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Legendre Transforms in Chemical Thermodynamics

Robert A. Alberty

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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I. Introduction

One of the first things to be clear about before making a thermodynamic measurement, an equilibrium calculation, or a statistical mechanical prediction is the answer to the question "What are the independent variables?" Gibbs[1] showed that the number of independent variables can be calculated by use of the phase rule, but the choice of independent variables is to some extent arbitrary. A major reason for selecting one independent variable over another is simply convenience. It is easy to hold the temperature constant and impossible to hold the entropy constant, except in adiabatic processes. It is easier to hold the pressure of a liquid constant than to hold the volume constant when the temperature is varied. However, there is a more insightful way to put the above question, and that is "What are the natural variables?" To explain what natural variables are, we start with the combined first and second laws for a closed system involving only PV work:

$$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V \qquad \text{(I-1)}$$

Here U is the internal energy and S is the entropy. The natural variables for the internal energy are S and V because their differentials are on the right side of eq I-1. If U could be determined as a function of S and V, then T and P could be obtained by taking partial derivatives of U with respect to S and V. If this could be done, we would have all of the thermodynamic properties of the system. The natural variables are also important because they are the variables that are held constant in stating the equilibrium condition in terms of the thermodynamic potential on the left side. The fundamental equation for U can be used to derive two criteria for equilib-

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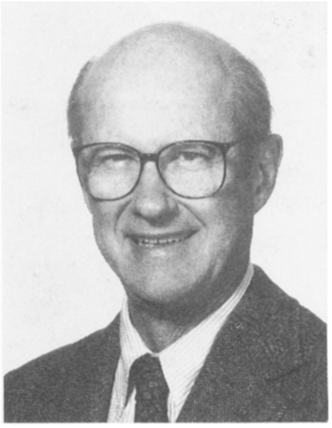

Robert A. Alberty was born in Winfield, KS, in 1921. He earned his doctorate at the University of Wisconsin in Physical Chemistry in 1947 and stayed there on the faculty. In 1955 he joined Professor Farrington Daniels as a coauthor of *Physical Chemistry*. He has been with this textbook through eight editions, and Robert J. Silbey joined him as a coauthor in 1992. At the University of Wisconsin, he carried out research on electrophoresis, enzyme kinetics, and thermodynamics of enzyme-catalyzed reactions. In 1963 he became Dean of the Graduate School at the University of Wisconsin. In 1967 he moved to the Massachusetts Institute of Technology to be Dean of Science, a position he held for 15 years. When he returned to research and teaching in 1982, he worked on the thermodynamics of hydrocarbon systems of interest in petroleum refining and combustion. When he became Professor Emeritus in 1991, he worked on the thermodynamics of biochemical reactions with new ideas from petroleum thermodynamics. Professor Alberty is a member of the National Academy of Sciences and the American Academy of Arts and Sciences, and has just completed a term as President of the Physical Chemistry Division of IUPAC.

rium and spontaneous change in a closed system involving only PV work. The internal energy can be used when the entropy and the volume are held constant; $(\mathrm{d}U)_{S,V} \le 0$. Under these conditions the internal energy can only decrease, and the equality applies at equilibrium because the internal energy is at a minimum. This criterion is not very useful in chemistry because there is no way to hold the entropy constant. The entropy can be used to state a criterion for spontaneous change when the internal energy and volume are constant: $(\mathrm{d}S)_{U,V} \ge 0$. Under these conditions the entropy can only increase, and the equality applies at equilibrium. This criterion applies to isolated systems because the internal energy and volume are constant, but the use of this criterion for systems at constant temperature and constant pressure is difficult because heat and pressure reservoirs have to be included in the isolated system in addition to the system of interest. Equation I-1 shows that the variables come in conjugate pairs (T, S and P, V) in which one variable is intensive (T and P) and the other is extensive (S and V); note that the natural variables for U are both extensive.

Legendre transforms are important because they provide the way to solve the problems mentioned in the preceding paragraph. A Legendre transform is a linear change in variable that involves adding or subtracting the product of conjugate variables from an extensive property of a system. The enthalpy, H, the Helmholtz energy, A, and the Gibbs energy, G, are defined by use of the following Legendre transforms:

$$H = U + PV \tag{I-2}$$

$$A = U - TS \tag{I-3}$$

$$G = U + PV - TS \tag{I-4}$$

Note that we are going to stick with these definitions throughout this paper and recommend that they not be altered. These simple linear transformations have remarkable effects on the fundamental equation. To see this, consider the enthalpy. To obtain the fundamental equation for the enthalpy, we take the differential of H in eq I-2:

$$\mathrm{d}H = \mathrm{d}U + P\,\mathrm{d}V + V\,\mathrm{d}P \tag{I-5}$$

Substituting eq I-1 yields the fundamental equation for the enthalpy of a closed system involving only PV work:

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}P \tag{I-6}$$

Note that the PV term in eq I-2 led to a $V\,\mathrm{d}P$ term in eq I-6, so that there is now a term proportional to the differential of an intensive variable P in a fundamental equation, rather than a term proportional to the differential of an extensive variable V, as in eq I-1. In other words, the Legendre transform in eq I-2 has interchanged the roles of P and V by making P a natural variable, rather than V. The fundamental equations for A and G for a closed system involving only PV work are derived using eqs I-3 and I-4:

$$\mathrm{d}A = -S\,\mathrm{d}T - P\,\mathrm{d}V \tag{I-7}$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P \tag{I-8}$$

The natural variables of A are T and V, and the natural variables of G are T and P.

Equations I-6 through I-8 make it possible to derive the following criteria of spontaneous change: $(\mathrm{d}H)_{S,P} \le 0$, $(\mathrm{d}A)_{T,V} \le 0$, and $(\mathrm{d}G)_{T,P} \le 0$, of which the last two are useful and the last one is especially useful since so many equilibrium measurements are made at constant T and P.

Equation I-8 indicates that if we can determine G of a closed system involving only PV work as a function of T and P, we can calculate all of the thermodynamic properties of the system because

$$S = -(\partial G/\partial T)_P \tag{I-9}$$

$$V = (\partial G/\partial P)_T \tag{I-10}$$

The enthalpy H can be calculated by use of the Legendre transform $H = G + TS$ (this is the difference between eqs I-2 and I-4) or by its equivalent, the Gibbs–Helmholtz equation:

$$H = -T^2[\partial(G/T)/\partial T]_P \tag{I-11}$$

If G is only known as an explicit function of T and V or of P and V, all of the thermodynamic properties of the system cannot be calculated. There is a very important lesson here. If a thermodynamic potential can be determined as a function of its natural variables, all of the thermodynamic properties of the system can be calculated; but if some of the independent variables are not natural variables, they cannot.

The state of a system can be defined in terms of any sufficient set of independent variables, but the reason for specifying the natural variables is that all of the thermodynamic properties of the system can be obtained by determining the thermodynamic potential as a function of its natural variables. Another way to say this is that when certain independent variables can be controlled, the thermodynamic potential for which they are the natural variables should be calculated from the experimental data.

A closed system involving only PV work has four thermodynamic potentials (U, H, A, G) because U depends on the two conjugate pairs of independent variables (T, S) and (P, V), and there are four possible combinations of independent variables when one is taken from each pair. The fact that the natural variables of the internal energy are the two extensive properties S and V is represented by $U(S,V)$. The natural variables of the enthalpy are one extensive variable and one intensive variable, which is represented by $H(S,P)$. The natural variables of the Helmholtz energy are one intensive and one extensive variable, which is represented by $A(T,V)$. The natural variables of the Gibbs energy are two intensive variables, which is represented by $G(T,P)$. Thus, the Legendre transforms of U given in eqs I-2 to I-4 replace extensive natural variables with intensive natural variables. In general, intensive variables are easier to control in the laboratory than extensive variables. The reason for introducing the additional thermodynamic potentials H, A, and G is the convenience of having the intensive variables T and P as natural variables.

When a system involves work in addition to PV work, there is an opportunity to make further Legendre transforms, and this article is about how and why this is done. For open systems and systems involving work in addition to PV work, the fundamental equation of thermodynamics for the internal energy may include additional work terms. For example, if chemical work, gravitational work, work of electrical transport, work of elongation, surface work, work of electric polarization, and work of magnetic polarization are involved and are independent, the fundamental equation for the internal energy can be written as

$$dU = T\,dS - P\,dV + \sum_{i=1}^{N}\mu_i\,dn_i + \psi\,dm + \sum_{i=1}^{N}\phi_i\,dQ_i + f\,dL + \gamma\,dA_s + \boldsymbol{E}\cdot d\boldsymbol{p} + \boldsymbol{B}\cdot d\boldsymbol{m} \quad \text{(I-12)}$$

This equation applies to a multiphase system and is really more complex than it appears. Equation I-12 does not apply to any actual system, but it is a good place to start to discuss the general nature of the terms that are discussed in more detail in the following sections. When a system has more than one phase, each species contributes a chemical work term for each phase in which it is present. The chemical potential of species i is represented by μ_i if the non-PV work terms are independent of the amount n_i of species i in a phase; later we will add a prime when other work terms involve n_i. When there is a single phase, N is the number of species in the system, but N can be as large as the number of species times the number of phases. In the gravitational work term, ψ is the gravitational potential and m is mass. The electrical work term is like the chemical work term in that each species contributes a term for each phase in which it is present; the electric work term depends on the charge Q_i that species i contributes to the electric charge of the phase and the electric potential ϕ_i of the phase. The mechanical work term can be much more complicated because a solid can be distorted in various ways. In general this term requires tensors, but the work term shown here deals with the force of extension f and the change in length L of the sample in the direction of the force. The surface work term also depends on the geometry of the system; γ is surface tension or interfacial tension and A_s is surface area. The last two terms deal with the work of polarization. $\boldsymbol{E}$ is electric field strength, $\boldsymbol{p}$ is the dipole moment of the system, $\boldsymbol{B}$ is magnetic field strength (magnetic flux density), and $\boldsymbol{m}$ is the magnetic moment of the system. The dots indicate scalar products of vectors. The chemical terms are sometimes written as a scalar product, but, as we will see in eqs III-38, III-39, and III-40, it is better to write the chemical terms as a matrix product. Equation I-12 indicates that the work terms are independent, but some of the terms may not be independent and must be combined with other terms, as described below.

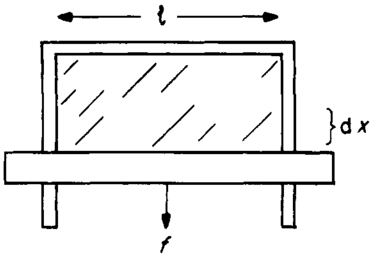

Figure 1. Work on a liquid film performed by a force f on a sliding bar.

It is perhaps puzzling that there are three types of work terms. The terms $P\,dV$, $f\,dL$, and $\gamma\,dA_s$ all amount to force time distance. Figure 1 illustrates this for work done on a liquid film against surface tension. The work performed by the force f on the sliding bar is $2\gamma l\,dx = 2\gamma\,dA_s$, where γ is the surface tension, l is the length of the interface, dx is the distance in the direction of the force, and $dA_s = l\,dx$. The 2 comes from the fact that the liquid film has two surfaces. The terms $\mu_i\,dn_i$, $\psi\,dm$, and $\phi_i\,dQ_i$ are of a different type; they are of the form (potential) d(capacity factor). The terms $\boldsymbol{E}\cdot d\boldsymbol{p}$ and $\boldsymbol{B}\cdot d\boldsymbol{m}$ are of the form (field)·d(polarization). Feynman[2] gives a detailed explanation of these three types of work terms and writes the potential energy U of an object in a field $\boldsymbol{C}$ at a point where the potential is ψ as

$$U = -\int \boldsymbol{F}\cdot d\boldsymbol{s} = -m\int \boldsymbol{C}\cdot d\boldsymbol{s} = m\psi \quad \text{(I-13)}$$

where $\boldsymbol{F}$ is a force, $\boldsymbol{s}$ is a distance vector, and m is the energy divided by a potential ψ. In using these work terms, we will assume that work is performed in a quasi-static process in which the system is at equilibrium at each infinitesimal step, so that exact differentials can be used.

It does not seem possible to imagine a system in which all these kinds of work terms are independent, but eq I-12 reminds us that several types of work may be involved in a single thermodynamic system. It is important to notice that the work terms in the fundamental equation for U are all of the form (intensive variable) d(extensive variable). The natural variables for U for the hypothetical system described by eq I-12 are indicated by $U(S, V, n_i, m, Q_i, L, A_s, \boldsymbol{p}, \boldsymbol{m})$, where n_i represents the amounts of all of the species in the system. When eq I-12 is written for an actual system, it is important that these extensive variables be independent of each other. When some of them are not independent, dependent variables must be eliminated from the fundamental equation; for example, the charge Q_i contributed by species i to a phase may be expressed in terms of the amount n_i of species i in the phase.

Temperature and pressure can be introduced as natural variables by use of eqs I-2, I-3, and I-4. The intensive variables like the chemical potential of a species μ_i, the gravitational potential ψ, the electric potential ϕ_i of a phase, the force of extension f, the surface tension γ, the electric field strength $\boldsymbol{E}$, and the magnetic field strength $\boldsymbol{B}$ can be introduced as natural variables only by defining new thermodynamic potentials by use of further Legendre transforms.

Since the natural variables for U are all extensive, eq I-12 can be integrated while holding all of the intensive variables constant. This yields

$$U = TS - PV + \sum_{i=1}^{N} n_i\mu_i + \psi m + \sum_{i=1}^{N}\phi_i Q_i + fL + \gamma A_s + \boldsymbol{E}\cdot\boldsymbol{p} + \boldsymbol{B}\cdot\boldsymbol{m} \quad \text{(I-14)}$$

Alternatively, this equation can be derived by use of Euler's theorem. A function $f(x_1,x_2,\ldots,x_N)$ is said to be homogeneous of degree n if

$$f(kx_1,kx_2,\ldots,kx_N) = k^n f(x_1,x_2,\ldots,x_N) \quad \text{(I-15)}$$

For such a function, Euler's theorem states that

$$nf(x_1,x_2,\ldots,x_N) = \sum_{i=1}^{N} x_i \frac{\partial f}{\partial x_i} \quad \text{(I-16)}$$

Thermodynamic potentials like U, H, A, and G are homogeneous of degree 1 in terms of extensive thermodynamic properties, and so eq I-12 leads to eq I-14. The absolute value of the internal energy of a system is unknown, but eq I-14 can be used in thermodynamic derivations because actual measurements and calculations are concerned with changes from one equilibrium state to another equilibrium state.

It is important to note that the intensive variables (T, P, μ_i, ψ, ϕ_i, f, γ, $\boldsymbol{E}$, and $\boldsymbol{B}$) for the system described by eq I-12 are each partial derivatives of the internal energy when the other variables are held constant. For example,

$$\mu_i = (\partial U/\partial n_i)_{S,V,n_j,m,Q_i,L,A_s,\boldsymbol{p},\boldsymbol{m}} \quad \text{(I-17)}$$

where $n_j \neq n_i$. This equation is written on the assumption that the various extensive variables are independent, but they may not be independent for an actual system. Note that only the natural variables for U for the system are included in the subscripts. Thus, if the internal energy were known as an explicit function of its natural variables, the corresponding intensive properties of the system could be calculated by partial differentiation of this function. From the standpoint of the fundamental equation for U, the symbols T, P, μ_i, ψ, ϕ_i, f, γ, $\boldsymbol{E}$, and $\boldsymbol{B}$ are simply symbols for partial derivatives.

The fundamental equations for H, A, and G for a system involving the various kinds of work described above can be obtained by using the Legendre transforms I-2 to I-4. For example,

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \sum_{i=1}^{N}\mu_i\,\mathrm{d}n_i + \psi\,\mathrm{d}m + \sum_{i=1}^{N}\phi_i\,\mathrm{d}Q_i + f\,\mathrm{d}L + \gamma\,\mathrm{d}A_s + \boldsymbol{E}\cdot\mathrm{d}\boldsymbol{p} + \boldsymbol{B}\cdot\mathrm{d}\boldsymbol{m} \quad \text{(I-18)}$$

Thus the natural variables of G for this hypothetical system are indicated by $G(T, P, n_i, m, Q_i, L, A_s, \boldsymbol{p}, \boldsymbol{m})$. Again we observe that the coefficients of the differential terms can be obtained as derivatives of G with respect to T, P, n_i, m, Q_i, L, A_s, $\boldsymbol{p}$, and $\boldsymbol{m}$, when the natural variables other than the one varied are held constant.

When the intensive variables are held constant, eq 18 can be integrated to

$$G = \sum_{i=1}^{N} n_i\mu_i + \psi m + \sum_{i=1}^{N}\phi_i Q_i + fL + \gamma A_s + \boldsymbol{E}\cdot\boldsymbol{p} + \boldsymbol{B}\cdot\boldsymbol{m} \quad \text{(I-19)}$$

Note that when P and T are introduced as natural variables, their terms in the expression for the integrated thermodynamic potential are eliminated; thus, eq I-19 has two fewer terms than eq I-14. This reduction will continue as further intensive variables are introduced as natural variables because the integration of a fundamental equation is always carried out with the intensive natural variables held constant.

Equations I-12 and I-18 and the corresponding equations for H and A are useful for the definitions (see eq I-17) they give for the coefficients of the differentials, and they provide useful Maxwell equations. However, in a given experimental situation, it may be much more convenient to control one or more of the intensive variables μ_i, ψ, ϕ_i, f, γ, $\boldsymbol{E}$, and $\boldsymbol{B}$. Therefore, Legendre transforms are used to define additional thermodynamic potentials that have some of these intensive variables as natural variables. This is simply a continuation of the process started with eqs I-2 to I-4. A number of these additional thermodynamic potentials are described in sections III–IX. It is evident that there is a very large number of thermodynamic potentials that can be defined by Legendre transforms; actually the number is infinite because the chemical potential of any species or combination of chemical potentials of species can be chosen as natural variables. This raises a serious nomenclature problem. There is a solution in principle to this problem that is discussed in the next section; however, more discussion is needed on the nomenclature for thermodynamic potentials.

The Legendre transforms in eqs I-2 to I-4 and in sections III–IX can be referred to as partial Legendre transforms. The complete Legendre transform of U replaces all of the extensive natural variables with intensive natural variables. The complete Legendre transform of the internal energy is

$$U' = U - TS + PV - \sum_{i=1}^{N} n_i\mu_i - \psi m - \sum_{i=1}^{N} \phi_i Q_i - fL - \gamma A_s - \boldsymbol{E}\cdot\boldsymbol{p} - \boldsymbol{B}\cdot\boldsymbol{m} = 0 \quad \text{(I-20)}$$

where U' is a transformed internal energy, which is equal to zero (see eq I-14). Taking the differential of U' and inserting eq I-12 for dU yields

$$-S\,dT + V\,dP - \sum_{i=1}^{N} n_i\,d\mu_i - m\,d\psi - \sum_{i=1}^{N} Q_i\,d\phi_i - L\,df - A_s\,d\gamma - \boldsymbol{p}\cdot d\boldsymbol{E} - \boldsymbol{m}\cdot d\boldsymbol{B} = 0 \quad \text{(I-21)}$$

This is the Gibbs–Duhem equation for the system. It shows that at equilibrium there is a relation between the intensive variables for a system. This particular system involves $N + 8$ intensive variables, and so only $N + 7$ of them are independent. This is of course true only if the extensive variables are independent. If there are two phases at equilibrium, there are only $N + 6$ independent intensive variables because there is an additional Gibbs–Duhem equation to be satisfied for the second phase. Therefore, the number F of intensive degrees of freedom for this system with p phases is $F = N - p + 8$, where 8 is the number of conjugate pairs in addition to the chemical work terms. This is the extended Gibbs phase rule. For the one-phase system, $F = N + 7$. Since F is the number of intensive degrees of freedom required to describe the intensive state of the system, one extensive variable has to be added to describe the extensive state of the system.

Equations I-12 to I-21 apply when there are no chemical reactions, but when chemical reactions are at equilibrium, eqs I-12 to I-21 must be written in terms of components. At chemical equilibrium it is necessary to use components rather than species because only the components are independent. If reactions occur and the system is at chemical equilibrium, the amounts of N species are not independent variables because their equilibrium chemical potentials are related through $\sum\nu_i\mu_i = 0$, where ν_i is the stoichiometric number for species i, for each independent reaction. If there are R independent reactions, there are $N - R$ independent species or combinations of species, which are referred to as components. Thus the number of independent chemical work terms is $C = N - R$, where C is the number of components. The number of components is defined as the number of species (or combinations of species) required to describe the composition of the reaction system at chemical equilibrium. The determination of the number of components and the selection of a suitable set of components really requires the use of matrices (see section III.A.2). If the first C species in a system can be selected as a set of components, the summation of chemical terms in eqs I-12, I-14, I-18, I-19, I-20, and I-21 has to be replaced with

$$\sum_{i=1}^{C} \mu_i\,dn_{Ci} \quad \text{(I-22)}$$

where μ_i is the chemical potential of a species selected as a component and n_{Ci} is the amount of the component with that chemical potential. If charge balance is independent of the atom balances, the number of components is $C = N - R - 1$. The Gibbs–Duhem equation for a system with chemical reactions at equilibrium is

$$-S\,dT + V\,dP - \sum_{i=1}^{C} n_{Ci}\,d\mu_i - m\,d\psi - \sum_{i=1}^{C} Q_i\,d\phi_i - L\,df - A_s\,d\gamma - \boldsymbol{p}\cdot d\boldsymbol{E} - \boldsymbol{m}\cdot d\boldsymbol{B} = 0 \quad \text{(I-23)}$$

This system involves $C + 8$ intensive variables, and so only $C + 7$ of them are independent. The number F of intensive degrees of freedom for this system with p phases is $F = C - p + 8$. For the one-phase system, the phase rule would be $F = C + 7$ if the work terms were independent. The use of matrices to determine the number of components in a system is discussed in section III.B. The choice of components is to some extent arbitrary, but the number of components is unique. For example, in a system consisting of CO, CO_2, H_2, H_2O, and CH_4, the components can be taken to be C, O, and H or CO, CO_2, and H_2.

Equations for differentials of thermodynamic potentials, like those above, lead to a large number of Maxwell equations. If there are n terms, there are 2^n thermodynamic potentials and $n(n - 1)/2$ Maxwell relations. There are three types of Maxwell equations; both partial derivatives may be with respect to an extensive variable, one of the partial derivatives may be with respect to an extensive variable and the other with respect to an intensive variable, or both partial derivatives may be with respect to intensive variables. The latter type is generally more useful because it is usually easier to control intensive variables in the laboratory. In order to obtain this type of Maxwell equation, it is necessary to use Legendre transforms.

No references have been given above to Legendre transforms because the treatment hardly goes beyond that of textbooks. All of the concepts described above go back to Gibbs.[1] The uses of Legendre transforms are discussed by Callen;[3,10] Tisza;[4] McQuarrie;[5] Beattie and Oppenheim;[6] Van Ness and Abbott;[7] Modell and Reid;[8] Adkins;[9] Chandler;[11] Couture, Chahine, and Zitoun;[12] and Bertin, Faroux, and Renault.[13]

II. Callen's Nomenclature for Legendre Transformed Thermodynamic Potentials

The purpose of this section is to introduce the infinite number of thermodynamic potentials that can be defined by Legendre transforms and to describe a nomenclature that can be used to designate any possible thermodynamic potential. It is not necessary to understand this section in detail in order to be able to use Legendre transforms, but it is important to see that it is possible to give systematic symbols for an infinite number of thermodynamic potentials and an infinite number of fundamental equations.

Callen[3,10] uses the nomenclature $U(X_0,X_1,\ldots,X_t)$ that we have used above to indicate that the internal energy has the natural extensive variables X_0 to X_t. The corresponding intensive variables are represented by P_k so that the fundamental equation for U (cf., eq I-12) is represented by

$$\mathrm{d}U = \sum_{k=0}^{t} P_k\,\mathrm{d}X_k \qquad \text{(II-1)}$$

Callen uses P_0 to represent T and X_0 to represent S. Chemical work terms can be treated like the other work terms; for example, $P_j = \mu_j$ and $X_j = n_j$. The extensive variables X_i must be independent. The intensive variables P_k can be calculated from the equation for the internal energy U as a function of X_0, ..., X_t by use of the partial derivatives

$$P_k = \partial U/\partial X_k \qquad \text{(II-2)}$$

where all of the extensive variables other than X_k have to be held constant for the differentiation. The integrated form of eq II-1 (cf., eq I-14) is

$$U = \sum_{k=0}^{t} P_k X_k \qquad \text{(II-3)}$$

Callen uses the symbol $U[P_i]$ to represent the transformed internal energy that has P_i as a natural variable. This is accomplished by defining $U[P_i]$ with the Legendre transform

$$U[P_i] = U - P_i X_i \qquad \text{(II-4)}$$

The symbol $U[P_i]$ for the new thermodynamic potential is used to indicate that P_i has been introduced as a natural intensive variable by subtracting the term P_iX_i from U to define the new thermodynamic potential. It is important to note the use of square brackets in this notation. The new thermodynamic potential $U[P_i]$ has the natural variables indicated by $U[P_i](X_0,X_1,\ldots,X_{i-1},P_i,X_{i+1},\ldots,X_t)$; note that the extensive variable X_i has been replaced by the intensive variable P_i. Callen's symbols for the basic thermodynamic potentials are $H = U[P]$, $A = U[T]$, and $G = U[T,P]$.

Additional thermodynamic potentials can be defined by use of the Legendre transform

$$U[P_0,P_1,\ldots,P_s] = U - \sum_{k=0}^{s} P_k X_k \qquad \text{(II-5)}$$

The symbol for the new thermodynamic potential $U[P_0,P_1,\ldots,P_s]$ shows the intensive natural variables introduced by the Legendre transform. This transform replaces the natural extensive variables X_0, X_1, ..., X_s of U with the intensive natural variables P_0, P_1, ..., P_s of $U[P_0,P_1,\ldots,P_s]$. If P_0 is T, X_0 is S, P_1 is P, and X_1 is V, then $U[P_0,P_1] = U[T,P] = G$. The partial derivatives of the new thermodynamic potential are

$$\frac{\partial U[P_0\ldots P_s]}{\partial P_k} = -X_k \qquad k = 0, 1, \ldots, s \qquad \text{(II-6)}$$

$$\frac{\partial U[P_0\ldots P_s]}{\partial X_k} = P_k \qquad k = s+1, \ldots, t \qquad \text{(II-7)}$$

The fundamental equation for the new thermodynamic potential is

$$\mathrm{d}U[P_0\ldots P_s] = \sum_{k=0}^{s}(-X_k)\,\mathrm{d}P_k + \sum_{k=s+1}^{t} P_k\,\mathrm{d}X_k \qquad \text{(II-8)}$$

The integration of this fundamental equation at constant values of the intensive variables P_0 to P_s yields the following equation for the new thermodynamic potential:

$$U[P_0\ldots P_s] = \sum_{k=s+1}^{t} P_k X_k \qquad \text{(II-9)}$$

The fundamental equations are written in terms of differentials of natural variables because the state of a system is described completely only by a thermodynamic potential written as a function of its natural variables. The new thermodynamic potential has the natural variables P_0, ..., P_s, X_{s+1}, ..., X_t.

$$U[P_0,\ldots,P_s] = U[P_0,\ldots,P_s](P_0,\ldots,P_s,X_{s+1},\ldots,X_t) \qquad \text{(II-10)}$$

The following are some examples of Callen's nomenclature for the usual thermodynamic potentials H and G for a one-phase system and their counterparts when other kinds of work are involved:

Closed system with only PV work: $H(S,P) = U[P]$, $G(T,P) = U[T,P]$.

Open system with only PV work: $H(S,P,n_i) = U[P]$, $G(T,P,n_i) = U[T,P]$.

Open system with PV and ϕQ work: $H(S,P,n_i,Q_i) = U[P]$, $G(T,P,n_i,Q_i) = U[T,P]$.

Open system with PV and ϕQ work at specified ϕ_i: $H'(S,P,n_i,\phi_i) = U[P,\phi_i] = H[\phi_i]$, $G'(T,P,n_i,\phi_i) = U[T,P,\phi_i] = G[\phi_i]$. Note that the convention followed here is that H and G are used in writing the fundamental equation when other kinds of work are involved and are written in the form $P_k\,\mathrm{d}X_k$, that is in the form (intensive property) d(extensive property). A prime is used to indicate that a Legendre transform has been used to make an intensive property other than T and P a natural variable. Callen's nomenclature can be extended by using H, A, and G with square brackets, in addition to U. If the definitions of H, A, and G in eqs I-2 to I-4 are adhered to, we can use U', H', A', and G' for Legendre transformed thermodynamic potentials and indicate the intensive variables introduced in addition to T and P by square brackets. The use of $H' = H[\phi_i]$ and $G' = G[\phi_i]$ is a logical extension of Callen's system, which uses $U[P,\phi_i]$ and $U[T,P,\phi_i]$, respectively.

In this section we have seen that even though there is an infinite number of thermodynamic potentials, each can be represented by a distinctive symbol that tells how it is defined.

III. Transforms for Chemical Work

A. Gas Reactions

1. Derivations

Chemical reaction systems are generally considered thermodynamically as batch processes under specified conditions of T and P or T and V, and the chemical potential of a reactant has not often been considered as an independent variable. The idea of using the chemical potential of a species as an independent variable is more familiar in statistical mechanics, where a semigrand isothermal–isobaric ensemble is one in which a species is available from a reservoir through a semipermeable membrane at a specified chemical potential. Semigrand ensembles have been used in statistical mechanical theories of solutions,[14] the study of the relationship between light scattering and composition fluctuations,[15] constant pressure solution theory,[16-19] studying molecular changes in hemoglobin,[20,21] cooperativity theory in biochemistry,[22] linear aggregation theory in cell biology,[23] solubility in monolayers,[24] and calculating the equilibrium distribution of hydrocarbons in homologous series.[25] Also, there have been equilibrium calculations on hydrocarbon processing at a specified partial pressure of molecular hydrogen.[26,27] This type of equilibrium calculation can be extended to reactants that are not elements.[28,29] For example, equilibrium compositions within a whole homologous series can be calculated at a specified partial pressure of ethylene.[30,31]

Alberty and Oppenheim[32] used a Legendre transform involving the chemical potential of gaseous ethylene to define a transformed Gibbs energy that is minimized at equilibrium in the alkylation of benzene. They[33] went on to derive the semigrand partition function for this system. Later, they[34,35,36] gave the seven Legendre transforms that apply to this system and wrote out the eight forms of the fundamental equation. They showed that for making calculations, it is more practical to use the partial pressure of a reactant as a natural variable, rather than its chemical potential. This brings in a transformed entropy S' and a transformed enthalpy H', as well as the transformed Gibbs energy G'. Alberty[37] used a Legendre transform involving the chemical potentials of acetylene and molecular hydrogen to discuss the equilibrium polymerization of polycyclic aromatic hydrocarbons in flames.

When chemical reactions occur in a reaction chamber that is connected with a large reservoir of one of the reactants through a semipermeable membrane, the Gibbs energy G of the contents of the reaction chamber is not minimized at equilibrium and the atoms of the elements in the reactant in the reservoir are not conserved in the reaction chamber. However, the atoms of the elements that are not in the reactants in the reservoir are conserved, and it can be shown that the transformed Gibbs energy defined below is minimized.

The derivation[34] of the fundamental equation for the transformed Gibbs energy of a gaseous reaction system is most easily illustrated by considering the reaction

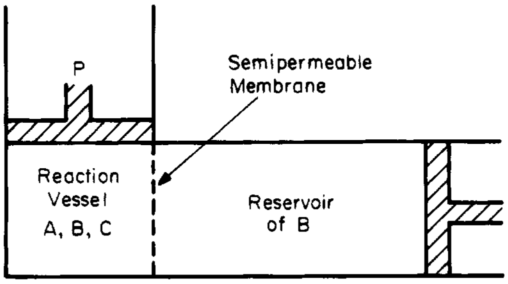

Figure 2. The reaction vessel contains gaseous species A, B, and C at T and P connected to a reservoir of B at P_B through a semipermeable membrane permeable only to B. The heat reservoir is not shown.

$$A + B = C \tag{III-1}$$

The fundamental equation for G is

$$dG = -S\,dT + V\,dP + \mu_A\,dn_A + \mu_B\,dn_B + \mu_C\,dn_C \tag{III-2}$$

If the reaction does not occur, five variables have to be specified to describe the extensive state of the system; this is in agreement with the phase rule that the number of degrees of freedom is given by

$$F = C - p + 2 \tag{III-3}$$

where C is the number of components and p is the number of phases. For the nonreacting system described by eq III-2, $F = 3 - 1 + 2 = 4$ intensive variables are required to describe the intensive state of the system. To describe the extensive state of the system, it is necessary to include one extensive variable. However, if reaction III-1 is at equilibrium, the number of components is $C = N - R = 3 - 1 = 2$ where R is the number of independent reactions, and $F = 2 - 1 + 2 = 3$ intensive variables are required. To describe the extensive state of the system, it is necessary to include one extensive variable. At chemical equilibrium the extensive state of the system could be described by specifying T, P, $n_C{}^\circ/n_A{}^\circ$, and $n_A{}^\circ$. There is another way to look at this system that is illustrated in Figure 2. The reaction system is connected to a reservoir of species B through a semipermeable membrane that is only permeable to B. Now P_B is an independent variable like T and P. The extensive state of the system can be described by specifying T, P, P_B, and $n_A{}^\circ$.

When the reaction system is at equilibrium, it is necessary to write the fundamental equation in terms of components, rather than species. This can be done by use of the equilibrium condition

$$\mu_A + \mu_B = \mu_C \tag{III-4}$$

to eliminate μ_C from eq III-2 to obtain

$$dG = -S\,dT + V\,dP + \mu_A(dn_A + dn_C) + \mu_B(dn_B + dn_C) = -S\,dT + V\,dP + \mu_I{}'dn_I{}' + \mu_B\,dn_B{}' \tag{III-5}$$

where $\mu_I{}' = \mu_A$ is the transformed chemical potential of the pseudoisomer group; at specified μ_B, A and C are called pseudoisomers. Note that eq III-5 is in terms of amounts of two components rather than three species. The amount of the pseudoisomer group is

$$n_{\mathrm{I}}' = n_{\mathrm{A}} + n_{\mathrm{C}} \qquad \text{(III-6)}$$

so that

$$\mathrm{d}n_{\mathrm{I}}' = \mathrm{d}n_{\mathrm{A}} + \mathrm{d}n_{\mathrm{C}} \qquad \text{(III-7)}$$

The total amount (bound and free) of B in the system is

$$n_{\mathrm{B}}' = n_{\mathrm{B}} + n_{\mathrm{C}} \qquad \text{(III-8)}$$

so that

$$\mathrm{d}n_{\mathrm{B}}' = \mathrm{d}n_{\mathrm{B}} + \mathrm{d}n_{\mathrm{C}} \qquad \text{(III-9)}$$

At chemical equilibrium,

$$(\partial G/\partial n_{\mathrm{I}}')_{T,P,n_{\mathrm{B}}'} = \mu_{\mathrm{I}}' = \mu_{\mathrm{A}} \qquad \text{(III-10)}$$

$$(\partial G/\partial n_{\mathrm{B}}')_{T,P,n_{\mathrm{I}}'} = \mu_{\mathrm{B}} \qquad \text{(III-11)}$$

This is an example of the theorems of Beattie and Oppenheim[6] that "(1) the chemical potential of a component of a phase is independent of the choice of components and (2) the chemical potential of a constituent of a phase when considered to be a species is equal to its chemical potential when considered to be a component".

Now we use the Legendre transform

$$G' = G - n_{\mathrm{B}}'\mu_{\mathrm{B}} \qquad \text{(III-12)}$$

to make μ_{B} a natural variable for the transformed Gibbs energy G'. A possible alternative symbol for the transformed Gibbs energy, which is close to Callen's symbol $U[T,P,\mu_{\mathrm{B}}]$, is $G[\mu_{\mathrm{B}}]$. Taking the differential of G' and substituting eq III-5 yields

$$\mathrm{d}G' = -S\,\mathrm{d}T + V\,\mathrm{d}P - n_{\mathrm{B}}'\,\mathrm{d}\mu_{\mathrm{B}} + \mu_{\mathrm{I}}'\,\mathrm{d}n_{\mathrm{I}}' \qquad \text{(III-13)}$$

Thus at a specified T, P, and μ_{B}, the system behaves like a one-component system; the pseudoisomer group I is that component. At chemical equilibrium,

$$(\partial G/\partial n_{\mathrm{I}}')_{T,P,\mu_\beta} = \mu_{\mathrm{I}}' = \mu_{\mathrm{A}} \qquad \text{(III-14)}$$

The above treatment is completely general, but now we assume that the gases are ideal so that

$$\mu_{\mathrm{i}} = \mu_{\mathrm{i}}^{\circ} + RT\ln(P_{\mathrm{i}}/P^{\circ}) \qquad \text{(III-15)}$$

where P° is the standard-state pressure. In order to use P_{B} as an independent variable in the fundamental equation, $\mathrm{d}\mu_{\mathrm{B}}$ in eq III-15 is replaced with the expression for the total differential:

$$\mathrm{d}\mu_{\mathrm{B}} = (\partial\mu_{\mathrm{B}}/\partial T)_{P_{\mathrm{B}}}\,\mathrm{d}T + (\partial\mu_{\mathrm{B}}/\partial P_{\mathrm{B}})_T\,\mathrm{d}P_{\mathrm{B}} \qquad \text{(III-16)}$$

When the derivatives of μ_{B} are taken and eq III-16 is substituted in eq III-13, we obtain

$$\mathrm{d}G' = -S'\,\mathrm{d}T + V\,\mathrm{d}P' - (n_{\mathrm{C}}RT/P_{\mathrm{B}})\,\mathrm{d}P_{\mathrm{B}} + \mu_{\mathrm{I}}'\,\mathrm{d}n_{\mathrm{I}}' \qquad \text{(III-17)}$$

where the transformed entropy of the system is

$$S' = S - n_{\mathrm{B}}'\overline{S}_{\mathrm{B}} \qquad \text{(III-18)}$$

The partial molar entropy of B is represented by $\overline{S}_{\mathrm{B}}$. The partial pressure P' of the pseudoisomer group is given by

$$P' = P_{\mathrm{A}} + P_{\mathrm{C}} = P - P_{\mathrm{B}} \qquad \text{(III-19)}$$

We can use a further Legendre transform to define the transformed enthalpy H'.

$$H' = G' + TS' \qquad \text{(III-20)}$$

Equations III-12, III-18, and III-20 indicate that

$$H' = H - n_{\mathrm{B}}'\overline{H}_{\mathrm{B}} \qquad \text{(III-21)}$$

Taking the differential of eq III-20 and substituting eq III-17 yields

$$\mathrm{d}H' = T\,\mathrm{d}S' + V\,\mathrm{d}P' - (n_{\mathrm{C}}RT/P_{\mathrm{B}})\,\mathrm{d}P_{\mathrm{B}} + \mu_{\mathrm{I}}'\,\mathrm{d}n_{\mathrm{I}}' \qquad \text{(III-22)}$$

The pseudoisomer group contributes a single term to $(\mathrm{d}G')_{T,P',P_{\mathrm{B}}}$, but now we must consider how this term is to be calculated given the thermodynamic properties of A, B, and C. This term can be written in several different ways:

$$(\mathrm{d}G')_{T,P',P_{\mathrm{B}}} = \mu_{\mathrm{I}}'\,\mathrm{d}n_{\mathrm{I}}' = \mu_{\mathrm{A}}(\mathrm{d}n_{\mathrm{A}} + \mathrm{d}n_{\mathrm{C}}) = \mu_{\mathrm{A}}\,\mathrm{d}n_{\mathrm{A}} + (\mu_{\mathrm{C}} - \mu_{\mathrm{B}})\,\mathrm{d}n_{\mathrm{C}} = \mu_{\mathrm{A}}'\,\mathrm{d}n_{\mathrm{A}} + \mu_{\mathrm{C}}\,\mathrm{d}n_{\mathrm{C}} \qquad \text{(III-23)}$$

Thus we see that the contributions of A and C to G' are proportional to the transformed chemical potentials $\mu_{\mathrm{A}}' = \mu_{\mathrm{A}}$ and $\mu_{\mathrm{C}}' = \mu_{\mathrm{C}} - \mu_{\mathrm{B}}$. When this equation is written in terms of the transformed chemical potentials of A and C there are two terms, but the transformed chemical potential of the pseudoisomer group can be written as

$$\mu_{\mathrm{I}}' = \mu_{\mathrm{I}}'^{\circ} + RT\ln\left[\left(\frac{n_{\mathrm{I}}'}{n_{\mathrm{A}} + n_{\mathrm{C}}}\right)\frac{P'}{P^{\circ}}\right] \qquad \text{(III-24)}$$

Thus the question is "How is $\mu_{\mathrm{I}}'^{\circ}$ related to $\mu_{\mathrm{A}}'^{\circ}$ and $\mu_{\mathrm{C}}'^{\circ}$?" The following derivation is given by Smith and Missen[38] for the closely related problem of representing the standard chemical potential of an isomer group at equilibrium in terms of the standard chemical potentials of the individual isomers. The transformed chemical potentials of A and C are given by

$$\mu_{\mathrm{A}}' = \mu_{\mathrm{A}}'^{\circ} + RT\ln\left[\left(\frac{n_{\mathrm{A}}}{n_{\mathrm{A}} + n_{\mathrm{C}}}\right)\frac{P'}{P^{\circ}}\right] \qquad \text{(III-25)}$$

$$\mu_{\mathrm{C}}' = \mu_{\mathrm{C}}'^{\circ} + RT\ln\left[\left(\frac{n_{\mathrm{C}}}{n_{\mathrm{A}} + n_{\mathrm{C}}}\right)\frac{P'}{P^{\circ}}\right] \qquad \text{(III-26)}$$

Equations III-24, III-25, and III-26 can be written in terms of amounts as follows:

$$n_{\mathrm{I}}' = \frac{n_{\mathrm{A}} + n_{\mathrm{C}}}{P'/P^{\circ}}\exp\left[\frac{\mu_{\mathrm{I}}' - \mu_{\mathrm{I}}'^{\circ}}{RT}\right] \qquad \text{(III-27)}$$

$$n_A = \frac{n_A + n_C}{P'/P^\circ} \exp\left[\frac{\mu_A{'} - \mu_A{'}^\circ}{RT}\right] \qquad \text{(III-28)}$$

$$n_C = \frac{n_A + n_C}{P'/P^\circ} \exp\left[\frac{\mu_C{'} - \mu_C{'}^\circ}{RT}\right] \qquad \text{(III-29)}$$

Substituting these three equations in $n_I' = n_A + n_C$ (eq III-6) yields

$$\mu_I{'}^\circ = -RT \ln[\exp(-\mu_A{'}^\circ/RT) + \exp(-\mu_C{'}^\circ/RT)] \qquad \text{(III-30)}$$

where $\mu_A{'}^\circ = \mu_A{}^\circ$ and $\mu_C{'}^\circ = \mu_C{}^\circ - \mu_B$. Of course, standard Gibbs energies of formation would be used in actual calculations, rather than standard chemical potentials. This important equation is reminiscent of statistical mechanics in that the term in brackets is a partition function, and taking derivatives yields the other standard thermodynamic properties of the isomer group. The equilibrium mole fraction of A within the pseudoisomer group is given by

$$r_A = \exp[(\mu_I{'}^\circ - \mu_A{'}^\circ)/RT] \qquad \text{(III-31)}$$

This is the Boltzmann distribution for this system. There is, of course, a similar equation for C. It can be shown[39] that the standard transformed enthalpy for the pseudoisomer group is given by

$$\Delta_f H'^\circ(\mathrm{I}) = r_A \Delta_f H'^\circ(\mathrm{A}) + r_C \Delta_f H'^\circ(\mathrm{C}) \qquad \text{(III-32)}$$

where r_A and r_C are the equilibrium mole fractions of A and C within the isomer group and $\Delta_f H'^\circ(\mathrm{A}) = \Delta_f H^\circ(\mathrm{A})$ and $\Delta_f H'^\circ(\mathrm{C}) = \Delta_f H^\circ(\mathrm{C}) - \Delta_f H^\circ(\mathrm{B})$.

Equation III-17 can be generalized to apply to a system with N' reactants (pseudoisomer groups) by writing it as follows:

$$dG' = -S\, dT + V\, dP' - (n_{Bb}RT/P_B)\, dP_B + \sum_{i=1}^{N'} \mu_i{'}\, dn_i{'} \qquad \text{(III-33)}$$

Here, P' is the sum of the partial pressures of species other than B. In this case the transformed entropy of the system is given by

$$S' = S - (n_B + n_{Bb})\bar{S}_B \qquad \text{(III-34)}$$

where n_{Bb} is the total amount of B bound in the system, and

$$n_{Bb} = \sum_{i=1}^{N'} \bar{N}_i n_i{'} \qquad \text{(III-35)}$$

where $\bar{N}_i$ is the average number of B molecules in pseudospecies i.

2. Matrix Notation and Degrees of Freedom

The general case described by fundamental eq III-33 brings up difficult questions like "What is N' for a specific system and how many components and how many independent reactions are there?" The same type of question has to be answered for systems where the partial pressure of a species is not held constant. These questions can best be answered by use of matrices.

Since atoms of elements are conserved in chemical reactions, a reaction system has[38,40,41] a conservation matrix A and a stoichiometric number matrix $\boldsymbol{\nu}$. These ways of representing the conservation of atoms of elements are equivalent, but one or the other may be more convenient in a given case. The A matrix is made up of the numbers of atoms of the elements in the various species and the coefficients of the amounts of species in any additional conservation equations. Redundant rows must be eliminated, and the number of independent rows is equal to the number of components C; thus, C is equal to the rank of the $\boldsymbol{A}$ matrix, and so the $\boldsymbol{A}$ matrix is $C \times N$, where N is the number of species. The $\boldsymbol{\nu}$ matrix is made up of the stoichiometric numbers, arranged in columns, in a set of independent chemical equations for the system. The number R of independent reactions is equal to the rank of the $\boldsymbol{\nu}$ matrix, and so it is $N \times R$. These matrices are related through

$$\boldsymbol{A\nu} = \boldsymbol{0} \text{ or } \boldsymbol{\nu}^{\mathrm{T}}\boldsymbol{A}^{\mathrm{T}} = \boldsymbol{0} \qquad \text{(III-36)}$$

where the superscript T indicates the transpose. The number N of species in the system is given by

$$N = C + R = \operatorname{rank} \boldsymbol{A} + \operatorname{rank} \boldsymbol{\nu} \qquad \text{(III-37)}$$

The stoichiometric number matrix $\boldsymbol{\nu}$ is the null space of the $\boldsymbol{A}$ matrix, and $\boldsymbol{A}^{\mathrm{T}}$ is the null space of the $\boldsymbol{\nu}^{\mathrm{T}}$ matrix. Therefore, one can be calculated from the other by use of a computer program, like *Mathematica*,[42] that does matrix operations.

Equations III-36 and III-37 can be illustrated by considering a gaseous reaction system containing CO, CO_2, H_2, H_2O, and CH_4. The conservation matrix is

$$\begin{array}{cc} & \begin{array}{ccccc} \mathrm{CO} & \mathrm{CO_2} & \mathrm{H_2} & \mathrm{H_2O} & \mathrm{CH_4} \end{array} \\ \boldsymbol{A} = \begin{array}{c} \mathrm{C} \\ \mathrm{O} \\ \mathrm{H} \end{array} & \left[\begin{array}{ccccc} 1 & 1 & 0 & 0 & 1 \\ 1 & 2 & 0 & 1 & 0 \\ 0 & 0 & 2 & 2 & 4 \end{array}\right] \end{array} \qquad \text{(III-38)}$$

Making a Gaussian reduction yields

$$\begin{array}{cc} & \begin{array}{ccccc} \mathrm{CO} & \mathrm{CO_2} & \mathrm{H_2} & \mathrm{H_2O} & \mathrm{CH_4} \end{array} \\ \boldsymbol{A} = \begin{array}{c} \mathrm{CO} \\ \mathrm{CO_2} \\ \mathrm{H_2} \end{array} & \left[\begin{array}{ccccc} 1 & 0 & 0 & -1 & 2 \\ 0 & 1 & 0 & 1 & -1 \\ 0 & 0 & 1 & 1 & 2 \end{array}\right] \end{array} \qquad \text{(III-39)}$$

Since no row is redundant, the rank of this matrix is $C = 3$, and these components can be taken as C, O, and H or CO, CO_2, and H_2. Actually there is an infinite number of choices of components because the conservation matrix can be multiplied by any 3 × 3 matrix without affecting its suitability as a conservation matrix. The last two columns indicate that H_2O and CH_4 are made up of CO, CO_2, and H_2. The null space of $\boldsymbol{A}$ is the stoichiometric number matrix $\boldsymbol{\nu}$.

$$\boldsymbol{\nu} = \begin{array}{c} \mathrm{CO} \\ \mathrm{CO_2} \\ \mathrm{H_2} \\ \mathrm{H_2O} \\ \mathrm{CH_4} \end{array} \left[\begin{array}{cc} 1 & -2 \\ -1 & 1 \\ -1 & -2 \\ 1 & 0 \\ 0 & 1 \end{array}\right] \quad \text{(III-40)}$$

This indicates that the chemical equations are

$$\mathrm{CO + H_2O = CO_2 + H_2} \quad \text{(III-41)}$$

$$\mathrm{CO_2 + CH_4 = CO + 2H_2} \quad \text{(III-42)}$$

These equations are not unique.

It is convenient to write chemical work terms with matrix notation, and this can be done in terms of amounts of species or extents of reaction.[32,38] For the Gibbs energy in a one-phase system where only PV work is involved, the fundamental equation can be written in matrix notation as follows:

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \boldsymbol{\mu}\,\mathrm{d}\boldsymbol{n} \quad \text{(III-43)}$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \boldsymbol{\mu\nu}\,\mathrm{d}\boldsymbol{\xi} \quad \text{(III-44)}$$

where $\boldsymbol{\mu}$ is the $1 \times N$ chemical potential matrix, $\boldsymbol{n}$ is the $N \times 1$ amount matrix, and $\boldsymbol{\xi}$ is the $R \times 1$ extent of reaction matrix. It is known that the fundamental equation can be written in terms of components,[6,43,44] and this can be expressed in matrix notation as follows:

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \boldsymbol{\mu}_c\boldsymbol{A}\,\mathrm{d}\boldsymbol{n} \quad \text{(III-45)}$$

where $\boldsymbol{\mu}_c$ is the $1 \times C$ chemical potential matrix for the C components. The chemical potentials of the components follow the rules of Beattie and Oppenheim[6] that is mentioned in connection with eq III-11.

When the partial pressure of reactant B is specified, the conservation matrix $\boldsymbol{A}$ is converted to the apparent conservation matrix $\boldsymbol{A}'$ by deleting the row and column for B and deleting redundant columns.[37] The $\boldsymbol{\nu}$ matrix is correspondingly changed to the $\boldsymbol{\nu}'$ matrix. The number C' of apparent components is equal to the rank of the $\boldsymbol{A}'$ matrix, and the number R' of apparent independent reactions is equal to the rank of the $\boldsymbol{\nu}'$ matrix. These matrices are related through

$$\boldsymbol{A}'\boldsymbol{\nu}' = \boldsymbol{0} \text{ or } (\boldsymbol{\nu}')^{\mathrm{T}}(\boldsymbol{A}')^{\mathrm{T}} = \boldsymbol{0} \quad \text{(III-46)}$$

The number N' of pseudospecies (reactants that are sums of species) in the system is given by

$$N' = C' + R' = \operatorname{rank} \boldsymbol{A}' + \operatorname{rank} \boldsymbol{\nu}' \quad \text{(III-47)}$$

It is convenient to be able to write the fundamental equation for the transformed Gibbs energy in matrix form.[44] When the partial pressure of species B is specified, the fundamental equation of thermodynamics for the transformed Gibbs energy (see eq III-33) can be written in matrix form as

$$\mathrm{d}G' = -S'\,\mathrm{d}T + V\,\mathrm{d}P' - (n_{\mathrm{Bb}}RT/P_{\mathrm{B}})\,\mathrm{d}P_{\mathrm{B}} + \boldsymbol{\mu}'\,\mathrm{d}\boldsymbol{n}' \quad \text{(III-48)}$$

The apparent chemical potential matrix $\boldsymbol{\mu}'$ is $1 \times N'$, and the apparent amount matrix $\boldsymbol{n}'$ is $N' \times 1$. Equation III-43 can be written in terms of the apparent extent of reaction matrix $\boldsymbol{\xi}'$, which is $R' \times 1$.

$$\mathrm{d}G' = -S'\,\mathrm{d}T + V\,\mathrm{d}P' - (n_{\mathrm{Bb}}RT/P_{\mathrm{B}})\,\mathrm{d}P_{\mathrm{B}} + \boldsymbol{\mu}'\boldsymbol{\nu}'\,\mathrm{d}\boldsymbol{\xi}' \quad \text{(III-49)}$$

This equation can also be written in terms of components as

$$\mathrm{d}G' = -S\,\mathrm{d}T + V\,\mathrm{d}P' - (n_{\mathrm{Bb}}RT/P_{\mathrm{B}})\,\mathrm{d}P_{\mathrm{B}} + \boldsymbol{\mu}'_{C'}\boldsymbol{A}'\,\mathrm{d}\boldsymbol{n}' \quad \text{(III-50)}$$

where C' is the apparent number of components. The Gibbs–Duhem equation at chemical equilibrium is

$$0 = -S'\,\mathrm{d}T + V\,\mathrm{d}P' - (\mathrm{d}\boldsymbol{\mu}_{C'})\boldsymbol{n}_{C'} \quad \text{(III-51)}$$

This equation indicates that at chemical equilibrium, there are $C' + 2$ independent intensive variables. For a one-phase system there are $C' + 1$ independent variables, and for a two-phase system there are C' independent variables since there is an additional Gibbs–Duhem equation. Thus the number F' of apparent independent degrees of freedom at specified partial pressures of one or more species *after* the specification of P_{B} is given by

$$F' = C' - p + 2 \quad \text{(III-52)}$$

where p is the number of phases, C' is the apparent number of components *after* specifying the partial pressure of B, and F' is the number of intensive degrees of freedom *after* specifying the partial pressure of B. Note that F' does not count P_{B}, but adding P_{B} gives the number of degrees of freedom $F = 3 = F' + 1$. Note that $C = C' + 1$, $R = R'$, $F = F' + 1$, and $N = N' + 1$ in this case.

Thus we have seen that the specification of the partial pressure of a species at equilibrium leads to a reconceptualization of the calculation of the equilibrium composition, new thermodynamic properties, new fundamental equations, a new Gibbs–Duhem equation, and a new phase rule, in short a whole new world of thermodynamics. When the partial pressures of one or more species are specified, attention is focused on reactants (sums of species) rather than species. The number of reactants (sum of species) N' may be considerably less than the number N of species. For example, a whole homologous series becomes a reactant when the partial pressure of ethylene is specified. The number R' of apparent independent reactions may be much smaller than the number R of independent reactions. The reason for using transformed thermodynamic properties is convenience, the same reason that G is used to state the criterion for equilibrium at specified T and P, rather than using S.

Symbols that do not involve G, S, and H could be used rather than G', S', and H'. The symbols G', S', and H' have the advantage that these transformed properties behave in a similar way to the thermodynamic properties G, S, and H. In fact, G', S', and H' for pseudospecies (sums of species) can be calculated from G, S, and H for the species. It is necessary to specify what partial pressures are held constant.

B. Biochemical Reactions

The thermodynamics of many biochemical reactions is complicated by the fact that the reactants are often weak acids and may form complex ions with metal ions that are present and may be necessary for the catalytic action. At pH values and concentrations of free metal ions where a reactant exists as an equilibrium mixture of species containing different numbers of protons and metal ions, there is a complication that has to be dealt with, and so first we consider a reaction under conditions where this is not the case. When adenosine triphosphate (ATP) is hydrolyzed at high pH in the absence of Mg^{2+}, the chemical equation is

$$ATP^{4-} + H_2O = ADP^{3-} + HPO_4^{\ 2-} + H^+ \quad \text{(III-53)}$$

which represents the element balance for all of the elements and electric charge balance.

The corresponding equilibrium constant expression is

$$K = \frac{[ADP^{3-}][HPO_4^{\ 2-}][H^+]}{[ATP^{4-}](c^\circ)^2} \quad \text{(III-54)}$$

where the brackets represent molar concentrations at equilibrium and c° is the standard state concentration (1 M). The $(c^\circ)^2$ in the denominator is required to make the equilibrium constant K dimensionless. The activity coefficients of the ions depend on the electrolyte and are usually taken to be functions of the ionic strength I, as given by the extended Debye–Hückel theory. In the laboratory, it is convenient to use an equilibrium constant K that depends on the ionic strength; thus K depends on the ionic strength as well as on T and P, and so the ionic strength must be specified. However, the ionic strength is a different kind of variable than T and P and does not appear directly in the fundamental equation; the ionic strength is like the specification that K is the equilibrium constant for the reaction in water, rather than methanol, for example.

At lower pH values and in the presence of Mg^{2+}, adenosine triphosphate exists as an equilibrium mixture of ATP^{4-}, $HATP^{3-}$, H_2ATP^{2-}, $MgATP^{2-}$, $MgHATP^-$, and Mg_2ATP. Analytical procedures for ATP yield the sum of these concentrations, which is represented by [ATP]. Similar remarks apply to ADP and inorganic phosphate P_i.

Biochemists have known for some time that apparent equilibrium constants K' can be written for biochemical reactions in terms of sums of concentrations of species. For example, the hydrolysis of adenosine triphosphate to adenosine diphosphate and inorganic phosphate at specified pH and pMg is represented by the biochemical equation

$$ATP + H_2O = ADP + P_i \quad \text{(III-55)}$$

The expression for the apparent equilibrium constant is

$$K' = \frac{[ADP][P_i]}{[ATP]c^\circ} \quad \text{(III-56)}$$

where ATP, ADP, and P_i represent sums of species and c° is the standard state concentration. K' is referred to as the apparent equilibrium constant because it is a function of pH and the free concentrations of metal ions that are bound by the reactants, as well as T, P, and ionic strength. Here we will assume that pMg is specified. When the pH and pMg are treated as independent variables, we can imagine the experiment was carried out in a reaction chamber connected with a pH reservoir through a semipermeable membrane that is permeable to hydrogen ions and a pMg reservoir through a semipermeable membrane that is permeable to magnesium ions. In this thought experiment, which is shown in Figure 3, hydrogen and magnesium are not conserved in the reaction chamber, and so a biochemical equation, like eq III-55, should not indicate that hydrogen is balanced. Another consequence of this thought experiment is that the Gibbs energy G of the material in the reaction chamber is not minimized at equilibrium. The same ideas apply to other metal ions that are bound by the reactants.

The apparent equilibrium constant K' is a function of pH and pMg as well as T and P. The dependency of K' on pH and pMg can be calculated if the acid dissociation constants and magnesium complex dissociation constants are known. There has been international agreement[45] on this nomenclature since 1976. The prime on the equilibrium constant in eq III-56 has been used for some time, but K_{obs} and K_{app} have also been used for this quantity.

When a biochemical reaction is studied in the laboratory, there is no question about the fact that the Gibbs energy G is minimized at equilibrium. If the experiment is interpreted in terms of equilibrium constants in terms of species and conservation relations in terms of species, the appropriate thermodynamic potential is G. This analysis can be made;[46] however, it requires detailed information on all of the equilibria in terms of species. On the other hand, when the analytical results at equilibrium are interpreted by use of an apparent equilibrium constant expression like eq III-56, it is not the actual experiment that is being analyzed, but the thought experiment in Figure 3. In this thought experiment, the Gibbs energy G of the system in the reaction chamber is not minimized at equilibrium because the concentrations of H^+ and Mg^{2+} are fixed. When the chemical potentials of H^+ and Mg^{2+} are specified at equilibrium as well as T and P, the thermodynamic potential that is minimized at equilibrium is the transformed Gibbs energy G' defined by the Legendre transform[47,48,49]

$$G' = G - n'(H^+)\mu(H^+) - n'(Mg^{2+})\mu(Mg^{2+}) \quad \text{(III-57)}$$

where $n'(H^+)$ is the total amount of H^+ in the system (free and bound). It is convenient to use the prime on G' to indicate that the equilibrium concentrations are specified for some species. A symbol for the transformed Gibbs energy that is an extension of Callen's recommendations is $G[\mu(H^+), \mu(Mg^{2+})]$. Equa-

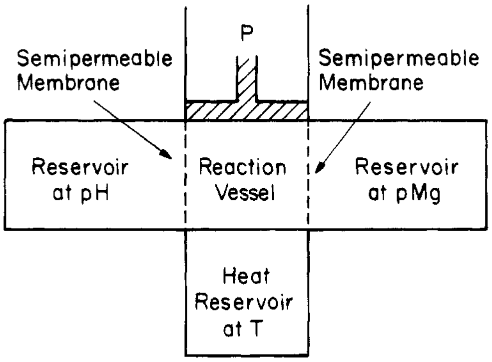

Figure 3. Reaction vessel for a biochemical reaction that is in contact with pH and pMg reservoirs through semipermeable membranes, as well as heat and pressure reservoirs.

tion III-57 involves the total amounts $n'(\mathrm{H}^+)$ and $n'(\mathrm{Mg}^{2+})$ because at chemical equilibrium only components can be used as independent variables. The amount of the hydrogen component in the reaction chamber is given by

$$n'(\mathrm{H}^+) = \sum_{i=1}^{N} N_i(\mathrm{H}^+)n_i \qquad (\text{III-58})$$

where $N_i(\mathrm{H}^+)$ is the number of hydrogen atoms in species i and n_i is the amount of i. The amount of the magnesium component in the reaction chamber is given by

$$n'(\mathrm{Mg}^{2+}) = \sum_{i=1}^{N} N_i(\mathrm{Mg}^{2+})n_i \qquad (\text{III-59})$$

where $N_i(\mathrm{Mg}^{2+})$ is the number of magnesium atoms in species i. Substituting this and $G = \sum n_i\mu_i$ into the Legendre transform yields

$$\begin{aligned} G' &= \sum n_i\mu_i - \sum N_i(\mathrm{H}^+)\mu(\mathrm{H}^+)n_i - \sum N_i(\mathrm{Mg}^{2+}) \times \mu(\mathrm{Mg}^{2+})n_i \\ &= \sum n_i[\mu_i - N_i(\mathrm{H}^+)\mu(\mathrm{H}^+) - N_i(\mathrm{Mg}^{2+})\mu(\mathrm{Mg}^{2+})] \\ &= \sum n_i\mu_i' \end{aligned} \qquad (\text{III-60})$$

where the transformed chemical potential μ_i' of species i is given by

$$\mu_i' = \mu_i - N_i(\mathrm{H}^+)\mu(\mathrm{H}^+) - N_i(\mathrm{Mg}^{2+})\mu(\mathrm{Mg}^{2+}) \qquad (\text{III-61})$$

Equation III-60 shows that the transformed Gibbs energy G' of a thermodynamic system is equal to the sum of amounts of the various species each multiplied by its transformed chemical potential μ_i', just like the Gibbs energy G is equal to the sum of amounts of the various species, each multiplied by its chemical potential μ_i. If the differential of G' in eq III-57 is taken and the fundamental equation for G is substituted, the following fundamental equation is obtained for G':

$$\mathrm{d}G' = -S\,\mathrm{d}T + V\,\mathrm{d}P - n'(\mathrm{H})\,\mathrm{d}\mu(\mathrm{H}^+) - n'(\mathrm{Mg}^{2+})\,\mathrm{d}\mu(\mathrm{Mg}^{2+}) + \sum_{i=1}^{N-2} \mu_i'\,\mathrm{d}n_i \qquad (\text{III-62})$$

Here N is the number of species.

When the effect of temperature is to be studied, it is better to use $\mathrm{pH} = -\log([\mathrm{H}^+]/c°)$ and $\mathrm{pMg} = -\log([\mathrm{Mg}^{2+}]/c°)$ as independent variables, rather than $\mu(\mathrm{H}^+)$ and $\mu(\mathrm{Mg}^{2+})$, and this change in variables (see eq III-16) leads to

$$\mathrm{d}G' = -S'\,\mathrm{d}T + V\,\mathrm{d}P + 2.303n'(\mathrm{H}^+)RT\,\mathrm{dpH} + 2.303n'(\mathrm{Mg}^{2+})RT\,\mathrm{dpMg} + \sum_{i=1}^{N-2} \mu_i'\,\mathrm{d}n_i \qquad (\text{III-63})$$

The transformed entropy S' of the system is defined by

$$S' = S - n'(\mathrm{H}^+)\bar{S}(\mathrm{H}^+) - n'(\mathrm{Mg}^{2+})\bar{S}(\mathrm{Mg}^{2+}) \qquad (\text{III-64})$$

Defining the transformed enthalpy with $H' = G' + TS'$ yields

$$H' = H - n'(\mathrm{H}^+)\bar{H}(\mathrm{H}^+) - n'(\mathrm{Mg}^{2+})\bar{H}(\mathrm{Mg}^{2+}) \qquad (\text{III-65})$$

Equation III-63 is written in terms of species, but the terms for pseudoisomers can be collected together because pseudoisomers have the same transformed chemical potential at equilibrium. This yields

$$\mathrm{d}G' = -S'\,\mathrm{d}T + V\,\mathrm{d}P + 2.303n'(\mathrm{H}^+)RT\,\mathrm{dpH} + 2.303n'(\mathrm{Mg}^{2+})RT\,\mathrm{dpMg} + \sum_{i=1}^{N'} \mu_i'\,\mathrm{d}n_i' \qquad (\text{III-66})$$

where N' is the number of reactants (sums of species) in the system and n_i' is the amount of reactant i (sum of species). This equation can be compared with eq III-33 above. Thus the natural variables for G' are T, P, pH, pMg, and n_i'.

Equation III-66 can be used to derive the expression for K' at specified T, P, pH, and pMg. The standard transformed Gibbs energy of reaction can be calculated using

$$\Delta_\mathrm{r}G'° = -RT\ln K' \qquad (\text{III-67})$$

If the standard transformed enthalpy of reaction is essentially constant in the range T_1 to T_2, it can be calculated using

$$\Delta_\mathrm{r}H'° = \frac{RT_1T_2}{(T_2 - T_1)}\ln\left(\frac{K_2'}{K_1'}\right) \qquad (\text{III-68})$$

The standard transformed enthalpy of reaction can also be determined calorimetrically, but corrections have to be made for the heat of reaction of the buffer with the H^+ and Mg^{2+} produced in the reaction.[50]

The standard transformed Gibbs energy of formation and the standard transformed enthalpies of formation of reactants at specified pH and pMg are defined by

$$\Delta_r G'^\circ = \sum \nu_i' \Delta_f G'^\circ(i) \qquad \text{(III-69)}$$

$$\Delta_r H'^\circ = \sum \nu_i' \Delta_f H'^\circ(i) \qquad \text{(III-70)}$$

where the ν_i' are the apparent stoichiometric numbers of the reactant i in a biochemical equation, like eq III-55, written in terms of reactants.

The standard transformed Gibbs energy of formation and standard transformed enthalpy of formation of a reactant at specified pH and pMg can be calculated if the thermodynamic properties are known for the species involved. These properties can be calculated for species by use of formation reactions in which the usual standard state of molecular hydrogen is replaced by hydrogen ions at the desired pH and the usual standard state for magnesium is replaced by magnesium ions at the desired pMg. When a reactant consists of several species, the next question is "Given the standard transformed thermodynamic properties of the species, what are the values of the standard transformed properties for the reactant?" This question is answered, as it was in the preceding section on gas reactions, by pointing out that this requires the same calculation as the calculation of the standard thermodynamic properties of an isomer group at equilibrium. Therefore, eqs III-30, III-31, and III-32 are used.

Table 1 shows the standard formation properties of a number of species involved in the hydrolysis of glucose 6-phosphate. The first two columns show properties of species at zero ionic strength, as in the usual thermodynamic tables. The second two columns show the transformed properties of reactants at pH 7, pMg 3, and 0.25 M ionic strength.

A chemical equation can be written for the hydrolysis of glucose 6-phosphate:

$$\mathrm{G6P}^{2-} + \mathrm{H_2O} = \text{glucose} + \mathrm{HPO_4}^{2-} \qquad \text{(III-71)}$$

The equilibrium constant for this chemical reaction can be calculated from values in Table 1:

$$K(298.15\text{ K, 1 bar}, I = 0) = \frac{[\text{glucose}][\mathrm{HPO_4}^{2-}]}{[\mathrm{G6P}^{2-}]c^\circ} = 80 \qquad \text{(III-72)}$$

The standard state concentration c° is 1 M. The biochemical equation for the hydrolysis of glucose 6-phosphate is

$$\mathrm{G6P} + \mathrm{H_2O} = \text{glucose} + \mathrm{P_i} \qquad \text{(III-73)}$$

The apparent equilibrium constant for this biochemical reaction can be calculated from values in Table 1:

$$K'(298.15\text{ K, 1 bar, pH 7, pMg 3}, I = 0.25\text{ M}) = \frac{[\text{glucose}][\mathrm{P_i}]}{[\mathrm{G6P}]c^\circ} = 108 \qquad \text{(III-74)}$$

These equilibrium constants are not very different because insignificant amounts of H^+ and Mg^{2+} are produced by this reaction at pH 7, but much larger differences are found for the hydrolysis of ATP, for example.

The standard formation properties have been calculated for the reactants in the ATP series[51] at 298.15 K, 1 bar, pH = 7, pMg = 3, and $I = 0.25$ M. Since it has not been possible to calculate the standard formation properties of any species in the ATP series, these calculations have been made with the convention that the uncharged species of adenosine has $\Delta_f G^\circ = \Delta_f H^\circ = 0$ at 298.15 K, 1 bar, and $I = 0$.

For many biochemical reactants, the acid and magnesium dissociation constants have not been measured, but their standard transformed Gibbs energies and enthalpies under specified conditions can be determined experimentally. If apparent equilibrium constants are measured for reactions of that reactant under the specified conditions, eqs III-69 and III-70 can be used directly to calculate the transformed formation properties.

The changes in binding[52,53,54] of H^+ and Mg^{2+} in a biochemical reaction at specified pH and pMg can be calculated from the changes in K' with pH and pMg at the specified pH and pMg. This is possible through Maxwell equations of eq III-62. This equation for a single reaction in terms of reactants can be written

$$(\mathrm{d}G')_{T,P} = 2.303n'(\mathrm{H^+})RT\,\mathrm{dpH} + 2.303n'(\mathrm{Mg^{2+}})RT\,\mathrm{dpMg} + \Delta_r G'\,\mathrm{d}\xi' \qquad \text{(III-75)}$$

where $\Delta_r G'$ is the reaction Gibbs energy given by

$$\Delta_r G' = \left(\frac{\partial G'}{\partial \xi'}\right)_{T,P,\mathrm{pH},\mathrm{pMg}} = \Delta_r G'^\circ + RT \ln Q' \qquad \text{(III-76)}$$

where Q' is the apparent reaction quotient written in terms of sums of concentrations of reactants, each divided by c°. The Maxwell equation for the first and third terms is

$$2.303RT\left(\frac{\partial n'(\mathrm{H^+})}{\partial \xi'}\right)_{T,P,\mathrm{pH},\mathrm{pMg}} = \left(\frac{\partial \Delta_r G'}{\partial \mathrm{pH}}\right)_{T,P,\mathrm{pMg},\xi'} \qquad \text{(III-77)}$$

The derivative on the left side is the change in binding of hydrogen ions $\Delta_r N(H^+)$ in the biochemical reaction:

$$\Delta_r N(\mathrm{H^+}) = -\left(\frac{\partial \log K'}{\partial \mathrm{pH}}\right)_{T,P,\mathrm{pMg}} \qquad \text{(III-78)}$$

where

$$\Delta_r N(\mathrm{H^+}) = \sum \nu_i' \bar{N}_i(\mathrm{H^+}) \qquad \text{(III-79)}$$

There is, of course, a similar equation for the change in binding of magnesium ions. Taking the cross derivatives yields

$$\left(\frac{\partial \Delta_r N(\mathrm{H^+})}{\partial \mathrm{pMg}}\right)_{T,P,\mathrm{pH}} = \left(\frac{\partial \Delta_r N(\mathrm{Mg^{2+}})}{\partial \mathrm{pH}}\right)_{T,P,\mathrm{pMg}} \qquad \text{(III-80)}$$

This expresses the linkage between the change in binding of H^+ and Mg^{2+} in the biochemical reaction.

The comments about the conservation matrix $\boldsymbol{A}$, the stoichiometric number matrix $\boldsymbol{\nu}$, apparent conservation matrix $\boldsymbol{A}'$, and apparent stoichiometric

Table 1. Standard Formation Properties and Standard Transformed Formation Properties at 298.15 K and 1 Bar

	$\Delta_f H^\circ$ (kJ mol^{-1}) $I = 0$	$\Delta_f G^\circ$ (kJ mol^{-1}) $I = 0$	$\Delta_f H'^\circ$ (kJ mol^{-1}) pH 7, pMg 3, $I = 0.25$ M	$\Delta_f G'^\circ$ (kJ mol^{-1}) pH 7, pMg 3, $I = 0.25$ M
H^+	0	0		
Mg^{2+}	−467.00	−455.30		
H_2O	−285.83	−237.19	−286.65	−155.66
$HPO_4{}^{2-}$	−1299.00	−1096.10	−1299.12	−1059.55
$H_2PO_4{}^-$	−1302.60	−1137.30		
$MgHPO_4$	−1753.80	−1566.87		
Glucose	−1262.19	−915.90	−1267.11	−426.70
$G6P^{2-}$	−2276.44	−1763.94	−2279.09	−1318.99
$HG6P^-$	−2274.64	−1800.59		
MgG6P	−2732.04	−2234.08		

matrix ν' in section III.A.2 apply to biochemical reactions at specified pH and pMg as well as gas reactions at specified partial pressures of reactants.[55] The apparent number F' of degrees of freedom after specifying pH and pMg are given by equation III-52: $F' = C' - p + 2$. Chemical equations satisfy element and change conservation equations, but generally do not satisfy additional independent conservation equations. Biochemical equations at a specified pH satisfy conservation equations for elements other than hydrogen, but they often satisfy additional independent conservation equations because of the coupling of reactions through the enzymatic mechanism.[56]

In making equilibrium calculations on systems of biochemical reactions, like glycolysis, for example, it is sometimes convenient to make calculations at steady-state concentrations of ATP and ADP because these reactants are provided by other series of biochemical reactions. This can be done by making a further Legendre transform to make [ATP] and [ADP] at specified pH natural variables of a further transformed Gibbs energy.[57] This is referred to as a level 3 calculation, where level 1 is in terms of species and level 2 is in terms of reactants at specified pH.

The Panel on Biochemical Thermodynamics of the IUBMB-IUPAC Joint Commission on Biochemical Nomenclature has made *Recommendations for Nomenclature and Tables in Biochemical Thermodynamics*.[58]

C. Ligand Binding and Denaturation of Macromolecules

Wyman[59−61] used Legendre transforms in the thermodynamic treatment of the binding of ligands by hemoglobin and other macromolecules. This is not the place to review that large field of activity, but it is necessary to comment on the relation of Wyman's treatment to that discussed in this section. As pointed out by Schellman,[62] Wyman's binding potential is a transformed Gibbs energy that has as independent variables the intensive properties of ligands (concentrations or activities), rather than the usual extensive composition variables, which characterize the Gibbs energy. Schellman goes on to show that the equations used by Wyman can be obtained by defining a transformed Gibbs energy by subtracting $n_i\mu_i$ for all species except for the macromolecule and then dividing by the amount of the macromolecule to obtain an apparent chemical potential which contains the binding potential defined by Wyman. He points out the strong connection between the binding potential and the grand partition function. Schellman[63,64] has shown that these methods can also be applied to the thermodynamic analysis of denaturation of proteins by solute. A solution containing water (species 1), macromolecules (species 2), and small molecule solutes (species 3 and higher) was treated by use of a transformed Gibbs energy $G(1,2)$ defined by

$$G(1,2) = G - \sum_{j>2} \mu_j n_j \qquad \text{(III-81)}$$

The differential of $G(1,2)$ at constant T and P is

$$\mathrm{d}G(1,2) = \mu_1\,\mathrm{d}n_1 + \mu_2\,\mathrm{d}n_2 - \sum n_j\,\mathrm{d}\mu_j \qquad \text{(III-82)}$$

This approach had been used by Schellman[65] to investigate the interaction of two solution components, A and B, with the macromolecule and with each other. Three cases were considered: (1) A and B are ligands that bind stoichiometrically to the macromolecule, as in Wyman's binding polynomial analysis. (2) A and B are two substances (at high concentrations) that interact selectively with the macromolecule. (3) A is a species that binds stoichiometrically to the macromolecule, while B is a component at high concentration that interacts weakly with the macromolecule.

IV. Transforms for Gravitational and Centrifugal Work

A. Gravitational Work

1. The Fundamental Equation for the Gibbs Energy

When gravitational work is involved, the fundamental equation for G can be written[66,67]

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \sum_{i=1}^{N} \mu_i{}'\,\mathrm{d}n_i + \psi\,\mathrm{d}m \qquad \text{(IV-1)}$$

where ψ is the gravitational potential (gh, where g is the acceleration of gravity and h is the height above the surface of the earth) and m is the mass of the system. A prime has been put on μ_i because we are considering work in addition to PV work and want to save μ_i for later use in eq IV-3. The gravitational work term can be written $\psi\sum M_i\,\mathrm{d}n_i$, where M_i is the molar mass of species i, so that

$$dG = -S\,dT + V\,dP + \sum_{i=1}^{N}(\mu_i' + \psi M_i)\,dn_i \quad \text{(IV-2)}$$

Since the natural variables are T, P, and n_i, this equation can be written

$$dG = -S\,dT + V\,dP + \sum_{i=1}^{N}\mu_i\,dn_i \quad \text{(IV-3)}$$

so that the familiar form of the fundamental equation is retained with

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \mu_i \quad \text{(IV-4)}$$

where $j \neq i$ and $G = \sum n_i\mu_i$. G can be used to express the criterion of equilibrium at specified T and P; $(dG)_{T,P} \leq 0$.

According to eqs IV-2 and IV-3, the chemical potential μ_i involves two contributions when gravitational work is included:

$$\mu_i = \mu_i' + \psi M_i \quad \text{(IV-5)}$$

Riedi[68] generalizes on this equation by pointing out that the chemical potential of a species in a system with potential differences may be written as the sum of an internal contribution (in this case μ_i') and an external contribution (in this case, ψM_i). As he states, since μ_i must be constant throughout the system, it follows that the internal contribution (μ_i') is a function of the potential. Gibbs[1] referred to μ_i' as an intrinsic potential. In this case the chemical potential μ_i of a species is independent of its height above the surface of the earth. This fact is used below to derive the barometric formula for an ideal gas in an isothermal atmosphere. Equation IV-3 can be integrated at constant T, P, and composition to obtain

$$G = \sum n_i\mu_i \quad \text{(IV-6)}$$

The expression for the entropy of the system can be obtained by use of

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,n_i} = \sum n_i\bar{S}_i = \sum n_i\bar{S}_i' \quad \text{(IV-7)}$$

where the second form comes from taking the derivative of the right side of eq IV-5. The expression for the enthalpy of the system can be obtained by use of the Gibbs–Helmholtz equation

$$H = -T^2\left[\frac{\partial(G/T)}{\partial T}\right]_{P,n_i} = \sum n_i\bar{H}_i = \sum n_i(\bar{H}_i' + \psi M_i) \quad \text{(IV-8)}$$

where the second form comes from using the right side of eq IV-5. Thus $\bar{H}_i$'s is a function of the gravitational potential, but $\bar{S}_i'$ is not.

2. The Fundamental Equation for the Transformed Gibbs Energy

In order to learn more about the nature of μ_i', let us make the following Legendre transform in order to interchange the roles of ψ and m in the fundamental equation of thermodynamics.

$$G' = G - \psi m \quad \text{(IV-9)}$$

Taking the differential of the transformed Gibbs energy yields

$$dG' = dG - \psi\,dm - m\,d\psi \quad \text{(IV-10)}$$

Substituting eq IV-1 yields

$$dG' = -S\,dT + V\,dP + \sum_{i=1}^{N}\mu_i'\,dn_i - m\,d\psi \quad \text{(IV-11)}$$

Thus the natural variables of the transformed Gibbs energy G' are T, P, n_i, and ψ. G' can be used to express the criterion of equilibrium at specified T, P, and ψ; $(dG')_{T,P,\psi} \leq 0$. Equation IV-11 shows that

$$\left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_j,\psi} = \mu_i' \quad \text{(IV-12)}$$

where $j \neq i$, and so μ_i' is a function of ψ. Thus μ_i' is the transformed chemical potential of i at specified T, P, ψ, and composition. Equation IV-12 shows exactly what μ_i' is. Equation IV-11 can be integrated at constant T, P, ψ, and composition to obtain

$$G' = \sum n_i\mu_i' \quad \text{(IV-13)}$$

Another way to derive this equation, which perhaps gives more insight, is to substitute $G = \sum n_i\mu_i$ and $m = \sum n_iM_i$ into the Legendre transform (eq IV-9) to obtain

$$G' = \sum n_i\mu_i - \psi\sum n_iM_i = \sum n_i(\mu_i - \psi M_i) = \sum n_i\mu_i' \quad \text{(IV-14)}$$

As in the case where the chemical potential of H^+ was specified, the Legendre transform leads immediately to an expression for a transformed chemical potential of a species (see eq III-60).

It is instructive to use eq IV-11 to calculate the thermodynamic properties S, V, μ', and m for a one-component ideal gas system in a gravitational field. The Gibbs energy of the system is given by

$$G = n[\mu^\circ + RT\ln(P/P^\circ)] \quad \text{(IV-15)}$$

where P° is the standard state pressure. The transformed Gibbs energy is given by eq IV-9, which becomes

$$G' = n[\mu^\circ + RT\ln(P/P^\circ) - \psi M] \quad \text{(IV-16)}$$

We can take the partial derivatives of G' according to eq IV-11 to obtain the values of S, V, μ', and m:

$$(\partial G'/\partial T)_{P,n,\psi} = -S = n[-\bar{S}^\circ + R\ln(P/P^\circ)] \quad \text{(IV-17)}$$

$$(\partial G'/\partial P)_{T,n,\psi} = V = nRT/P \quad \text{(IV-18)}$$

$$(\partial G'/\partial n)_{T,P,\psi} = \mu' = \mu - \psi M \quad \text{(IV-19)}$$

$$(\partial G'/\partial \psi)_{T,P,n} = m = nM \qquad \text{(IV-20)}$$

The second form on the right in these four equations was determined by taking the indicated derivative of eq IV-16. The transformed enthalpy is defined by

$$H' = G' + TS \qquad \text{(IV-21)}$$

Substituting $n\mu' = n\mu - m\psi$ for G' and $n[\bar{S}^\circ - R\ln(P/P^\circ)]$ for S yields

$$H' = n\mu - m\psi + nT\bar{S} = H - m\psi \qquad \text{(IV-22)}$$

where $H = G + TS$. Thus the gravitational potential affects the transformed Gibbs energy G' and transformed enthalpy H', but does not affect S and V of an ideal gas.

3. Derivation of the Barometric Formula

In the earth's gravitational field, the gravitational potential is proportional to the height h above the surface for distances above the surface that are small in comparison with the radius of the earth. For an ideal gas the eq IV-5 can be written

$$\mu_i = \mu_i'^\circ + RT\ln(P_i/P^\circ) + hgM_i \qquad \text{(IV-23)}$$

Since μ_i is independent of h and μ_i° is a constant, P_i decreases as h increases. Taking the derivative of eq IV-23 yields

$$\left(\frac{\partial \mu_i}{\partial h}\right)_T = \frac{RT}{P_i}\left(\frac{\partial P_i}{\partial h}\right)_T + gM_i = 0 \qquad \text{(IV-24)}$$

and

$$\frac{\mathrm{d}P_i}{P_i} = -\frac{gM_i}{RT}\,\mathrm{d}h \qquad \text{(IV-25)}$$

Integrating yields

$$P_i = P_i(h{=}0)\exp\left(-\frac{gM_ih}{RT}\right) \qquad \text{(IV-26)}$$

The exponential drop in pressure with height in an idealized atmosphere is illustrated in Figure 4.

For a chemical reaction at a specified gravitational potential ψ, the equilibrium criterion is $(\mathrm{d}G')_{T,P,\psi} = 0$. Equation IV-11 indicates that

$$\sum \mu_i'\nu_i = \sum(\mu_i - \psi M_i)\nu_i = \sum \mu_i\nu_i = 0 \qquad \text{(IV-27)}$$

since $\sum M_i\nu_i = 0$. Thus we obtain the familiar equation for chemical equilibrium; the effect of the gravitational potential ψ on the products of a reaction is balanced by the effect of ψ on the reactants, so that there is no effect of a gravitational field on the equilibrium constant.

B. Centrifugal Work

The potential ψ in a centrifugal field is given by[66]

$$\psi = -{}^1/_2\omega^2r^2 \qquad \text{(IV-28)}$$

where ω is the angular velocity and r is the distance from the axis of rotation. Since the treatments of gravitational and centrifugal fields in terms of the potential are the same, there is no need to repeat the equations of the preceding section. The equation for sedimentation equilibrium in a centrifuge is well known.[69]

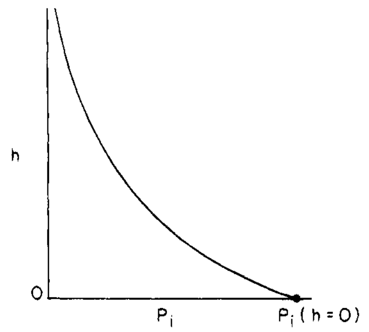

Figure 4. Partial pressure of ideal gas i in the earth's atmosphere assuming the temperature and acceleration of gravity are independent of height.

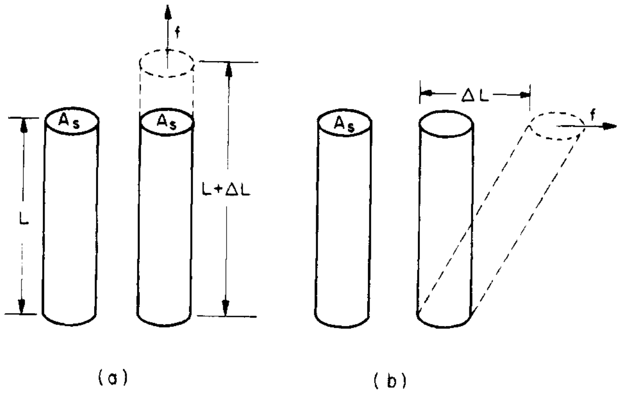

Figure 5. Two ways in which a solid might change it dimensions under the action of force f: (a) tensile stress resulting in elongation by ΔL, and (b) shearing stress resulting in displacement ΔL. The cross sectional area is represented by A_s.

V. Transforms for Mechanical Work

A. Work of Tensile Stress

1. Without Coupling to the Chemical Work[41,70,71]

When a solid is compressed uniformly, the work of $-P\,\mathrm{d}V$ is included in eq I-1. But there are two other ways a solid might change its dimensions under the action of a force, as shown in Figure 5. When a solid is subjected to a tensile stress, it is elongated by ΔL, the strain, as shown in a. (Normal stress σ is defined as force per unit area, but here we will simply represent the differential work with $f\,\mathrm{d}L$.) When a solid is subjected to a shearing stress, it deforms like a deck of playing cards, as shown in b. Here we will be interested only in the elastic region so that the changes are reversible. Actually the deformation of a solid is much more complicated and requires the use of tensors, and only two simple examples are considered here.

When an isotropic solid is under tension in one direction, it is convenient to use the internal energy U and the Helmholtz energy A, rather than the enthalpy H and Gibbs energy G, because PV work is not involved to an appreciable extent. Thus the fundamental equations for U and A can be written

$$\mathrm{d}U = T\,\mathrm{d}S + f\,\mathrm{d}L \qquad \text{(V-1)}$$

and

$$\mathrm{d}A = -S\,\mathrm{d}T + f\,\mathrm{d}L \qquad \text{(V-2)}$$

where f is the tension force and L is the length of the solid in the direction it is being stretched. Note that the force is given by the derivative of A with respect to length at constant temperature:

$$f = (\partial A/\partial L)_T \qquad \text{(V-3)}$$

Equation V-1 can be used to derive the following thermodynamic equation of state for the solid:

$$(\partial U/\partial L)_T = T(\partial S/\partial L)_T + f \qquad \text{(V-4)}$$

The following Maxwell equation can be obtained from eq V-2:

$$(\partial f/\partial T)_L = -(\partial S/\partial L)_T \qquad \text{(V-5)}$$

This is important because it provides an experimental means for evaluating the rate of change of the entropy with respect to length at constant temperature. Substituting this relation in eq V-4 yields

$$(\partial U/\partial L)_T = f - T(\partial f/\partial T)_L \qquad \text{(V-6)}$$

Now all of the terms on the right-hand side are measurable. For rubber, it is found that the force at constant length is proportional to the temperature so that $f = T\theta(L)$, where $\Theta(L)$ is a function of L that has to be measured experimentally. Inserting this relation in eq V-6 shows that

$$(\partial U/\partial L)_T = f - f = 0 \qquad \text{(V-7)}$$

Thus the internal energy of the rubber does not change with extension. Equation V-5 shows that the force exerted by the stretched rubber is given by

$$f = -T(\partial S/\partial L)_T \qquad \text{(V-8)}$$

Thus to the extent that the force is proportional to T, the tension is an entropy effect. The chains between attachment points in the rubber have many configurations with very nearly the same energy. This model can be treated by statistical mechanics.[5]

In order to obtain a thermodynamic potential with f as a natural variable, the following Legendre transform can be used:

$$A' = A - fL \qquad \text{(V-9)}$$

Taking the differential of A' and substituting eq V-2 yields

$$\mathrm{d}A' = -S\,\mathrm{d}T - L\,\mathrm{d}f \qquad \text{(V-10)}$$

Note that this is a complete Legendre transform. It yields the Maxwell equation

$$(\partial S/\partial f)_T = (\partial L/\partial T)_f \qquad \text{(V-11)}$$

2. With Coupling to Chemical Work

The contraction of muscle and the rotation of flagella are examples of the conversion of chemical energy into mechanical work. The fundamental equation for the Gibbs energy for a system involving a single chemical reaction and mechanical work is

$$\mathrm{d}G_{\mathrm{sys}} = -S\,\mathrm{d}T + V\,\mathrm{d}P + \Delta_{\mathrm{r}}G\,\mathrm{d}\xi - f\,\mathrm{d}L \qquad \text{(V-12)}$$

where $\Delta_{\mathrm{r}}G$ is the reaction Gibbs energy at specified concentrations of the reactant species and ξ is the extent of reaction. A negative sign is used in the work term so that the force can be taken as positive; thus $\mathrm{d}L < 0$ corresponds to mechanical work done on the system. If the chemical reaction is coupled with the decrease in length, as it is in muscle, $\mathrm{d}L = -k\,\mathrm{d}\xi$, where k is a constant. In this case eq V-12 becomes

$$\mathrm{d}G_{\mathrm{sys}} = -S\,\mathrm{d}T + V\,\mathrm{d}P + (\Delta_{\mathrm{r}}G + kf)\,\mathrm{d}\xi \qquad \text{(V-13)}$$

so that the natural variables of G are T, P, and ξ. At constant T, P, and concentrations of the reactant species,

$$(\partial G_{\mathrm{sys}}/\partial\xi)_{T,P} = \Delta_{\mathrm{r}}G_{\mathrm{sys}} = \Delta_{\mathrm{r}}G + kf \qquad \text{(V-14)}$$

At equilibrium this quantity is equal to zero, and so that the force at equilibrium is given by

$$f = -\Delta_{\mathrm{r}}G/k \qquad \text{(V-15)}$$

where $\Delta_{\mathrm{r}}G$ is negative. In biochemical examples, the pH is generally constant so that a Legendre transform should be used to make pH an independent variable, as discussed in section III.B. A more detailed model is needed to discuss muscle contraction, but this simple example indicates how the force might be related to the thermodynamics of the reaction.

B. Work of Shear Stress

The shear stress τ is defined as force per unit area, but the force vector lies in the plane of the area rather than perpendicular to it (see Figure 5b). The shear strain is usually taken to be $\Delta L/L$, but we will simply use the expression $\tau A_{\mathrm{s}}\Delta L$ for the work. When PV work is not involved to an appreciable extent, the fundamental equations for U and A can be written

$$\mathrm{d}U = T\,\mathrm{d}S + \mu\,\mathrm{d}n + \tau A_{\mathrm{s}}\,\mathrm{d}L \qquad \text{(V-16)}$$

and

$$\mathrm{d}A = -S\,\mathrm{d}T + \mu\,\mathrm{d}n + \tau A_{\mathrm{s}}\,\mathrm{d}L \qquad \text{(V-17)}$$

It is convenient to use a Legendre transformed Helmholtz energy defined by

$$A' = A - n\mu - \tau A_{\mathrm{s}}L \qquad \text{(V-18)}$$

Taking the differential of A' and substituting eq V-17

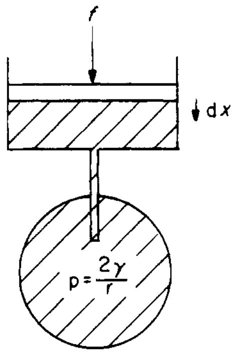

Figure 6. Expansion of a drop of liquid in the absence of a gravitational field. Surface tension causes a pressure in the drop that is inversely proportional to the radius of curvature r.

yields

$$dA' = -S\,dT - n\,d\mu - \tau L\,dA_s - A_s L\,d\tau \quad \text{(V-19)}$$

where τL is a kind of surface tension. This approach can even be used to study liquids when the distances between the parallel planes are only a few molecular diameters, because stick–slip motion occurs.[72,73]

VI. Transforms for Surface Work

A. One-Component Systems

The fundamental equation for the Gibbs energy of a one-component system involving surface work[66,67,74] is a special case of eq I-3. However, for certain geometries of the system,[75] dA_s may be proportional to dn. Figure 6 shows a spherical drop in the absence of a gravitational field. The work of expanding the surface area against surface tension can be measured by the force on a piston and the distance traveled.

$$dw = f\,dx = P\,dV = P4\pi r^2\,dr \quad \text{(VI-1)}$$

since $V = (4/3)\pi r^3$. The differential work is also given by $dw = \gamma dA_s$. Equating two expressions for dw with dA_s replaced with $A_s = 4\pi r^2$ and $dA_s = 8\pi r\,dr$ yields the following expression for the pressure in the drop:

$$P = 2\gamma/r \quad \text{(VI-2)}$$

The differential of the volume of the sphere is $dV = 4\pi^2\,dr$ and the differential of the surface area is $dA_s = 8\pi r\,dr$, and so

$$dA_s = (2/r)\,dV = (2/r)\bar{V}\,dn \quad \text{(VI-3)}$$

where $\bar{V}$ is the molar volume of the pure liquid and the differential volume can be written as $dV = \bar{V}\,dn$. Thus, the differential of the surface area is proportional to the differential of the amount of substance in the sphere. The fundamental equation for G can be written as

$$dG = -S\,dT + V\,dP + \mu'\,dn + (2\gamma\bar{V}/r)\,dn \quad \text{(VI-4)}$$

where a prime is put on the μ' so that μ can be saved for its usual meaning. Since the derivative of the Gibbs energy with respect to amount of liquid at specified T and P is the chemical potential μ of the liquid:

$$\mu = \mu' + 2\gamma\bar{V}/r \quad \text{(VI-5)}$$

The chemical potential μ of the liquid is equal to the chemical potential of the vapor with which it is in equilibrium.

Equation VI-5 can be used to derive the Kelvin equation for the vapor pressure of the sphere of liquid by assuming that the vapor (with pressure p) is an ideal gas so that

$$\mu = \mu^\circ + RT\ln(p/P^\circ) \quad \text{(VI-6)}$$

where P° is the standard state pressure (1 bar). At equilibrium, the chemical potential μ is the same for the liquid and the vapor in equilibrium with it. Therefore, the vapor pressure will be higher than that over a planar surface because the liquid is squeezed by the surface tension. Setting the chemical potential in eq VI-5 equal to the chemical potential in eq VI-6 yields

$$\mu' + 2\gamma\bar{V}/r = \mu^\circ + RT\ln(p/P^\circ) \quad \text{(VI-7)}$$

As $r \to \infty$, $\mu' \to \mu^\circ + RT\ln(p_0/P^\circ)$, where p_0 is the vapor pressure of a planar surface. Thus the transformed chemical potential μ' is given by

$$\mu' = \mu^\circ + RT\ln(p_0/P^\circ) \quad \text{(VI-8)}$$

Substituting this equation in eq VI-5 yields the Kelvin equation

$$\ln(p/p_0) = (2\gamma\bar{V}/rRT) \quad \text{(VI-9)}$$

which gives the vapor pressure p of the spherical mass of liquid as a function of its radius of curvature r. (The Kelvin equation can be applied to a bubble in a liquid by changing the sign of the radius of curvature.)

The integration of eq VI-4 yields

$$G = n(\mu' + 2\gamma\bar{V}/r) = n\mu \quad \text{(VI-10)}$$

Thus the Gibbs energy of the liquid in a spherical drop is made up of two contributions.

A Legendre transform can be used to find the definition of the transformed chemical potential μ'. The obvious Legendre transform is $G' = G - \gamma A_s$, but this is not satisfactory because γ is not an independent variable. Since we want to interchange the extensive variable with the intensive variable in the $(2\gamma\bar{V}/r)\,dn$ term of eq VI-4, the following Legendre transform is used:

$$G' = G - 2\gamma\bar{V}n/r \quad \text{(VI-11)}$$

Taking the differential of G' and substituting eq VI-4 yields

$$dG' = -S\,dT + V\,dP + (2\gamma\bar{V}n/r^2)\,dr + \mu'\,dn \quad \text{(VI-12)}$$

Thus the natural variables of G' are T, P, r, and n. Equation VI-12 shows that the transformed chemical potential μ' of the liquid is defined by

$$(\partial G'/\partial n)_{T,P,r} = \mu' \qquad \text{(VI-13)}$$

Note that dividing eq VI-11 by n yields VI-5, as expected.

The integration of eq VI-12 at constant T, P, and r yields

$$G' = n\mu' = n(\mu - 2\gamma\bar{V}/r) \qquad \text{(VI-14)}$$

where the second form has been obtained by substituting eq VI-5.

B. Multicomponent Systems

Multicomponent systems can be treated in terms of surface excess properties (defined by using the Gibbs surface and designated by a superscript σ) or in terms of thermodynamic properties of an interfacial layer (designated by a superscript s) when there is a physical model of the interfacial layer.[74,76] In both of these cases the IUPAC Recommendations by Everett[76] use the concept that a Legendre transform of the internal energy by PV or γA_s yields an enthalpy. This practice is not consistent with the recommendation in connection with eqs I-2 to I-4 that these definitions always be adhered to. In discussing surface excess properties, which are designated by a superscript σ, Everett writes

$$H^{\sigma} = U^{\sigma} - \gamma A_s \qquad \text{(VI-15)}$$

According to the conventions advocated here, this Legendre transform would be considered to be the definition of a transformed surface excess internal energy.

$$U^{\sigma\prime} = U^{\sigma} - \gamma A_s \qquad \text{(VI-16)}$$

Since $V^{\sigma} = 0$, this distinction may not appear to be important, but for the properties of an interfacial layer, $V^s \neq 0$, and so the distinction is important. For example, Everett defines the following three interfacial enthalpies:

$$\mathscr{H}^s = U^s + PV^s \qquad \text{(VI-17)}$$

$$\hat{H}^s = U^s - \gamma A^s \qquad \text{(VI-18)}$$

$$H^s = U^s + PV^s - \gamma A^s \qquad \text{(VI-19)}$$

with the names interfacial PV–enthalpy, interfacial γA–enthalpy, and interfacial $PV\gamma A$–enthalpy, respectively. According to the recommendations given here, these quantities would be referred to as the interfacial enthalpy H^s, transformed interfacial internal energy $U^{s\prime}$, and transformed interfacial enthalpy$H^{s\prime}$. The same types of comments apply to the surface excess Gibbs energies.

Lee, Klingler, and McConnell[77] have recently studied electric field induced concentration gradients in lipid monolayers. They found it convenient to use a chemical potential for dihydroxycholesterol in the monolayers that is linear in the surface pressure and has an additional contribution due to the applied electric field.

VII. Transforms for Work of Electrical Transport

A. The Fundamental Equations

For a multiphase system involving electrical work,[66,78,79] eq I-12 is

$$dG = -S\,dT + V\,dP + \sum_{i=1}^{N}\mu_i'\,dn_i + \sum_{i=1}^{N}\phi_i\,dQ_i \qquad \text{(VII-1)}$$

where each species contributes a term for each phase in which it exists. If each species exists in each phase, N is the number of species times the number of phases. The electric potential ϕ_i of an ion depends upon the phase. A prime has been put on the chemical potential because the charge Q_i contributed by an ion is not independent of its amount n_i, and we want to save the symbol μ_i for its usual meaning. The charge contributed by an ion to a phase is given by $Q_i = Fz_in_i$, where F is the Faraday constant and z_i is the charge on the ion. Substituting this expression in the fundamental equation yields

$$dG = -S\,dT + V\,dP + \sum_{i=1}^{N}(\mu_i' + Fz_i\phi_i)\,dn_i = -S\,dT + V\,dP + \sum_{i=1}^{N}\mu_i\,dn_i \qquad \text{(VII-2)}$$

where the chemical potential μ_i of a species is given by

$$\mu_i = \mu_i' + z_iF\phi_i \qquad \text{(VII-3)}$$

Thus the natural variables of G for the system are T, P, and n_i. The chemical potential of species i in a particular phase is defined by the second form of eq VII-2, which shows that

$$(\partial G/\partial n_i)_{T,P,n_j} = \mu_i \qquad \text{(VII-4)}$$

where $j \neq i$. Here G is the Gibbs energy of the whole system, but n_i is the amount of species i in a particular phase. Since the Gibbs energy of the system is equal to the sum of the Gibbs energies of the phases, G can also be interpreted as the Gibbs energy of the phase containing species i in amount n_i. We can interpret eq VII-4 as the change in the Gibbs energy when a small but macroscopic amount of an ion is added to a particular phase of such a large system that we do not have to worry about the change in the electric potential of the phase due to this tiny addition of ions. This derivative is essentially $G(N + 1) - G(N)$, where N is the number of particles and is a very large number. The reason for electroneutrality is that small net charges lead to large electric potentials, which cannot ordinarily be maintained in real systems. Nevertheless, phases can have different electric charges, and necessarily do when they have different electric potentials.

The usual integrated form of eq VII-2 applies: $G = \sum n_i\mu_i$. G can be used to express the criterion of spontaneous change at specified T and P; $(\mathrm{d}G)_{T,P} \leq 0$. Equation VII-2 can be used to show that at equilibrium the chemical potential of a species is the same in each phase.

The two contributions to the chemical potential of an ion in a phase are sometimes referred to as the internal (μ_i') and external ($Fz_i\phi_i$) contributions.[78] Gibbs[1] referred to μ_i' as an intrinsic potential. Equation VII-17, given later, shows that μ_i' is a transformed chemical potential. When a system is at equilibrium, the chemical potential μ_i of a species is independent of where it is in the system, no matter how many phases there are, whether they are solid, liquid, or gas, and what their electric potentials are. After eq VI-5 we noted that the chemical potential of a species is the same in two phases at different pressures. This is also true of the solvent in an osmotic pressure experiment. Since the chemical potential of an ion is independent of the electric potential of the phase at equilibrium, eq VII-3 shows that the transformed chemical potential μ_i' depends on ϕ_i according to

$$\mu_i' = \mu_i - z_iF\phi_i \tag{VII-5}$$

where μ_i is constant throughout a multiphase system at equilibrium.

Electrochemists[80,81,82] write eq VII-3 as

$$\tilde{\mu}_i = \mu_i + z_iF\phi_i \tag{VII-6}$$

where $\tilde{\mu}_i$ is referred to as the electrochemical potential and μ_i is referred to as the chemical potential. From the standpoint of eqs VII-1 to VII-4 there are two problems with this equation. The first problem is that the derivative defining $\tilde{\mu}_i$ is exactly that used to define the chemical potential μ_i (cf., eq VII-4), and so two symbols and two names are currently being used for this derivative. The second problem is that the chemical potential μ_i in eq VII-6 is not the usual chemical potential and has different properties; it is defined by a different partial derivative, as shown below in eq VII-17. The usual chemical potential μ_i has the same value throughout the phases of a multiphase system at equilibrium, and so we would expect that μ_i in eq VII-6 to have this property, but it does not. The property μ_i in eq VII-6 has different values in different phases that are in equilibrium but have different electric potentials.

The activity of a species is defined by

$$\mu_i = \mu_i^\circ + RT\ln a_i \tag{VII-7}$$

Therefore, eq VII-5 for the transformed chemical potential can be written

$$\mu_i' = \mu_i^\circ + RT\ln a_i - z_iF\phi_i = \mu_i'^\circ + RT\ln a_i \tag{VII-8}$$

where the second form is obtained by taking

$$\mu_i'^\circ = \mu_i^\circ - z_iF\phi_i \tag{VII-9}$$

Thus the standard transformed chemical potential $\mu_i'^\circ$ of an ion is equal to the standard chemical potential μ_i° adjusted to potential ϕ_i. Since the standard transformed chemical potential $\mu_i'^\circ$ depends on the electric potential, the electric potential has to be part of the specification of the standard state for ion i when dealing with the transformed chemical potential. Substituting the second form of eq VII-8 into eq VII-3 for the chemical potential of a species yields

$$\mu_i = \mu_i'^\circ + RT\ln a_i + z_iF\phi_i \tag{VII-10}$$

This equation can be compared with the following equation

$$\tilde{\mu}_i = \mu_i^\circ + RT\ln a_i + z_iF\phi_i \tag{VII-11}$$

that is currently used by electrochemists. In a recent book in electrochemistry, Rieger[83] uses $\mu_i = \mu_i^\circ + RT\ln a_i + z_iF\phi_i$. Equation VII-10 has the advantage that μ_i is the same in the various phases of a multiphase system, even if they have different electric potentials, and the symbol $\mu_i'^\circ$ reminds us that the standard transformed chemical potential depends on the electric potential.

The other thermodynamic properties of an ion in a phase at electric potential ϕ_i can be calculated from eq VII-10:

$$\overline{S}_i = -\left(\frac{\partial\mu_i}{\partial T}\right)_{P,n_i} = \overline{S}_i'^\circ - R\ln a_i - RT\left(\frac{\partial\ln a_i}{\partial T}\right)_{P,n_i} = \overline{S}_i' \tag{VII-12}$$

$$\overline{H}_i = -T^2\left[\frac{\partial(\mu_i/T)}{\partial T}\right]_{P,n_i} = \overline{H}_i'^\circ - RT^2\left(\frac{\partial\ln a_i}{\partial T}\right)_{P,n_i} + z_iF\phi_i = \overline{H}_i' + z_iF\phi_i \tag{VII-13}$$

Thus the molar entropy of an ion is not affected by the electric potential, but the molar enthalpy is. The standard transformed molar entropy is equal to the standard molar entropy because the electric potential has no effect on it; $\overline{S}_i'^\circ = \overline{S}_i^\circ$. The standard transformed molar enthalpy is given by $\overline{H}_i'^\circ = \overline{H}_i^\circ - z_iF\phi_i$.

In order to learn more about the nature of μ_i', we use the following Legendre transform to make the electric potentials of the phases natural variables:

$$G' = G - \sum_{i=1}^{N}\phi_iQ_i = G - F\sum_{i=1}^{N}\phi_iz_in_i \tag{VII-14}$$

Since n_i and ϕ_i are both variables, the differential of G' is

$$\mathrm{d}G' = \mathrm{d}G - F\sum_{i=1}^{N}z_i\phi_i\,\mathrm{d}n_i - F\sum_{i=1}^{N}z_in_i\,\mathrm{d}\phi_i \tag{VII-15}$$

Substituting the expression for $\mathrm{d}G$ from the first form of eq VII-2 yields

$$\mathrm{d}G' = -S\,\mathrm{d}T + V\,\mathrm{d}P + \sum_{i=1}^{N}\mu_i'\,\mathrm{d}n_i - F\sum_{i=1}^{N}z_in_i\,\mathrm{d}\phi_i \tag{VII-16}$$

The natural variables of the transformed Gibbs energy G' are T, P, n_i, and ϕ_i. G' can be used to express the criterion of equilibrium at specified T, P, and ϕ; $(\mathrm{d}G')_{T,P,\phi_i} \le 0$. According to eq VII-16,

$$(\partial G'/\partial n_i)_{T,P,n_j,\phi_i} = \mu_i' \qquad \text{(VII-17)}$$

where $j \ne i$. This emphasizes again that μ_i' is a function of T, P, ϕ_i, and composition. Since μ_i' is the partial derivative of the transformed Gibbs energy G', it is called the transformed chemical potential of i at specified T, P, ϕ_i, and amounts of other species in the phase. Equation VII-16 can be integrated at constant T, P, ϕ_i, and composition to obtain

$$G' = \sum n_i \mu_i' \qquad \text{(VII-18)}$$

This equation can also be derived by substituting $G = \sum n_i\mu_i$ in the second form of eq VII-14.

The transformed molar entropies and enthalpies of an ion in a phase with an electric potential can be calculated by starting with eq VII-5.

$$\overline{S}_i' = \left(\frac{\partial \mu_i'}{\partial T}\right)_{P,n_i,\phi_i} = \overline{S}_i^\circ - R\ln a_i - RT\left(\frac{\partial \ln a_i}{\partial T}\right)_{P,n_i} = \overline{S}_i \qquad \text{(VII-19)}$$

The transformed molar entropy is not affected by the electric potential and is equal to the molar entropy, as previously shown in eq VII-12. The transformed molar enthalpy is defined by

$$\overline{H}_i' = -T^2\left[\frac{\partial(\mu_i'/T)}{\partial T}\right]_{P,n_i} = \overline{H}_i^\circ - RT^2\left(\frac{\partial \ln a_i}{\partial T}\right)_{P,n_i} - z_iF\phi_i = \overline{H}_i - z_iF\phi_i \qquad \text{(VII-20)}$$

Thus, the transformed molar enthalpy of an ion depends on the electric potential in the same way as the transformed chemical potential.

B. Thermodynamic Properties and Chemical Reactions

Since $G = \sum n_i\mu_i$, the expressions for the entropy S and enthalpy H for an open system involving electrical work can be obtained in the usual way. Equation VII-2 can be used to derive the equilibrium constant expression for a chemical reaction involving ions in different phases. Since $\sum \nu_i z_i = 0$, there is no effect of the electric potential on the equilibrium constant of a reaction that occurs in a single phase. But when some of the reactants and products in a chemical reaction are ions that are in a phase at a different electric potential, the equilibrium constant K for the reaction will be a function of the difference in potentials.

An issue that has not been discussed much in this review is the form of the phase rule when work in addition to PV work is involved. Rock[84] has called attention to the fact that the phase rule for an electrochemical cell is $F = C - p + 3$.

C. Derivation of the Equation for the Membrane Potential

When there is equilibrium between phases α and β that involve the same solvent but are separated by a membrane and have different electric potentials, the fundamental equation for G for the two-phase system is

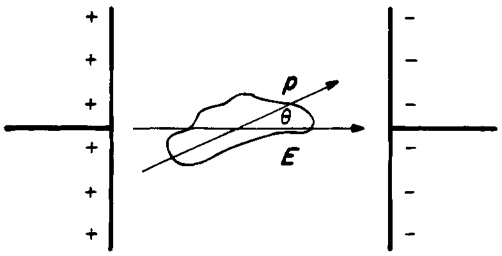

Figure 7. A sample with electric dipole moment $\boldsymbol{p}$ is shown at an angle θ with respect to the electric field. The energy of the dipole in the field is $\boldsymbol{E}\cdot\mathrm{d}\boldsymbol{p} = Ep\cos\theta$.

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \sum \mu_i(\alpha)\,\mathrm{d}n_i(\alpha) + \sum \mu_i(\beta)\,\mathrm{d}n_i(\beta) \qquad \text{(VII-21)}$$

If the membrane is permeable to ion i, then it can be shown that at equilibrium

$$\mu_i(\alpha) = \mu_i(\beta) \qquad \text{(VII-22)}$$

Substituting eq VII-10 yields

$$\mu_i'^\circ(\alpha) + RT\ln a_i(\alpha) + z_iF\phi(\alpha) = \mu_i'^\circ(\beta) + RT\ln a_i(\beta) + z_iF\phi(\beta) \qquad \text{(VII-23)}$$

When the solvent is the same on both sides of the membrane, the standard transformed chemical potentials of i in the two phases are equal because they are defined at the same electric potential. In this case, eq VII-23 can be rearranged to

$$\phi(\beta) - \phi(\alpha) = -\frac{RT}{z_iF}\ln\frac{a_i(\beta)}{a_i(\alpha)} \qquad \text{(VII-24)}$$

VIII. Transforms for Work of Electric Polarization

The thermodynamics of electrical polarization has been treated authoritatively in a number of places.[66,85,86] The energy due to the electric polarization of a body in an electric field is given by the dot product $\boldsymbol{E}\cdot\mathrm{d}\boldsymbol{p} = Ep\cos\theta$, where $\boldsymbol{E}$ is the vector electric field strength, $\boldsymbol{p}$ is the vector total dipole moment of the system, E is the magnitude of the electric field, p is the magnitude of the total dipole moment, and θ is the angle between the vectors (Figure 7). Thus the fundamental equation for the internal energy U of a closed system without chemical reaction is

$$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V + \boldsymbol{E}\cdot\mathrm{d}\boldsymbol{p} \qquad \text{(VIII-1)}$$

Integration of this equation yields

$$U = TS - PV + \boldsymbol{E}\cdot\boldsymbol{p} \qquad \text{(VIII-2)}$$

For an isotropic system, the differential of polarization work can be written $E\,\mathrm{d}p$.

In statistical mechanics it is more convenient to take the electric field strength as a natural variable, and this corresponds with making the Legendre transform

$$U' = U - \boldsymbol{E}\cdot\boldsymbol{p} \qquad \text{(VIII-3)}$$

This yields the following fundamental equation for the transformed internal energy.

$$dU' = T\,dS - P\,dV - \boldsymbol{p}\cdot d\boldsymbol{E} \qquad \text{(VIII-4)}$$

The difference between U and U' is simply $\boldsymbol{E}\cdot\boldsymbol{p}$, and for some purposes this is not a significant difference, since the absolute value of U is unknown. The integration of eq VIII-4 at a constant electric field strength yields

$$U' = TS - PV \qquad \text{(VIII-5)}$$

It is of interest to consider polarizable systems involving elongation work, but negligible PV work. The fundamental equation for U for such a system is

$$dU = T\,dS + f\,dL + \boldsymbol{E}\cdot d\boldsymbol{p} \qquad \text{(VIII-6)}$$

As usual the natural variables are all extensive. In discussions of thermoelectric, pyroelectric, and piezoelectric effects, it is advantageous to use a fundamental equation with intensive variables as natural variables. It is therefore convenient to use the transformed Gibbs energy defined by

$$G' = G - fL - \boldsymbol{E}\cdot\boldsymbol{p} = 0 \qquad \text{(VIII-7)}$$

This is actually a complete Legendre transform, and so the result of taking the differential of G' and substituting eq VIII-6 is the Gibbs–Duhem equation:

$$0 = -S\,dT + V\,dP - L\,df - \boldsymbol{p}\cdot d\boldsymbol{E}$$
$$\text{or } 0 = -S\,dT + V\,dP - L\,df - p\,dE \qquad \text{(VIII-8)}$$

where the last form applies to an isotropic system. This equation yields three Maxwell equations:[86]

thermoelastic

$$(\partial S/\partial f)_{E,T} = (\partial L/\partial T)_{f,E} \qquad \text{(VIII-9)}$$

pyroelectric

$$(\partial S/\partial E)_{T,f} = (\partial p/\partial T)_{f,E} \qquad \text{(VIII-10)}$$

piezoelectric

$$(\partial L/\partial E)_{T,f} = (\partial p/\partial f)_{T,E} \qquad \text{(VIII-11)}$$

Piezoelectricity is electricity or electric polarity due to pressure on a solid. Pyroelectricity is the electric polarization produced by a change in temperature. Thermoelasticity is the change in length due to temperature in an electric field. These closely related phenomena are a good example of the usefulness of Legendre transforms to obtain Maxwell equations with derivatives with respect to intensive variables and with the other intensive variables held constant.

Another Maxwell equation of the Gibbs–Duhem equation can be used[12,13] to treat electrostriction, namely $(\partial V/\partial E)_{T,P}$, where E is the magnitude of the electric field strength.

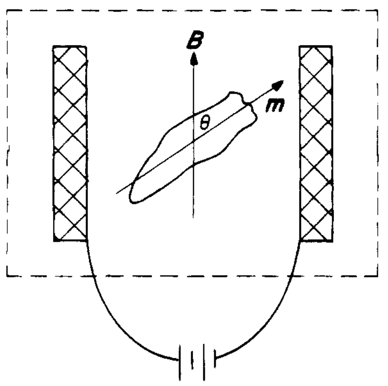

Figure 8. A sample with a magnetic dipole moment $\boldsymbol{m}$ is shown at an angle θ to the magnetic field of a solenoid. The energy of the magnetic dipole in the magnetic field is given by $\boldsymbol{B}\cdot\boldsymbol{m} = Bm\cos\theta$.

IX. Transforms for Work of Magnetic Polarization

Magnetic work is discussed authoritatively several places,[66,86–90] and so it is not necessary to go into all of the details here. The energy due to the magnetic polarization of a body in a magnetic field is given by the dot product $\boldsymbol{B}\cdot\boldsymbol{m} = Bm\cos\theta$, where $\boldsymbol{B}$ is the magnetic flux density (magnetic field strength), $\boldsymbol{m}$ is magnetic dipole moment (the total magnetic moment of the system), B is the magnitude of the magnetic field strength, m is the magnitude of the total magnetic moment of the system, and θ is the angle between the vectors (Figure 8). We will exclude ferromagnetic substances and substances exhibiting hysteresis effects from our considerations here. Thus, the fundamental equation for U can be written

$$dU = T dS + \boldsymbol{B}\cdot d\boldsymbol{m} \qquad \text{(IX-1)}$$

when PV work is ignored. For an isotropic sample, the work term can be written $B\,dm$, where B and m are the magnitudes of the vector quantities:

$$dU = T\,dS + B\,dm \qquad \text{(IX-2)}$$

In making statistical mechanical calculations[5,17] it is more convenient to use the magnetic field strength $\boldsymbol{B}$ as an independent variable. This can be done by making the Legendre transform

$$U' = U - \boldsymbol{B}\cdot\boldsymbol{m} \qquad \text{(IX-3)}$$

to obtain

$$dU' = T\,dS - \boldsymbol{m}\cdot d\boldsymbol{B} \text{ or } T\,dS - m\,dB \qquad \text{(IX-4)}$$

where the last form is for an isotropic system.

In order to treat adiabatic demagnetization, it is advantageous to also have temperature and magnetic field strength as intensive variables, and so for a closed system that does not involve PV work or chemical reaction, a transformed Gibbs energy is defined by

$$G' = G - Bm \qquad \text{(IX-5)}$$

This is a complete Legendre transform, and it yields the following Gibbs–Duhem equation:

$$0 = -S\,\mathrm{d}T - m\,\mathrm{d}B \tag{IX-6}$$

This yields the Maxwell equation

$$(\partial S/\partial B)_T = (\partial m/\partial T)_B \tag{IX-7}$$

The effect of a magnetic field on a chemical reaction producing a paramagnetic species from a diamagnetic species is small and readily calculated.

X. Discussion

There is another Legendre transform of the internal energy that was not discussed above, and that is a Legendre transform to bring in the velocity v of the system. A thermodynamic system may be moving with respect to some coordinate system. This was not discussed above because we are not interested in having the chemical properties of a system dependent on its velocity. However, this Legendre transform clarifies the significance of the internal energy. The energy E of a system can be considered to be made up of its internal energy U and its kinetic energy E_k.

$$E = U + E_k = U + (v^2/2)\sum n_i M_i \tag{X-1}$$

The differential of the energy is

$$\mathrm{d}E = \mathrm{d}U + (v^2/2)\sum M_i\,\mathrm{d}n_i + v\,\mathrm{d}v\sum n_i M_i \tag{X-2}$$

Substituting the expression for $\mathrm{d}U$ for a system involving chemical work yields

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V + \sum(\mu_i + v^2M_i/2)\mathrm{d}n_i + v\,\mathrm{d}v\sum n_i M_i \tag{X-3}$$

At constant velocity the last term disappears, but we are not interested in a chemical potential that is a function of the velocity.

Legendre transforms are important because they can be used to define thermodynamic potentials that have intensive variables as natural variables. In general, intensive variables are easier to control in the laboratory than extensive variables. The natural variables of the internal energy are all extensive variables, but Legendre transforms can be used to define thermodynamic potentials with one or more natural variables that are intensive. Any combination of extensive and intensive variables can be used, with each natural variable coming from a different conjugate pair. When a thermodynamic potential of a system can be determined as a function of its natural variables, all of the thermodynamic properties of the system can be calculated by taking partial derivatives. A thermodynamic potential can be used to express the criterion for spontaneous change under the condition that its natural variables are held constant. Since there are so many thermodynamic potentials, actually an infinite number when chemical potentials of species are used as natural variables, it is necessary to be able to give them symbols that indicate their natural variables. Callen[10] has shown how to do this by using $U[P_0,...,P_s]$, where P_0, ..., P_s represent the intensive variables that have been introduced by Legendre transforms. Since many additional thermodynamic potentials that are like H, A, and G can be defined by Legendre transforms, Callen's nomenclature can be extended to utilize H, A, and G with an indication in brackets of the additional intensive variables that have been converted to natural variables by the use of a Legendre transform. In calculations using a particular set of natural variables, this nomenclature is clumsy, and so it is convenient to indicate the transformed thermodynamic properties with primes. For example U', H', A', and G' can be used to represent transformed internal energies, transformed enthalpies, transformed Helmholtz energies, and transformed Gibbs energies; when this is done it is important to show in the context which intensive variables have been introduced as natural variables.

Legendre transforms are also useful in irreversible thermodynamics.[91]

Since the structure of thermodynamics is mathematical, certain practices that are found in the literature should be avoided. Since H, A, and G are defined by well-known Legendre transforms, these definitions should always be followed. The thermodynamic potentials U, H, A, and G can have extensive natural variables arising from non-PV work, but when intensive natural variables arising from non-PV work are introduced, the symbols U, H, A, and G should not be used. In order to emphasize the natural variables for a thermodynamic potential, it is convenient to simply indicate these variables in parentheses. In representing partial derivatives of thermodynamic potentials, only natural variables should be used as subscripts.

The concept that the chemical potential μ_i of a species is the same in all phases of a system at equilibrium is so important that it should not be lost by using μ_i for a different thermodynamic property, as it is currently in electrochemistry. It is confusing that in electrochemistry, the symbol μ_i and the term chemical potential are used for a property that depends on the electric potential of the phase, so that μ_i is not uniform throughout a system with phases at different electric potentials.

Whenever a non-PV work term is proportional to the amount of a species, the use of a Legendre transform leads to a transformed chemical potential. Examples, include

$$\mu_i' = \mu_i - N_i(\mathrm{H}^+)\mu(\mathrm{H}^+) - N_i(\mathrm{Mg}^{2+})\mu(\mathrm{Mg}^{2+}) \tag{III-61}$$

$$\mu_i' = \mu_i - \psi M_i \tag{IV-5}$$

$$\mu_i' = \mu_i - z_i F\phi_i \tag{VII-5}$$

These equations show how the transformed chemical potentials change with $\mu(\mathrm{H}^+)$ and $\mu(\mathrm{Mg}^{2+})$, gravitational potential ψ, and electric potential ϕ_i, since μ_i is constant throughout a system.

Wyman[92] has discussed the fact that the Legendre transforms applicable to any thermodynamic potential form a group. This is indicated by the fact that any number of separate transformations, each involving a single variable, are equivalent to a single transformation. Also two successive applications of the same transformation involving the same set of variables restores the initial thermodynamic potential to itself. Since the same result is obtained for all possible orders of the transformations, the group is Abelian.

Legendre transforms are used in thermodynamics to define thermodynamic potentials with intensive variables as natural variables. In statistical mechanics these various thermodynamic potentials are calculated by using different ensembles. Thus making Legendre transforms in thermodynamics has its counterpart in statistical mechanics in devising new ensembles. The thermodynamic potentials defined by use of Legendre transforms are represented by symbols and names, and the corresponding partition functions of statistical mechanics are represented by symbols and names. There are at least nine kinds of work that may be involved and each involves an intensive variable that can be introduced as a natural variable of a transformed thermodynamic potential. These intensive variables can be introduced in various combinations, and so there is a large number of thermodynamic potentials and corresponding partition functions. In fact the number of possible thermodynamic potentials and partition functions is infinite since chemical potentials of species can be specified. In statistical mechanics the symbols Ω, Q, and Δ are widely used for the microcanonical partition function, canonical ensemble partition function, and isothermal–isobaric partition function, respectively. Therefore, Ω', Q', and Δ' could be used for the ensembles that yield S', A', and G', respectively. Various Greek letters have been used for some of these, but symbols like $Q[\mu_1]$ and $\Delta[\gamma]$ are recommended here.

In writing this article, I have tried to follow certain principles, and I recommend them to others:

(1) The definitions $H = U + PV$, $A = U - TS$, and $G = U + PV - TS$ should not be altered.

(2) The fundamental equations for U, H, A, and G may contain terms for additional kinds of work where the differential quantities for these additional kinds of work are extensive variables. Thus the extensive variables in non-PV work are natural variables of U, H, A, and G, if they are independent of other natural variables.

(3) The chemical potential of species i is defined by

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j,X_i} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j,X_i} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j,X_i} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j,X_i} \qquad \text{(X-4)}$$

in a nonreaction system. Here X_i represents all of the independent extensive variables in non-PV and nonchemical work involved. It is important to retain μ_i for this purpose because μ_i is the same throughout a multiphase system at equilibrium, even if the phases are different states of matter, have different pressures, or different electric potentials. When a system involves chemical reactions at equilibrium, the n_i in the derivatives is replaced by the amount $n_{\mathrm{C}i}$ of component i and the n_j in the subscript is replaced with $n_{\mathrm{C}j}$. Even when chemical reactions are at equilibrium, the chemical potentials in eq X-4 are chemical potentials of species.

(4) In order to introduce the intensive variables of non-PV work as natural variables, it is necessary to define thermodynamic potentials in addition to U, H, A, and G with Legendre transforms. These additional thermodynamic potentials have intensive properties for non-PV work as natural variables. Legendre transformed thermodynamic potentials can be represented by U', H', A', and G', but it is necessary to specify the intensive variables that have been introduced. Examples are G[pH,pMg], $G[\phi]$, $A[f]$, $G[r]$, and $U[\boldsymbol{E}]$. In a given situation where it is clear from the context what intensive variables have been introduced by Legendre transforms, U', H', A', and G' are used to indicate transformed thermodynamic potentials, and it is not necessary to use the notation with brackets.

(5) The transformed chemical potential of species i is defined by

$$\mu_i' = \left(\frac{\partial U'}{\partial n_i}\right)_{S,V,n_j,X_i,P_j} = \left(\frac{\partial H'}{\partial n_i}\right)_{S,P,n_j,X_i,P_j} = \left(\frac{\partial A'}{\partial n_i}\right)_{T,V,n_j,X_i,P_j} = \left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_j,X_i,P_j} \qquad \text{(X-5)}$$

where the P_j represents intensive variables that have been introduced by Legendre transforms. The j is used to indicate that P_j is not in the conjugate pair with extensive variable X_i. If chemical reactions are at equilibrium, amounts of apparent components have to be used to express amounts, rather than amounts of species. However, the transformed chemical potentials of apparent components are the transformed chemical potentials of reactants (sums of species).

(6) Subscripts of partial derivatives are always natural variables. It is important to be sure that natural variables are independent. For a given system, the choice of natural variables may not be unique, but the number is.

XI. Nomenclature

Note: When primes are used on thermodynamic potentials, it is important to indicate in the context the intensive variables that have to be specified. This also applies when primes are used on equilibrium constants, amounts, or numbers like the number of components, degrees of freedom, and stoichiometric numbers. SI units are indicated in parentheses.

a_i	activity of species i (dimensionless)
A	Helmholtz energy (J)
A'	transformed Helmholtz energy (J)
A_s	surface area (m^2)
$\mathbf{A}$	conservation matrix ($C \times N$) (dimensionless)
$\mathbf{A}'$	apparent conservation matrix ($C' \times N'$) (dimensionless)
$\boldsymbol{B}$	magnetic flux density (magnetic field strength) (T)
B	magnitude of the magnetic flux density (magnetic field strength) (T)
C	number of components ($N - R$) (dimensionless)

C'	number of apparent components (pseudocomponents) ($N' - R'$) (dimensionless)
c°	standard-state concentration (mol L^{-1})
E	energy (J)
E_k	kinetic energy (J)
$\mathbf{E}$	electric field strength (V m^{-1})
E	magnitude of the electric field strength (V m^{-1})
f	force (N)
F	Faraday (96 485 C mol^{-1})
F	degrees of freedom (dimensionless)
F'	apparent degrees of freedom (dimensionless)
g	acceleration of gravity (m s^{-2})
G	Gibbs energy (J)
G'	transformed Gibbs energy (J)
$\Delta_r G^\circ$	standard Gibbs energy of reaction (J mol^{-1})
$\Delta_r G'^\circ$	standard transformed Gibbs energy of reaction at a specified concentration of a species (J mol^{-1})
$\Delta_r G'$	transformed Gibbs energy of reaction at a specified concentration of a species (J mol^{-1})
h	height above the surface of the earth (m)
H	enthalpy (J)
H'	transformed enthalpy (J)
$\overline{H}_i$	molar enthalpy of i (J mol^{-1})
$\overline{H}_i'$	molar transformed enthalpy of i (J mol^{-1})
$\Delta_r H^\circ$	standard enthalpy of reaction (J mol^{-1})
$\Delta_r H'^\circ$	standard transformed enthalpy of reaction at a specified concentration of a species (J mol^{-1})
$\Delta_f H_i^\circ$	standard enthalpy of formation of species i (J mol^{-1})
$\Delta_f H_i'^\circ$	standard transformed enthalpy of formation of i at a specified concentration of a species (J mol^{-1})
I	ionic strength (mol L^{-1})
K	equilibrium constant (dimensionless)
K'	apparent equilibrium constant (dimensionless)
L	elongation (m)
m	mass (kg)
$\mathbf{m}$	magnetic moment of the system (J T^{-1})
m	magnitude of the magnetic moment of the system (J T^{-1})
M_i	molar mass of i (kg mol^{-1})
n_i	amount of species i (mol)
$\mathbf{n}$	amount matrix ($N \times 1$) (mol)
n_i'	amount of reactant i (sum of species) (mol)
n_{Ci}	amount of component i (mol)
n_{Bb}	amount of B bound in the system (mol)
N	number of species when a single phase is involved and number of species in different phases for a multiphase system (dimensionless)
N'	number of reactants (pseudospecies) (dimensionless)
$N_i(H^+)$	number of hydrogen atoms in a molecule of i (dimensionless)
$N_i(Mg^{2+})$	number of magnesium atoms in a molecule of i (dimensionless)
$\bar{N}_i(H^+)$	average number of hydrogen atoms bound by a molecule of i (dimensionless)
$\Delta_r N(H^+)$	change in the binding of H^+ in a biochemical reaction (dimensionless)
$\Delta_r N(Mg^{2+})$	change in the binding of Mg^{2+} in a biochemical reaction (dimensionless)
P	pressure (bar)
P_i	partial pressure of i (bar)
P°	standard state pressure (1 bar)
P'	partial pressure of species other than the one with a specified pressure (bar)
P_k	intensive variable in Callen's nomenclature (varies)
$\mathbf{p}$	dipole moment of the system (C m)
p	magnitude of the dipole moment of the system (C m)
p	number of phases (dimensionless)
pH	$-\log([H^+]/c^\circ)$ (dimensionless)
pMg	$-\log([M^{2+}]/c^\circ)$ (dimensionless)
Q_i	electric charge contributed to a phase by species i (C)
Q'	reaction quotient at specified T, P, pH, pMg, and I (dimensionless)
r	distance from the axis of rotation (m)
r_i	equilibrium mole fraction of i within an isomer group or pseudoisomer group (dimensionless)
R	gas constant (8.314 51 J K^{-1} mol^{-1})
R	number of independent reactions (dimensionless)
R'	number of independent biochemical reactions in a system (dimensionless)
S	entropy (J K^{-1})
$\overline{S}_i$	molar entropy of i (J K^{-1} mol^{-1})
$\overline{S}_i'$	molar apparent entropy of i (J K^{-1} mol^{-1})
S'	transformed entropy (J K^{-1})
T	temperature (K)
U	internal energy (J)
U'	transformed internal energy (J)
$U[P_i]$	Callen's nomenclature for the transformed internal energy that has intensive variable P_i as a natural variable (J)
V	volume (m^3)
$\bar{V}$	molar volume (m^3 mol^{-1})
v	velocity (m s^{-1})
X_k	extensive variable in Callen's nomenclature (varies)
z_i	number of protonic charges on ion i (dimensionless)
γ	surface tension (N m^{-1})
μ_i	chemical potential of species i (J mol^{-1}); in electrochemistry this symbol and name are used for the property defined in eq VII-17 rather than eq VII-4 (kJ mol^{-1})
μ_i'	transformed chemical potential of reactant i (J mol^{-1})
$\boldsymbol{\mu}$	chemical potential matrix ($1 \times N$) (J mol^{-1})
$\boldsymbol{\mu}'$	transformed chemical potential matrix ($1 \times N'$) (J mol^{-1})
$\boldsymbol{\mu}_C$	component chemical potential matrix ($1 \times C$) (J mol^{-1})
$\boldsymbol{\mu}'_{C'}$	transformed component chemical potential matrix ($1 \times C'$) (J mol^{-1})
$\tilde{\mu}_i$	electrochemical potential of i defined by eq VII-6 (same definition as μ_i in eq VII-4) (J mol^{-1})
ν_i	stoichiometric number of species i (dimensionless)
ν_i'	stoichiometric number of reactant (sum of species) i (dimensionless)
$\boldsymbol{\nu}$	stoichiometric number matrix ($N \times R$) (dimensionless)
$\boldsymbol{\nu}'$	apparent stoichiometric number matrix ($N' \times R'$) (dimensionless)
ξ	extent of reaction (dimensionless)
$\boldsymbol{\xi}$	extent of reaction matrix ($R \times 1$) (dimensionless)
ξ'	apparent extent of reaction (dimensionless)
$\boldsymbol{\xi}'$	apparent extent of reaction matrix ($R' \times 1$) (dimensionless)
τ	shear stress (N m^{-2})
ϕ_i	electric potential of the phase containing species i (V, J C^{-1})

ψ	gravitational potential (J kg^{-1})
ω	angular velocity (s^{-1})

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