

3. What are the students' perceptions of the quality of the tapes?

An experimental design was employed to answer the first question. The students were randomly assigned to two groups. Group I was allowed to use the tapes for only the first and third topics and Group II was allowed to use the tapes during the second and fourth topics. (The fifth set of tapes had not yet been made.) The exam scores for both groups were compared following each test to see if normal use of the tapes had a significant effect on the student's achievement. There were 39 students in both groups who took all four exams. Each exam consisted of two or three problems. The average test score of a student throughout the semester was 75.6 when he was using the videotapes and 74.4 when he did not have access to the tapes. However, a t-test shows that the difference between these two numbers is not significant.

A survey was made of the spring '81 ChE 311 class. There were 84 students in the class and 63 responded to the anonymous questionnaire. At the time of the questionnaire 19 tapes were in use. A summary shows that 43% of the responders saw all 19 tapes, 81% saw more than 11 tapes, and 10% saw no tapes.

Comments from the questionnaire indicated that most students believe that using the tapes enabled them to learn the material more quickly. Many students viewed the tapes more than once. Typically they might view a tape once when the material was first discussed, and then view the same tape as a review just before the exam.

## CONCLUSIONS

The fact that no significant improvement in test performance attributable to the tapes was observed is not surprising. The tapes are but a small part of the course and similar problems are required of all students. We were encouraged that many students indicated that the tapes allowed them to understand the material more quickly.

That 43% of the class saw all of the tapes and 81% saw more than half of the tapes is our best indication that the students believed the tapes were worthwhile. (Remember that the tapes were not required and were not discussed in class.) At twenty minutes per tape, this level of viewing represents a significant amount of voluntarily committed time. We conclude that the tapes are a useful addition to the course and we plan to continue their use. If any other professors would like to use any or all of these tapes, copies can be obtained from Prof. Squires.

## ACKNOWLEDGMENTS

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## Applications...

### THE FUNDAMENTAL PROPERTY RELATION\*

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SUPPOSE ONE WERE TO try to describe the field of thermodynamics in as simple a manner as possible. It is likely he would start with the concise definition that thermodynamics is the science of energy as displayed in all of its forms, transfers, and transformations. He would probably then

invoke the famous "three laws" that are the result of observation and some intuition, and discuss how these lead to the field which is agreed to be the one in question, as judged from a study of the multitude of books that have been written on the subject.

An alternative approach would be to assume from prior knowledge the four basic equations of thermodynamics, thereby utilizing from the very start the powerful shorthand language of mathematics. This would be followed by an interpretation and explanation of each basic equation.

\*This paper was presented at the symposium prior to Professor Martins death on Dec. 13, 1982 (see *CEE* Vol. XVII, No. 2, pg. 73 for Memoriam).

Following the latter approach, the first and most used basic equation is the fundamental property relation,

$$dU = T dS - P dV + \sum_i \bar{G}_i dm_i \quad (1)$$

(See Nomenclature for definition of all symbols.) The second and more easily understood equation is the energy balance,

$$d\left(U + \frac{mu^2}{2} + mgz\right)_{\text{sys}} = \delta Q - \delta W + \sum_j \left(\frac{h}{T} + \frac{mu}{2} + gz\right)_j \delta m_j = dE_{\text{sys}} \quad (2)$$

The third equation is a little more sophisticated and is known as the entropy balance,

$$dS_{\text{sys}} = \sum_i \left(\frac{\delta Q}{T}\right)_i + \frac{\delta LW}{T_0} + \sum_j s_j \delta m_j \quad (3)$$

while the fourth equation is the simplest of all and is the mass balance\*,

$$dm_{\text{sys}} = \sum_j \delta m_j \quad (4)$$

It is the objective in this discourse to focus attention primarily on the fundamental property relation because of its great utility in problems of thermodynamic properties and physical and chemical equilibrium. As it stands in its simplest form,

\*The Einstein relation,  $m = E/c^2$  implies a transfer of mass associated with work and heat; however, except in nuclear reactions, the mass equivalent of energy is so minute due to the vast magnitude of the velocity of light that separate energy and mass balances are satisfactory.



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**An alternative approach would be to assume from prior knowledge the four basic equations of thermodynamics, thereby utilizing from the very start the powerful shorthand language of mathematics.**

Eq. (1) considers only thermal, compression, and mass change effects in any finite collection of matter or substance whose temperature, pressure, and chemical potentials are uniform throughout. Essentially, Eq. (1) says that thermodynamic properties of matter are not independent; that they are interrelated and locked together by a differential relationship such that if any property is changed, at least one other property must change to preserve the equality of the equation.

The generalization of Eq. (1) to include effects other than thermal, compression, and mass change has caused considerable confusion and difficulty, even though all writers agree on the implications of Eq. (1) in its simplest form. To understand the source of confusion, let us examine first the treatment of the gravitational effect in the pioneering work of Lewis and Randall as revised by Pitzer and Brewer [4]. They state without proof that the reversible lifting of a weight increases its free energy per molal mass  $M$  by an amount,

$$d\bar{G} = gMdz \quad (5)$$

or

$$\left(\frac{\delta \bar{G}}{\delta z}\right)_{P,T,\dots} = gM \quad (6)$$

It is interesting to note here they are implying there is a better or greater understanding of a quantity called free energy than there is of just energy. It is not meant that energy is a simple concept, but it is certainly simpler than free energy.

Preceding Eq. (6) it is emphasized that although potential energy and internal energy may be separated, their energy-content function  $E$  is to include gravitational energy.\* From their definition and later discussion the Gibbs free energy is defined as

$$G = E + PV - TS \quad (7)$$

\*This is the opposite approach from Gibbs [2] who wrote, "The energy of 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."

Their free energy relation when gravity is not of importance is

$$dG = -S dT + V dP + \sum_i \mu_i dm_i \quad (8)$$

which follows directly from Eq. (1) with  $G = U + PV - TS$  and the partial free energy  $\bar{G}_i$  identical to the chemical potential  $\mu_i$ . Now if any mass  $m = nM$  is lifted, Eq. (6) may be written

$$\left(\frac{\partial G}{\partial z}\right)_{P,T,\dots} = gm \quad \text{or} \quad dG = gmdz \quad (9)$$

and this may be added to Eq. (8) to give

$$dG = -S dT + V dP + \sum_i \mu_i dm_i + gmdz \quad (10)$$

If Eq. (7) is differentiated and combined with Eq. (10), we get

$$dE = T dS - P dV + \sum_i \mu_i dm_i + gmdz \quad (11)$$

In generalizing on the terms in Eq. (11), they present

$$dE = \sum_i X_i dx_i \quad (12)$$

where  $X_i$  is an intensive variable or force and  $x_i$  is its associated variable. A table of  $X_i$ 's and  $x_i$ 's is given so that one may readily construct the relation comparable to Eq. (11) as

$$dE = T dS - P dV + \sum_i \mu_i dm_i + gzdm \quad (13)$$

It is obvious there is a contradiction between Eq. (11) and Eq. (13) because the former contains  $gmdz$  while the latter contains  $gzdm$ . Thus, there is an outright error in their treatment of the gravitational effect.

As a second example of difficulty the book by Aston and Fritz [1] is considered. For a reversible process involving a closed system (the authors emphasize this restriction of a closed system) the generalized equation

$$dE = T dS - P dV - \sum_i X_i dx_i \quad (14)$$

is given with the  $X_i$ 's and  $x_i$ 's being respectively the intensive and extensive variables other than the usual ones associated with thermal and compression effects. In considering the gravitational effect they identify the intensive variable as

$$X_i = gz \quad (15)$$

and the associated extensive variable as

$$x_i = m \quad (16)$$

When these are inserted in Eq. (14), the result is

$$dE = T dS - P dV - gzdm \quad (17)$$

Now here is an obvious contradiction because the application is to a closed system where  $m$  cannot change. Furthermore, because of the minus sign, the equation implies that the energy somehow decreases if the mass is increased in a gravitational 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.

As a last example of difficulties with the treatment of effects other than thermal or compression, let us look at the highly regarded textbook by Guggenheim [3]. He considers the work done in transferring  $dn_i$  moles of  $i$  from phase  $\alpha$  to phase  $\beta$ , each with its own gravitational potential,

$$W = (\phi^\beta - \phi^\alpha)M_i dn_i \quad (18)$$

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  $\alpha$  (and chemical potential in place of partial free energy), so that

$$dU^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_i (\mu_i^\alpha + M_i \phi^\alpha) dn_i^\alpha \quad (19)$$

Guggenheim does not explicitly say whether his  $U$  is internal or the sum of internal and gravitational energy. However, in view of the way he treats electrical effects, it will first be assumed that he means all of the energy, which is the sum  $E$  of internal and potential energy. Consequently, Eq. (19) is rewritten as

$$dE^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_i (\mu_i^\alpha + M_i \phi^\alpha) dn_i^\alpha \quad (20)$$

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

$$E = U + m\phi = U + \sum_i M_i n_i \phi \quad (21)$$

and Eq. (20) may be written

$$\begin{aligned} dE^\alpha &= d(U^\alpha + \sum_i M_i n_i \phi^\alpha) \\ &= T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_i (\mu_i^\alpha + M_i \phi^\alpha) dn_i^\alpha \end{aligned} \quad (22)$$

This reduces to

$$dU^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_i \mu_i^\alpha dn_i^\alpha - \sum_i M_i n_i^\alpha d\phi^\alpha \quad (23)$$

Here is an equation, obtained simply by substituting the sum of internal and potential energy for the total energy, which must be flatly incorrect,



for it says that the internal energy of matter changes with the potential energy which is not in accord with observation.

Of course, one might interpret Guggenheim's  $U^\alpha$  in Eq. (19) to be strictly internal energy. In that event

$$\begin{aligned} dE^\alpha &= d(U^\alpha + \sum_i M_i n_i^\alpha \phi_i^\alpha) \\ &= T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_i (\mu_i^\alpha + M_i \phi_i^\alpha) dn_i^\alpha \\ &\quad + \sum_i M_i \phi_i^\alpha dn_i^\alpha + \sum_i M_i n_i^\alpha d\phi_i^\alpha \end{aligned} \quad (24)$$

This may be rearranged to

$$\begin{aligned} dE^\alpha &= T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_i M_i n_i^\alpha d\phi_i^\alpha \\ &\quad + \sum_i (\mu_i^\alpha + 2M_i \phi_i^\alpha) dn_i^\alpha \end{aligned} \quad (25)$$

This equation with its double potential energy term must be just as incorrect as Eq. (23), so that either interpretation of Guggenheim's energy term leads to ridiculous results.

**It is the objective in this discourse to focus attention primarily on the fundamental property relation because of its great utility in problems of thermodynamic properties and physical and chemical equilibrium.**

Now that erroneous treatments have been shown in three well-known textbooks, let us explore a logical approach to the development of the fundamental property relation where effects other than thermal, compression, and exchange of matter with the surroundings are considered.

Consider as a system a uniform collection of ponderable matter, where uniformity implies the same chemical composition, temperature, pressure, and any other intensive properties throughout all regions. Let the total energy (sum of intrinsic energy, potential energy due to position in any kind of force field, and energy due to massive macroscopic motion such as kinetic) be denoted by  $E$  as in Eq. (2). This total energy may be changed in three ways:

- (1) The mass of ponderable matter may exchange heat with its surrounding environment.
- (2) It may transfer work with its surroundings.
- (3) It may exchange matter with its surroundings.

The energy balance for these energy and mass transfers may be written

$$dE = \delta Q - \delta W + \sum_i \bar{E}_i dm_i \quad (26)$$

which is just an equivalent of Eq. (2). The energy of each component added per unit mass of that component is  $\bar{E}_i$  which is the partial total energy of the component. The accompanying entropy balance for the energy and mass transfer is the equivalent of Eq. (3) for a single heat transfer and  $\bar{S}_i$  the partial entropy per unit mass of each component added, or

$$dS = \frac{\delta Q}{T} + \frac{\delta LW}{T} + \sum_i \bar{S}_i dm_i \quad (27)$$

This equation simply means that the entropy change of a collection of matter is the sum of the heat transfer divided by the temperature, the lost work  $LW$  divided by the temperature, and the entropy carried in with any entering matter.

Let us now make all the energy and mass 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 any entering matter are identical to those of the system of matter under observation. This means that if the temperature of the matter is to rise, it rises uniformly throughout the whole mass of matter, if the pressure is to rise, it does so uniformly throughout, and if the concentration (and its associated chemical potential) changes, it does so uniformly everywhere, and if a component is added, it is at the same temperature, pressure, and chemical potential as in the system of matter. Such a requirement makes any process reversible because at no point is there allowed a finite difference in any potential driving force (i.e., all driving forces are infinitesimal in magnitude). For such a reversible process there will be no lost work so that Eq. (27) becomes in a rearranged form,

$$\delta Q = T dS - T \sum_i \bar{S}_i dm_i \quad (28)$$

Elimination of  $\delta Q$  between Eq. (26) and Eq. (28) gives

$$dE = T dS - T \sum_i \bar{S}_i dm_i - \delta W + \sum_i \bar{E}_i dm_i \quad (29)$$

The total energy  $E$  is the sum of the internal energy, the kinetic energy, and any potential energy due to position in force fields such as gravitational, electrical, and magnetic,

$$E = U + mu^2/2 + m\phi - \epsilon P - HM \quad (30)$$

Here by way of explanation  $\epsilon$  is the electric potential or field and  $P$  is the electric polarization while  $H$  is the magnetic field and  $M$  is the magnetic polarization. Eq. (30) may be differentiated to give

... these extended equations account for other effects such as surface tension, tensile stress, electric polarization, and magnetic polarization.

$$dE = dU + mdu + \frac{u^2}{2} dm + md\phi + \phi dm - \epsilon dP - Pd\epsilon - HdM - MdH \quad (31)$$

It may also be differentiated partially with respect to the mass of one component at constant values of all the intensive properties that determine the state of matter, so that

$$\bar{E}_i = \bar{U}_i + u^2/2 + \phi - \epsilon \bar{P}_i - H \bar{M}_i \quad (32)$$

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

$$\delta W = P dV - P \sum_i \bar{v}_i dm_i - \gamma d\alpha + \gamma \sum_i \bar{\alpha} dm_i - F d\ell + F \sum_i \bar{\ell}_i dm_i - md\phi - mdu + Pd\epsilon + MdH \quad (33)$$

Here the first term is the work done on the surroundings if the system expands. The second term is work done by the surroundings to force  $dm_i$  of matter into the system. The  $\gamma d\alpha$  term gives the work to overcome surface tension in creating new area while

$$\gamma \sum_i \bar{\alpha}_i dm_i$$

is the work to force  $dm_i$  into the system of matter when there is surface tension. The  $F d\ell$  term is the work to elongate the matter in tension while the

$$F \sum_i \bar{\ell}_i dm_i$$

is the tensile work delivered to the surroundings when  $dm_i$  is admitted to a system of matter under tension. An alternative more general approach here is to set up a strain tensor that gives the change in dimensions of an elastic material resulting from all components of stress. Such a tensor would account for tension, compression, expansion and the normal and shear components and would give terms of the same form as that for simple tension. The term  $md\phi$  accounts for the work to move the mass in a gravitational or centrifugal field. The term  $mdu$  accounts for the work to increase the kinetic energy of the whole mass of matter. The  $Pd\epsilon$  is the work involved in moving

polarizable matter in an electric field and the  $MdH$  is the same thing for motion in a magnetic field.

Now if Eqs. (30), (31), (32), and (33) are inserted into Eq. (29), and use is made of

$$dm = \sum_i dm_i$$

the complete property relation is obtained,

$$dU = T dS - P dV + \gamma d\alpha + F d\ell + \epsilon dP + HdM + \sum_i (\bar{U}_i + P \bar{V}_i - T \bar{S}_i - \gamma \bar{\alpha}_i - F \bar{\ell}_i - \epsilon \bar{P}_i - H \bar{M}_i) dm_i \quad (34)$$

It is worth noting that kinetic and gravitational energy terms do not appear in Eq. (34) so that internal energy is completely independent of these effects, as it should be.

If Gibbs free energy is defined as

$$G = U + PV - TS - \gamma\alpha - F\ell - \epsilon P - HM \quad (35)$$

it may be differentiated at constant  $T, P, \gamma, F, \epsilon, H$  and  $m_j$  to give the partial extensive quantity,

$$\bar{G}_i = \bar{U}_i + P \bar{V}_i - T \bar{S}_i - \gamma \bar{\alpha}_i - F \bar{\ell}_i - \epsilon \bar{P}_i - H \bar{M}_i \quad (36)$$

If Eq. (36) is inserted into Eq. (34),

$$dU = T dS - P dV + \gamma d\alpha + F d\ell + \epsilon dP + HdM + \sum_i \bar{G}_i dm_i \quad (37)$$

where the partial free energy  $\bar{G}_i$  is the previously used chemical potential  $\mu_i$ .

Since Eq. (37) is homogeneous in mass (i.e., doubling the mass at constant state of fixed  $T, P, \gamma, F, \epsilon, H$ , and  $\bar{G}_i$  doubles  $U, S, V, d, \ell, P, M$ , and  $m$ ), it may be integrated from zero to finite mass,

$$U = TS - PV + \gamma\alpha + F\ell + \epsilon P + HM_i + \sum_i \bar{G}_i m_i \quad (38)$$

and

$$G = \sum_i \bar{G}_i m_i \quad (39)$$

If Eq. (35) is differentiated and compared with Eq. (37) an alternate form of the fundamental property relation is obtained,

$$dG = -S dT + V dP - \alpha d\gamma - \ell dF - P d\epsilon - MdH + \sum_i \bar{G}_i dm_i \quad (40)$$

If Eq. (38) is differentiated and compared with Eq. (37), the result is

$$S dT - V dP + \alpha d\gamma + \ell dF + P d\epsilon + MdH + \sum_i m_i d\bar{G}_i = 0 \quad (41)$$

In summary Eqs. (34), (35), (36), (37), (38),

(40), and (41) are similar to the usual well-known equations when only thermal, compression, and mass transfer effects are involved, but these extended equations account for other effects such as surface tension, tensile stress, electric polarization, and magnetic polarization. The proper way to handle gravitation and other field effects has been shown and contrasted with the erroneous methods in three well-known books.

For a more complete discussion of this subject the reader is referred to the previous extensive treatment of The Symmetrical Fundamental Property Relation of Thermodynamics [5]. □

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#### NOMENCLATURE

C	Velocity of light
E	Total energy (internal + kinetic + potential of all kinds)
$\epsilon$	Electrical potential or field
F	Force
G	Gibbs free energy, $U + PV - TS$ , or $G = U$

	$+ PV - TS - \gamma\alpha - Fl - \epsilon P - HM$
g	Acceleration due to gravity
H	Enthalpy, $U + PV$
$H$	Magnetic potential or field
l	Length
LW	Lost work (irreversibility)
M	Molecular weight
$M$	Magnetic polarization
m	Mass
n	Number of moles
P	Pressure
$P$	Electrical polarization
Q	Heat flow
S	Entropy
T	Temperature (absolute)
U	Internal (intrinsic) energy of matter
u	Velocity
V	Volume
W	Work flow
Z	Height above a reference point
$\alpha$	Surface area
$\delta$	Quantity transferred (as heat $\delta Q$ and work $\delta W$ )
$\gamma$	Surface tension
$\Phi$	Potential energy ( $gz$ in gravitational field)
$\mu$	Chemical or mass potential ( $\mu_i = \bar{G}_i$ )

#### Superscript

—	Denotes partial extensive property
$\alpha, \beta$	Points in gravitation field

#### Subscripts

i	Denotes different chemical species
j	Denotes all chemical species except particular one i being examined.

## RESIDUAL FUNCTIONS AND FUGACITY

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TWO PROPERTIES WHICH generate considerable confusion in thermodynamics courses are residual functions and fugacity. They are, in fact, closely related concepts and, in this paper, we have developed them in a consistent manner. In this

way, the composition dependence of the fugacity coefficient of a component in a mixture appears in an unambiguous manner.

#### PROPERTY CHANGES

The property changes which we shall develop in this paper are all of the form: real fluid property less perfect gas property. The difference is either at the same temperature and pressure or at the same temperature and density. The definitions are (using M to denote U, H, A, G, S, V).