a given case depends upon the variables that can be held constant in a given experiment. For example, suppose the effect of electric field on tension in a solid of fixed composition is being investigated. It will be assumed that surface effects are negligible, and there is no magnetic field. The outside variables in Eqns. (78–81), which are all those except  $F$ ,  $l$ ,  $\varepsilon$  and  $\mathfrak{P}$ , are fixed first. If the temperature can be held constant,  $T$  is chosen from  $S$  and  $T$ . If the pressure is constant,  $P$  is chosen from  $P$  and  $V$ . Because of the assumptions,  $\alpha$  or  $\gamma$ , and  $\mathfrak{M}$  or  $\mathfrak{H}$  are out. Because of fixed composition  $m_1$  is chosen from  $m_1$  and  $\bar{G}_1$ . The inside or independent variables that are fixed in alternate experiments might be the electric potential and the force. Thus, Eqn. (79) would be the useful equation,

$$\left(\frac{\partial \mathfrak{P}}{\partial F}\right)_{\varepsilon, T, P, m_1} = \left(\frac{\partial l}{\partial \varepsilon}\right)_{F, T, P, m_1} \quad (82)$$

Up to this point it has been emphasized there is no necessity of defining new variables from the fundamental properties. Such definitions are convenient, however, so that it is sometimes rather efficient to know just which new variables to define. The possibilities are extremely great, but fortunately there are just three new variables that will handle all practical cases. We have seen already in Eqn. (41) how the definition of free energy  $G$  arises quite naturally. From previous thermodynamic experience it is recalled that enthalpy  $H$  is related to  $G$  as

$$H = G + TS \quad (83)$$

Consequently, Eqn. (41) and (83) give

$$H = U + PV - \gamma\alpha - Fl - \varepsilon\mathfrak{P} - \mathfrak{H}\mathfrak{M} \quad (84)$$

The work function  $A$  is defined exactly as before,

$$A = U - TS \quad (85)$$

and it is seen that  $A$  and  $G$  are related by the equation

$$G = A + PV - \gamma\alpha - \varepsilon\mathfrak{P} - \mathfrak{H}\mathfrak{M} - Fl \quad (86)$$

The Maxwell derivatives that can be obtained directly from differentials of the functions,  $U$ ,  $H$ ,  $G$ , and  $A$ , are included in the general Eqn. (66), (75), (76), and (77). The functions  $H$  and  $A$  may be differentiated and combined with Eqn. (43) to give new equations that may be considered fundamental in the sense of *Gibbs* [7], as exemplified by Eqn. (54). The usual Gibbs-Helmholtz type equations are obtained in exactly the same form as always, but at different restrictions. For example

$$dA = SdT - PdV + \gamma d\alpha + Fdl + \varepsilon d\mathfrak{P} + \mathfrak{H}d\mathfrak{M} + \sum_i \bar{G}_i dm_i \quad (87)$$

which at constant  $V$ ,  $\alpha$ ,  $\mathfrak{P}$ ,  $\mathfrak{M}$ , and  $m_1$  is

$$dA = -SdT \quad (88)$$

Eliminating  $S$  between Eqn. (85) and (88) gives

$$dA = \frac{A - U}{T} dT \quad (89)$$

which upon rearranging becomes

$$d\left(\frac{A}{T}\right) = -\frac{U dT}{T^2} \text{ at constant } V, \alpha, l, \mathfrak{P}, \mathfrak{M} \text{ and } m_1 \quad (90)$$

In summary one can say that many relations between thermodynamic properties can be developed, but they all have their origin in the fundamental Eqn. (40). *Gibbs* described the shorter version of this equation as an equation of equilibrium. In this paper the equation is referred to as a relation between thermodynamic properties of any homogeneous or uniform collection of matter. It is believed the latter description is more general and in fact indicative of applications not covered by previous description. For example, consider a uniform mixture of slowly reaction gases. Eqn. (40) tells exactly how the properties that are changing during the reaction are related to each other even though the system is not at equilibrium since a reaction is taking place. Furthermore, such a reaction is not occurring reversibly since it will not go backwards, and yet Eqn. (40) still applies, for it gives the relation between the changing properties. Because of this general applicability it is safe to say that Eqn. (40) is the most important relation in macroscopic thermodynamics.

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## Nomenclature

$A$	Helmholtz work function, $U - TS$
$c$	Velocity of light
$E$	Total energy (i. e., internal + potential of all kinds + kinetic)
$\varepsilon$	Electrical potential or field
$F$	Force
$G$	Gibbs free energy, $H - TS$
$g$	Acceleration due to gravity
$H$	Enthalpy, $U + PV$
$\mathfrak{H}$	Magnetic potential or field
$l$	Length
$LW$	Lost work in irreversible process
$\mathfrak{M}$	Molecular weight (i. e., mole mass)
$\mathfrak{M}$	Magnetic polarization
$m$	Mass
$n$	Number of moles
$P$	Pressure

$\mathcal{D}$	Electrical polarization
$Q$	Heat
$S$	Entropy
$T$	Temperature, absolute
$U$	Internal energy (intrinsic energy of matter irrespective of position in force field)
$u$	Velocity
$V$	Volume
$W$	Work
$X$	Intensive property or force
$x$	Extensive property or displacement
$z$	Height above reference point
$\alpha$	Surface area
$\delta$	Quantity transferred (as heat $\delta Q$ or work $\delta W$ )
$\gamma$	Surface tension
$\Phi$	Potential energy ( $gz$ in gravitational field, $-\omega^2 r^2/2$ in centrifugal field)
$\mu$	Chemical or mass potential, $\mu_i = \bar{G}_i$

#### Superscripts

$\alpha$	Phase at a point in gravitational field
$\beta$	Phase at a point in gravitational field
-	Denotes partial extensive property in mixture as, for example, $\bar{G}_i$ is partial free energy of $i$ -th component

#### Subscripts

$i$	Denotes different chemical species or different energy effects in property relation
$j$	Denotes all species but particular one under inspection or all energy effects except particular ones being examined

0	Refers to reference point for gravitational potential
-	Denotes extensive property per unit mole or mass as, for example $\bar{G}$

#### Literature

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## Über Strömung und Vermischung in Haufwerken \*

Sergei Traustel und Karl Briem \*\*

Herrn Prof. Dr.-Ing. Dr.-Ing. E. h. W. Ludewig zum 65. Geburtstag

Betrachtet wird ein Haufwerk aus festen Partikeln, das von einem Fluid durchströmt wird. An einer bestimmten Stelle tritt ein zweites, mit dem ersten unbegrenzt mischbares Fluid hinzu. Unter vereinfachenden Voraussetzungen wird das entstehende Strömungsbild und der Fortgang der Vermischung der Fluide theoretisch berechnet. In diesem Zusammenhang wird die Gattung der „konformen Modelle“ vorgestellt.

#### Voraussetzungen

Die Betrachtung beschränkt sich auf eine zweidimensionale (ebene) Strömung. Von örtlich veränderlichen Größen wird angenommen, daß sie von den zwei Koordinaten  $x$  und  $y$  einer Ebene, nicht aber von der dritten Koordinate  $z$  abhängig sind (alle  $\partial/\partial z = 0$ ).

Die Strömung durchs Haufwerk wird „unscharf“, d. h. als Strömung durch ein permeables Kontinuum gesehen, ohne Beachtung der lokalen Geometrie der Umströmung einzelner Haufwerksteilchen. Als Strömungs-Geschwindigkeit wird die auf den „leeren“ Gesamtquerschnitt bezogene

Volumenstromdichte bezeichnet. Von der Strömung wird angenommen, sie sei eine Potentialströmung. Das ist nur eine Näherung, deren technische Brauchbarkeit von *Radestock* [1] nachgewiesen wurde.

#### Ebene Potentialströmung

Die graphische Darstellung einer ebenen Potentialströmung ist ein beliebig feinmaschiges Netz von Potentiallinien ( $\varphi = \text{const}$ ) und Stromlinien ( $\psi = \text{const}$ ). Die Potential- und die Stromlinien schneiden sich überall unter einem rechten Winkel, auch wenn sie gekrümmt sind (orthogonales Netz).

Jeder Potentiallinie ist ein bestimmter Wert des Potentials  $\varphi$ , jeder Stromlinie ein bestimmter Wert der „Stromfunktion“  $\psi$  zuzuordnen. Zwischen zwei Potentiallinien besteht eine bestimmte Potentialdifferenz; Potentialdifferenzen sind die „treibenden Kräfte“ der Strömung.

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