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USE OF LEGENDRE TRANSFORMS IN CHEMICAL THERMODYNAMICS

(IUPAC Technical Report)

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Use of Legendre transforms in chemical thermodynamics

(IUPAC Technical Report)

Abstract: The fundamental equation of thermodynamics for the internal energy U may include terms for various types of work and involves only differentials of extensive variables. The fundamental equation for U yields intensive variables as partial derivatives of the internal energy with respect to other extensive properties. In addition to the terms from the combined first and second laws for a system involving PV work, the fundamental equation for the internal energy may involve terms for chemical work, gravitational work, work of electric transport, elongation work, surface work, work of electric and magnetic polarization, and other kinds of work. Fundamental equations for other thermodynamic potentials can be obtained by use of Legendre transforms that define these other thermodynamic potentials in terms of U minus conjugate pairs of intensive and extensive variables involved in one or more work terms. The independent variables represented by differentials in a fundamental equation are referred to as natural variables. The natural variables of a thermodynamic potential are important because if a thermodynamic potential can be determined as a function of its natural variables, all of the thermodynamic properties of the system can be obtained by taking partial derivatives of the thermodynamic potential with respect to the natural variables. The natural variables are also important because they are held constant in the criterion for spontaneous change and equilibrium based on that thermodynamic potential. By use of Legendre transforms any desired set of natural variables can be obtained. The enthalpy H , Helmholtz energy A , and Gibbs energy G are defined by Legendre transforms that introduce P , T , and P and T together as natural variables, respectively. Further Legendre transforms can be used to introduce the chemical potential of any species, the gravitational potential, the electric potentials of phases, surface tension, force of elongation, electric field strength, magnetic field strength, and other intensive variables as natural variables. The large number of transformed thermodynamic potentials that can be defined raises serious nomenclature problems. Some of the transforms of the internal energy can also be regarded as transforms of H , A , or G . Since transforms of U , H , A , and G are useful, they can be referred to as the transformed internal energy U' , transformed enthalpy H' , transformed Helmholtz energy A' , and transformed Gibbs energy G' in a context where it is clear what additional intensive natural variables have been introduced. The chemical potential μ_i of a species is an especially important intensive property because its value is uniform throughout a multiphase system at equilibrium even though the phases may be different states of matter or be at different pressures, gravitational potentials, or electric potentials. When the chemical potential of a species is held constant, a Legendre transform can be used to define a transformed Gibbs energy, which is minimized at equilibrium at a specified chemical potential of that species. For example, transformed chemical potentials are useful in biochemistry because it is convenient to use pH as an independent variable. Recommendations are made to clarify the use of transformed thermodynamic potentials of systems and transformed chemical potentials of species.

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1. FUNDAMENTAL EQUATIONS OF THERMODYNAMICS FOR SYSTEMS WITHOUT CHEMICAL REACTIONS

Thermodynamic properties such as the internal energy U , entropy S , temperature T , pressure P , and volume V behave like mathematical functions, and many relations between thermodynamic properties can be obtained by simply using the operations of calculus. As various types of work in addition to PV work are included, the number of thermodynamic properties is considerably expanded. Furthermore, Legendre transforms can be used to define thermodynamic potentials in addition to U and S . This is done to make it convenient to use certain intensive variables. Thermodynamic potentials are extensive properties that, like the potential energy in mechanics, give information about the most stable state of the system. When terms for non- PV work are introduced, the number of possible thermodynamic potentials increases exponentially, and this increases difficulties with nomenclature and terminology. This Technical Report has been written to promote discussion of these problems and agreements on their solution.

It is highly desirable that there be the widest possible general agreement about these basic matters because they affect nomenclature and terminology in various subfields of chemical thermodynamics. If these subfields were sufficiently isolated, they could develop independent nomenclature and terminology, but the subfields of thermodynamics are not isolated. Experiments often involve more than one type of work other than PV work. Research on chemical equilibria may involve surfaces or phases at different electric potentials. Electrochemistry may involve surfaces and chemical equilibria.

Biochemical applications may involve the coupling of reactions and mechanical work or the coupling of reactions with the transport of ions between phases at different electric potentials.

From a mathematical point of view, there is a great deal in common between the thermodynamic treatments of various types of work starting with the fundamental equations of thermodynamics. Thermodynamics involves a network of inter-related equations, and so the nomenclature in any one equation affects the nomenclature in many other equations. Different subfields of thermodynamics have different needs and different traditions, but this report deals with the basic nomenclature and terminology that underlies the treatment of all types of work in chemical thermodynamics.

Thermodynamics is such a large field that it is not possible to cover everything here. The interesting phenomena of critical regions are not discussed. Many future developments in nomenclature are to be expected. The emphasis of these recommendations is on the fundamental equations of thermodynamics and the introduction of intensive variables with Legendre transforms.

1.1 One-phase systems with N species

The differential of the internal energy U of an open one-phase system involving only PV work and changes in amounts of species is given by the fundamental equation [1].

$$dU = TdS - PdV + \sum_{i=1}^N \mu_i dn_i \quad (1.1-1)$$

where N is the number of species, μ_i is the chemical potential of species i , and n_i is the amount of species i . This equation shows that the thermodynamic properties of the system behave like mathematical functions and can be differentiated and integrated. The variables on the right-hand side of a fundamental equation occur as conjugate pairs. The internal energy can be considered to be a function of S , V , and $\{n_i\}$, where $\{n_i\}$ is the set of amounts of species, and calculus yields the following relation

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,\{n_i\}} dS + \left(\frac{\partial U}{\partial V}\right)_{S,\{n_i\}} dV + \sum_{i=1}^N \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} dn_i \quad (1.1-2)$$

where $j \neq i$. (Note that this convention is used throughout this report.) Comparison of eqs. 1.1-1 and 1.1-2 shows that

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,\{n_i\}} \quad (1.1-3)$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,\{n_i\}} \quad (1.1-4)$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} \quad (1.1-5)$$

The variables in the differentials on the right-hand side of the fundamental equation have a special significance and are referred to as natural variables [2–12]. For the system under consideration, the natural variables of U are S , V , and $\{n_i\}$. The natural variables of a thermodynamic potential are important because when a thermodynamic potential can be determined as a function of its natural variables, all of the thermodynamic properties of the system can be calculated, as illustrated by eqs. 1.1-3 to 1.1-5. All of the thermodynamic properties can be calculated if U is determined as a function of S , V , and $\{n_i\}$, but not if U is determined as a function of T , P , and $\{n_i\}$, or other set of $N + 2$ independent variables. The natural variables are also important because they are used in the criterion for spontaneous change and equilibrium based on a particular thermodynamic potential. The criterion for equilibrium

for a one-phase system without chemical reactions is $(dU)_{S,V,\{n_i\}} \leq 0$, which means that at constant S , V , and $\{n_i\}$, U can only decrease and is at a minimum at equilibrium. The natural variables of U are all extensive. As terms for additional types of work are added to eq. 1.1-1, they should each involve the differential of an extensive property (see Section 1.3).

Equation 1.1-1 can be integrated at constant values of the intensive properties to obtain

$$U = TS - PV + \sum_{i=1}^N \mu_i n_i \quad (1.1-6)$$

Alternatively, this equation can be viewed as a consequence of Euler's theorem. A function $f(x_1, x_2, \dots, x_N)$ is said to be homogeneous of degree n if

$$f(kx_1, kx_2, \dots, kx_N) = k^n f(x_1, x_2, \dots, x_N) \quad (1.1-7)$$

where k is a constant. For such a function, Euler's theorem states that

$$nf(x_1, x_2, \dots, x_N) = \sum_{i=1}^N x_i \frac{\partial f}{\partial x_i} \quad (1.1-8)$$

The internal energy of an open system is homogeneous of degree one in terms of the extensive properties S , V , and $\{n_i\}$, and so eq. 1.1-6 follows from Euler's theorem. The integrated forms of fundamental equations are sometimes referred to as Euler equations, but it is better to call them integrated equations to avoid confusion with Euler's theorem. It is important to remember that the intensive variables for a system are not all independent, as discussed later in connection with the Gibbs–Duhem equation.

Equation 1.1-1 has the following mixed cross derivatives (Maxwell equations), which indicate some of the relationships between the thermodynamic properties for this system:

$$\left(\frac{\partial T}{\partial V}\right)_{S,\{n_i\}} = -\left(\frac{\partial P}{\partial S}\right)_{V,\{n_i\}} \quad (1.1-9)$$

$$\left(\frac{\partial T}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial \mu_i}{\partial S}\right)_{V,\{n_i\}} \quad (1.1-10)$$

$$-\left(\frac{\partial P}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial \mu_i}{\partial V}\right)_{S,\{n_i\}} \quad (1.1-11)$$

$$\left(\frac{\partial \mu_j}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial \mu_i}{\partial n_j}\right)_{S,V,n_i} \quad (1.1-12)$$

Since S and V are often inconvenient natural variables from an experimental point of view, Legendre transforms are used to define further thermodynamic potentials that have P as a natural variable rather than V , T as a natural variable rather than S , and both T and P as natural variables. A Legendre transform is a linear change in variables in which one or more products of conjugate variables are subtracted from the internal energy to define a new thermodynamic potential [2–16]. The Legendre transforms that introduce P , T , and T and P together as natural variables are

$$H = U + PV \quad (1.1-13)$$

$$A = U - TS \quad (1.1-14)$$

$$G = U + PV - TS \quad (1.1-15)$$

They define the enthalpy H , the Helmholtz energy A , and the Gibbs energy G . Legendre transforms are also used in mechanics to obtain more convenient independent variables. The Lagrangian L is a func-

tion of coordinates and velocities, but it is often more convenient to define the Hamiltonian function H with a Legendre transform because the Hamiltonian is a function of coordinates and momenta. Quantum mechanics is based on the Hamiltonian rather than the Lagrangian function. The important thing about Legendre transforms is that the new thermodynamic potentials defined in this way all contain exactly the same information as U .

The fundamental equations for H , A , and G are obtained by taking the differentials of eqs. 1.1-13, 1.1-14, and 1.1-15, and substituting eq. 1.1-1. For example, the fundamental equation for G is

$$dG = -SdT + VdP + \sum_{i=1}^N \mu_i dn_i \quad (1.1-16)$$

Each of the fundamental equations for the thermodynamic properties defined by Legendre transforms provides more partial derivatives and more Maxwell equations. Some of the thermodynamic potentials are also linked by Gibbs–Helmholtz equations:

$$H = -T^2 \left(\frac{\partial(G/T)}{\partial T} \right)_{P, \{n_i\}} \quad (1.1-17)$$

$$U = -T^2 \left(\frac{\partial(A/T)}{\partial T} \right)_{V, \{n_i\}} \quad (1.1-18)$$

The integrated forms of the fundamental equations for H , A , and G are

$$H(S, P, \{n_i\}) = TS + \sum_{i=1}^N n_i \mu_i \quad (1.1-19)$$

$$A(T, V, \{n_i\}) = -PV + \sum_{i=1}^N n_i \mu_i \quad (1.1-20)$$

$$G(T, P, \{n_i\}) = \sum_{i=1}^N n_i \mu_i \quad (1.1-21)$$

Thus, only the Gibbs energy of this system is made up of additive contributions from species. The natural variables of H , A , and G are indicated by the variables in parentheses. The corresponding criteria of spontaneous change and equilibrium involve these natural variables; namely $(dH)_{S,P,\{n_i\}} \leq 0$, $(dA)_{T,V,\{n_i\}} \leq 0$, and $(dG)_{T,P,\{n_i\}} \leq 0$.

More Legendre transforms are possible for the system described by eq. 1.1-1 because chemical potentials can be introduced as natural variables by use of Legendre transforms; that is described in Sections 2.2 and 2.3.

Equations 1.1-13 to 1.1-15 define partial Legendre transforms. The complete transform is obtained by subtracting all of the conjugate pairs for a system from U . For the system under discussion, the complete Legendre transform [7,14] is

$$U' = U + PV - TS - \sum_{i=1}^N \mu_i n_i \quad (1.1-22)$$

Taking the differential of the transformed internal energy U' and substituting eq. 1.1-1 yields

$$0 = -SdT + VdP + \sum_{i=1}^N n_i d\mu_i \quad (1.1-23)$$

the differential of U' is zero because U' is equal to zero, as is evident from eqs. 1.1-6 and 1.1-22. Equation 1.1-23 is referred to as the Gibbs–Duhem equation for the system. Since it gives a relation between the intensive properties for the system, these properties are not independent for the system at equilibrium. For the one-phase system, the number of independent intensive properties is $N + 1$. The

Gibbs–Duhem equation can be regarded as the source of the phase rule, according to which the number f of independent intensive variables is given by $f = N - p + 2$, where p is the number of phases, for a system involving only PV work and chemical work, but no chemical reactions. If chemical reactions are involved, the phase rule is $f = N - R - p + 2 = C - p + 2$, where R is the number of independent reactions and $C = N - R$ is the number of components. Components are discussed later in connection with phase equilibria and chemical equilibria.

In view of the importance of natural variables, it is convenient to have a symbol for the number of natural variables, just as it is convenient to have a symbol f for the number of independent intensive variables (degrees of freedom), as given by the phase rule. It can be shown that the number D of natural variables (independent variables to describe the extensive state) for a system without chemical reactions is given by

$$D = f + p = N + 2 \quad (1.1-24)$$

For a system with chemical reactions,

$$D = f + p = N - R + 2 = C + 2 \quad (1.1-25)$$

The number of thermodynamic potentials for a system is given by 2^D , and the number of Legendre transforms is $2^D - 1$. The number of thermodynamic potentials includes the potential that is equal to zero and yields the Gibbs–Duhem equation. The number of Maxwell equations for each of the thermodynamic potentials is $D(D - 1)/2$, and the number of Maxwell equations for all of the thermodynamic potentials for a system is $[D(D - 1)/2]2^D$ [13]. When Legendre transforms are used to introduce two new natural variables (T, P), then $2^D = 2^2 = 4$ thermodynamic potentials are related by Legendre transforms, as we have seen with U, H, A , and G . There are four Maxwell equations.

This section has shown that intensive variables are introduced as natural variables only by use of Legendre transforms. Since a Legendre transform defines a new thermodynamic potential, it is important that the new thermodynamic property have its own symbol and name. The new thermodynamic potentials contain all the information in $U(S, V\{n_i\})$, and so the use of U, H, A, G , or other thermodynamic potential in place of U is simply a matter of convenience.

1.2 One-phase systems with one species

In order to discuss the complete set of Legendre transforms for a system, we consider a one-phase system with one species. The fundamental equation for U is

$$dU = TdS - PdV + \mu dn \quad (1.2-1)$$

The integration of this fundamental equation at constant values of the intensive variables yields

$$U = TS - PV + \mu n \quad (1.2-2)$$

Since $D = 3$, there are $2^3 - 1 = 7$ thermodynamic potentials defined by Legendre transforms and 24 Maxwell equations. There are not generally accepted symbols for all of these thermodynamic potentials, and so a suggestion made by Callen [3] is utilized here. Callen pointed out that all conceivable thermodynamic potentials can be represented by U followed by square brackets around a list of the intensive variables introduced as natural variables by the Legendre transform defining the new thermodynamic potential. For example, the thermodynamic potentials defined by Legendre transforms 1.1-13, 1.1-14, and 1.1-15 can be represented by $U[P] = H$, $U[T] = A$, and $U[T, P] = G$. The seven Legendre transforms for a one-phase system with one species are

$$H = U + PV \quad (1.2-3)$$

$$A = U - TS \quad (1.2-4)$$

$$G = U + PV - TS \quad (1.2-5)$$

$$U[\mu] = U - \mu n \quad (1.2-6)$$

$$U[P, \mu] = U + PV - \mu n \quad (1.2-7)$$

$$U[T, \mu] = U - TS - \mu n \quad (1.2-8)$$

$$U[T, P, \mu] = U + PV - TS - \mu n = 0 \quad (1.2-9)$$

The first three Legendre transforms introduce P , T , and T and P together as natural variables. The last four Legendre transforms introduce the chemical potential as a natural variable. Three of these thermodynamic potentials are frequently used in statistical mechanics, and there are generally accepted symbols for the corresponding partition functions [12]: $U[T] = A = -RT \ln Q$, where Q is the canonical ensemble partition function; $U[T, P] = G = -RT \ln \Delta$, where Δ is the isothermal-isobaric partition function; and $U[T, \mu] = -RT \ln \Xi$, where Ξ is the grand canonical ensemble partition function. The last thermodynamic potential $U[T, P, \mu]$ is equal to zero because it is the complete Legendre transform for the system, and this Legendre transform leads to the Gibbs–Duhem equation.

Taking the differentials of the seven thermodynamic potentials defined in eqs. 1.2-3 to 1.2-9 and substituting eq. 1.2-1 yields the fundamental equations for these seven thermodynamic potentials:

$$dH = TdS + VdP + \mu dn \quad (1.2-10)$$

$$dA = -SdT - PdV + \mu dn \quad (1.2-11)$$

$$dG = -SdT + VdP + \mu dn \quad (1.2-12)$$

$$dU[\mu] = TdS - PdV - nd\mu \quad (1.2-13)$$

$$dU[P, \mu] = TdS + VdP - nd\mu \quad (1.2-14)$$

$$dU[T, \mu] = -SdT - PdV - nd\mu \quad (1.2-15)$$

$$dU[T, P, \mu] = -SdT + VdP - nd\mu = 0 \quad (1.2-16)$$

The last fundamental equation is the Gibbs–Duhem equation for the system, which shows that only two of the three intensive properties are independent. Because of the Gibbs–Duhem equation, we can say that the chemical potential of a pure substance is a function of temperature and pressure. The number f of independent intensive variables is 2, and so $D = f + p = 2 + 1 = 3$. Each of these fundamental equations yields $D(D - 1)/2 = 3$ Maxwell equations. The criteria of equilibrium provided by these thermodynamic potentials are $(dU)_{S, V, n} \leq 0$, $(dH)_{S, P, n} \leq 0$, $(dA)_{T, V, n} \leq 0$, $(dG)_{T, P, n} \leq 0$, $(dU[\mu])_{S, V, \mu} \leq 0$, $(dU[P, \mu])_{S, P, \mu} \leq 0$, and $(dU[T, \mu])_{T, V, \mu} \leq 0$.

The integrated forms of the eight fundamental equations for this system are

$$U(S, V, n) = TS - PV + \mu n \quad (1.2-17)$$

$$H(S, P, n) = TS + \mu n \quad (1.2-18)$$

$$A(T, V, n) = -PV + \mu n \quad (1.2-19)$$

$$G(T, P, n) = \mu n \quad (1.2-20)$$

$$U[\mu](S, V, \mu) = TS - PV \quad (1.2-21)$$

$$U[P, \mu](S, P, \mu) = TS \quad (1.2-22)$$

$$U[T, \mu](T, V, \mu) = -PV \quad (1.2-23)$$

$$UT, P, \mu = 0 \quad (1.2-24)$$

The natural variables are shown in parentheses.

1.3 Other types of work

Table 1 shows a number of types of work terms that may be involved in a thermodynamic system [16]. The last column shows the form of work terms in the fundamental equation for the internal energy. When there are no chemical reactions, the amounts of species are independent variables, but when there are chemical reactions, the amounts of components are independent variables, as discussed in Section 2.1. In some cases, the extensive variables for other kinds of work are proportional to the amounts of species so that these work terms are not independent of the chemical work terms. In these cases, the other types of work do not introduce new natural variables for U .

Table 1 Conjugate pairs of variables in work terms for the fundamental equation for U^a .

Type of work	Intensive variable	Extensive variable	Differential work in dU
Mechanical			
Pressure-volume	$-P$	V	$-PdV$
Elastic	f	L	$f dL$
Gravitational	$\psi = gh$	$m = \sum M_i n_i$	$\psi dm = \sum gh M_i dn_i$
Surface	γ	A_s	γdA_s
Electromagnetic			
Charge transfer	ϕ_i	Q_i	$\phi_i dQ_i$
Electric polarization	\mathbf{E}	\mathbf{p}	$\mathbf{E} \cdot d\mathbf{p}$
Magnetic polarization	\mathbf{B}	\mathbf{m}	$\mathbf{B} \cdot d\mathbf{m}$
Chemical			
Chemical: no reactions	μ_i	n_i (species)	$\mu_i dn_i$
Chemical: reactions	μ_i	n_{ci} (components)	$\mu_i dn_{ci}$

^aHere $\psi = gh$ is the gravitational potential, g is the gravitational acceleration, h is height above the surface of the earth, m is mass, M_i is molar mass, ϕ_i is the electric potential of the phase containing species i , Q_i is the contribution of species i to the electric charge of a phase, z_i is the charge number, F is the Faraday constant, f is force of elongation, L is length in the direction of the force, γ is surface tension, A_s is surface area, \mathbf{E} is electric field strength, \mathbf{p} is the electric dipole moment of the system, \mathbf{B} is magnetic field strength (magnetic flux density), and \mathbf{m} is the magnetic moment of the system. In some electrochemical systems, $Q_i = Fz_i n_i$ so that $dQ_i = Fz_i dn_i$. The dots indicate scalar products of vectors. Some of the other work terms can be written in vector notation. Other types of work terms are possible, and some of the expressions for differential work are more complicated; for example, the force on a solid may be represented by a tensor and ψ may be a centrifugal potential. The term γdA_s applies to flat surfaces.

Note that each type of work term in the fundamental equation for U is written in the form (intensive variable)d(extensive variable). The intensive variables in the various work terms may be referred to as generalized forces, and the extensive variables may be referred to as generalized displacements. Several types of work terms may be involved in a single thermodynamic system. The first question that must be considered before writing the fundamental equation for an actual system is the possible dependence of the extensive variables m , Q_i , L , A_s , \mathbf{p} , \mathbf{m} on $\{n_i\}$. It is not possible to give a general answer to the question as to which extensive variables are independent because that depends on the system.

1.4 One-phase systems with N species and non- PV work

Here we consider an unspecified type of work $X dY$ in which the extensive property Y is independent of $\{n_i\}$. Phase equilibrium and chemical equilibrium are discussed in Sections 1.5 and 2.1. The fundamental equation for U for the system considered is

$$dU = TdS - PdV + \sum \mu_i dn_i + X dY \quad (1.4-1)$$

If we are only interested in specifying the chemical potential of one species (the s -th species), there are $D = 2^4 = 16$ possible thermodynamic potentials. The following equations give the integrated equation for U and the 15 Legendre transforms defining new thermodynamic potentials. In representing thermodynamic potentials, Callen's nomenclature [2,3] is extended by using H , A , and G with square brackets, as well as U . The use of $H[]$ indicates that P is introduced by the Legendre transform as well as the indicated variables, the use of $A[]$ indicates that T is introduced by the Legendre transform as well as the indicated variables, and the use of $G[]$ indicates that T and P are introduced as well as the indicated variables.

$$U = TS - PV + \sum \mu_i n_i + XY = f(S, V, \{n_i\}, Y) \quad (1.4-2)$$

$$H = U + PV = TS + \sum \mu_i n_i + XY = f(S, P, \{n_i\}, Y) \quad (1.4-3)$$

$$A = U - TS = -PV + \sum \mu_i n_i + XY = f(T, V, \{n_i\}, Y) \quad (1.4-4)$$

$$G = U + PV - TS = \sum \mu_i n_i + XY = f(T, P, \{n_i\}, Y) \quad (1.4-5)$$

$$U[X] = U - XY = TS - PV + \sum \mu_i n_i = f(S, V, \{n_i\}, X) \quad (1.4-6)$$

$$H[X] = H - XY = TS + \sum \mu_i n_i = f(S, P, \{n_i\}, X) \quad (1.4-7)$$

$$A[X] = A - XY = -PV + \sum \mu_i n_i = f(T, V, \{n_i\}, X) \quad (1.4-8)$$

$$G[X] = G - XY = \sum \mu_i n_i = f(T, P, \{n_i\}, X) \quad (1.4-9)$$

$$U[\mu_s] = U - n_s \mu_s = TS - PV + \sum \mu_i n_i + XY = f(S, V, \{n_i\}, \mu_s, Y) \quad (1.4-10)$$

$$H[\mu_s] = H - n_s \mu_s = TS + \sum \mu_i n_i + XY = f(S, P, \{n_i\}, \mu_s, Y) \quad (1.4-11)$$

$$A[\mu_s] = A - n_s \mu_s = -PV + \sum \mu_i n_i + XY = f(T, V, \{n_i\}, \mu_s, Y) \quad (1.4-12)$$

$$G[\mu_s] = G - n_s \mu_s = \sum \mu_i n_i + XY = f(T, P, \{n_i\}, \mu_s, Y) \quad (1.4-13)$$

$$U[\mu_s, X] = U - n_s \mu_s - XY = TS - PV + \sum \mu_i n_i = f(S, V, \{n_i\}, \mu_s, X) \quad (1.4-14)$$

$$H[\mu_s, X] = H - n_s \mu_s - XY = TS + \sum \mu_i n_i = f(S, P, \{n_i\}, \mu_s, X) \quad (1.4-15)$$

$$A[\mu_s, X] = A - n_s \mu_s - XY = -PV + \sum \mu_i n_i = f(T, V, \{n_i\}, \mu_s, X) \quad (1.4-16)$$

$$G[\mu_s, X] = G - n_s \mu_s - XY = \sum \mu_i n_i = f(T, P, \{n_i\}, \mu_s, X) \quad (1.4-17)$$

where $i \neq s$ in eqs. 1.4-1 to 1.4-17. Note that this last thermodynamic potential would be a complete Legendre transform if there was only one species present, and so it would lead to a Gibbs–Duhem equation in that case. When there are chemical reactions at equilibrium, we have to deal with components, and this requires further interpretation of n_i and μ_i in eqs. 1.4-10 to 1.4-18, which is discussed in Sections 2.2 and 2.3.

1.5 Phase equilibrium

Fundamental equation eq. 1.1-16 for G for an open system can be used for a system with multiple phases by counting each species in a different phase as a different species. This indicates that the system has $N + 2$ natural variables, but in order to identify the natural variables for the system at equilibrium and to write the criterion for equilibrium it is necessary to introduce the constraints, which are $\mu_{i\alpha} = \mu_{i\beta}$ for each species in a two-phase system. The fundamental equation for a thermodynamic potential like G can be written in terms of natural variables for the system at equilibrium by using the equilibrium constraints to reduce the number of terms. For example, consider a system with two species and two phases. Substituting $\mu_{1\alpha} = \mu_1$ and $\mu_{2\alpha} = \mu_{2\beta} = \mu_2$ yields

$$dG = -SdT + VdP + \mu_1 dn_{c1} + \mu_2 dn_{c2} \quad (1.5-1)$$

where $n_{c1} = n_{1\alpha} + n_{1\beta}$ and $n_{c2} = n_{2\alpha} + n_{2\beta}$ are the amounts of two components. Note that components are conserved. This form of the fundamental equation indicates that there are four natural variables for this system at equilibrium, which can be taken as T , P , n_{c1} , and n_{c2} . This is in agreement with $D = f + p = 2 + 2 = 4$, where $f = N - p + 2 = 2 - 2 + 2 = 2$. However, there is a choice of natural variables, and it may be more useful to write the fundamental equation for G as

$$dG = -SdT + VdP + \langle \mu_\alpha \rangle dn_\alpha + \langle \mu_\beta \rangle dn_\beta \quad (1.5-2)$$

where $n_\alpha = n_{1\alpha} + n_{2\alpha}$, $n_\beta = n_{1\beta} + n_{2\beta}$ are the amounts of the two phases. The average chemical potentials in the α and β phases are given by

$$\langle \mu \rangle_\alpha = \frac{\mu_1 n_{1\alpha} + \mu_2 n_{2\alpha}}{n_{1\alpha} + n_{2\alpha}} \quad (1.5-3)$$

$$\langle \mu \rangle_\beta = \frac{\mu_1 n_{1\beta} + \mu_2 n_{2\beta}}{n_{1\beta} + n_{2\beta}} \quad (1.5-4)$$

Equation 1.5-1 indicates that the criterion for spontaneous change and equilibrium can be written $(dG)_{T,P,n_{c1},n_{c2}} \leq 0$, and eq. 1.5-2 indicates that the criterion can alternatively be written $(dG)_{T,P,n_\alpha,n_\beta} \leq 0$. The fact that there are only two intensive properties for this system can also be understood by considering the two Gibbs–Duhem equations for the system. These equations for the separate phases both involve dT , dP , $d\mu_1$, and $d\mu_2$. The quantity $d\mu_2$ can be eliminated between these two equations, and the resulting equation can be solved for $d\mu_1$ as a function of T and P . Thus, μ_1 and μ_2 are both functions of T and P .

The integrated forms of fundamental eqs. 1.5-1 and 1.5-2 are

$$G = \mu_1 n_{c1} + \mu_2 n_{c2} \quad (1.5-5)$$

$$G = \langle \mu_\alpha \rangle n_\alpha + \langle \mu_\beta \rangle n_\beta \quad (1.5-6)$$

In concluding Section 1, the following points are emphasized. Legendre transforms provide the only means for introducing intensive variables into criteria for spontaneous change and equilibrium. Intensive variables are introduced because they are often easier to control than extensive variables. When various types of work terms are involved, the number of possible Legendre transforms is $2^D - 1$, and the number of thermodynamic potentials that can be used in criteria of spontaneous change and equilibrium is 2^D , where $D = f + p$ is the number of natural variables. Since each thermodynamic potential requires a symbol and name, there is a serious nomenclature problem. It is important to be aware of all the Legendre transforms that can be applied to a given system. The problem of the dependence of extensive variables in other types of work on $\{n_i\}$ has been pointed out.

2. FUNDAMENTAL EQUATIONS OF THERMODYNAMICS FOR SYSTEMS WITH CHEMICAL REACTIONS

2.1 Components in chemical reaction systems

In a one-phase reaction system, the natural variables appear to be T , P , and $\{n_i\}$, but because of the constraints of the chemical reactions, the $\{n_i\}$ are not independent variables for a closed reaction system. The amounts of components are independent variables [13,17–19]. The conversion from amounts of species to amounts of components in a chemical reaction system is illustrated by consideration of a closed system in which the reaction



occurs. The fundamental equation for G is

$$dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C \quad (2.1-2)$$

The equilibrium condition derived from this equation is

$$\mu_A + \mu_B = \mu_C \quad (2.1-3)$$

Using this constraint to eliminate μ_C from the fundamental equation for G yields

$$\begin{aligned} dG &= -SdT + VdP + \mu_A (dn_A + dn_C) + \mu_B (dn_B + dn_C) \\ &= -SdT + VdP + \mu_A dn_{cA} + \mu_B dn_{cB} \end{aligned} \quad (2.1-4)$$

where $n_{cA} = n_A + n_C$ and $n_{cB} = n_B + n_C$ are the amounts of components A and B. For this system, $f = N - R - p + 2 = 3 - 1 - 1 + 2 = 3$, and $D = f + p = 3 + 1 = 4$. The natural variables can be chosen to be T, P, n_{cA} , and n_{cB} , but this choice is not unique because μ_A or μ_B could have been eliminated using eq. 2.1-3. The amounts of components are constants for the system, and they need to be known in order to calculate the equilibrium composition [20]. The criterion for spontaneous change and equilibrium can be written $(dG)_{T,P,n_{cA},n_{cB}} \leq 0$. When a system involves chemical reactions, the amounts of species at any given time are given by

$$n_i = n_{i0} + \sum_{j=1}^R v_{ij} \xi_j \quad (2.1-5)$$

where n_{i0} is the initial amount of species i , v_{ij} is the stoichiometric number of species i in reaction j , ξ_j is the extent of reaction j , and R is the number of independent reactions. Since there are N species and R reactions, the number of components C is given by $C = N - R$.

In dealing with multireaction systems, it is useful to express eq. 2.1-5 in matrix form:

$$\mathbf{n} = \mathbf{n}_0 + \mathbf{v}\boldsymbol{\xi} \quad (2.1-6)$$

where \mathbf{n} is the $N \times 1$ matrix of amounts of species, \mathbf{n}_0 is the $N \times 1$ matrix of initial amounts of species, \mathbf{v} is the $N \times R$ matrix of stoichiometric numbers, and $\boldsymbol{\xi}$ is the $R \times 1$ matrix of extents of reactions. The fundamental equation for G for a multireaction system can be written

$$dG = -SdT + VdP + \boldsymbol{\mu}d\mathbf{n} = -SdT + VdP + \boldsymbol{\mu}v d\boldsymbol{\xi} \quad (2.1-7)$$

where $\boldsymbol{\mu}$ is the $1 \times N$ matrix of chemical potentials of species. This equation can be used to derive the equilibrium condition [17]

$$\boldsymbol{\mu}v = \mathbf{0} \quad (2.1-8)$$

where the zero matrix $\mathbf{0}$ is $1 \times R$. Equation 2.1-7 is useful for thinking about the equilibrium conditions, but to identify the natural variables and state the criterion of spontaneous change and equilibrium, it is necessary to use components.

At equilibrium, there are R known equations of the type

$$\sum_{i=1}^N v_{ij} \mu_i = 0 \quad (2.1-9)$$

Each equilibrium condition can be used to eliminate one chemical potential from eq. 2.1-1 so that the fundamental equation for G stated in terms of natural variables for a chemical reaction system is

$$dG = -SdT + VdP + \sum_{i=1}^C \mu_i dn_{c_i} \quad (2.1-10)$$

where μ_i is the chemical potential of a species and n_{c_i} is the amount of the component with that chemical potential. The number of components in a system is unique, but different sets of components can

be chosen [19]. When a system is at chemical equilibrium, the chemical potential of a component is given by

$$\mu_i = \left(\frac{\partial G}{\partial n_{ci}} \right)_{T,P,n_{cj}} \quad (2.1-11)$$

where $j \neq i$. Beattie and Oppenheim [13] discuss their two theorems on chemical potentials: (1) “The chemical potential of a component of a phase is independent of the choice of components”. (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”. Thus, for a chemical reaction system, the criterion for equilibrium is $(dG)_{T,P,\{c_i\}} \leq 0$.

The number of components is equal to the rank of the conservation matrix \mathbf{A} , which has a column for each species and a row for each independent conservation equation [17]. The conservation matrix is made up of the coefficients of the conservation equations for the system. In chemical reactions, atoms of elements and electric charge are conserved, and sometimes groups of atoms are conserved as well, so that conservation equations may not all be independent. If two elements always appear in the same ratio, they can be considered to be a pseudoelement. There may be additional conservation equations that arise from the mechanism of reaction. The independent conservation equations for a system are represented by

$$\mathbf{A}\mathbf{n} = \mathbf{n}_c \quad (2.1-12)$$

where \mathbf{A} is the $C \times N$ conservation matrix, \mathbf{n} is the $N \times 1$ matrix of amounts of species, and \mathbf{n}_c is the $C \times 1$ matrix of amounts of components. The conservation matrix for a system is related to the stoichiometric number matrix \mathbf{v} by

$$\mathbf{A}\mathbf{v} = \mathbf{0} \quad (2.1-13)$$

where \mathbf{v} is the $N \times R$ stoichiometric number matrix and the zero matrix is $C \times R$. The stoichiometric number matrix \mathbf{v} is in the null space of \mathbf{A} and can be calculated by hand for small matrices or by computer for large matrices. Alternatively, \mathbf{A}^T is the null space of \mathbf{v}^T , where T indicates the transpose. Neither \mathbf{A} nor \mathbf{v} for a system are unique, but their row-reduced forms are unique for a given order of species.

The fundamental equation for G in terms of components (eq. 2.1-10) can be written in matrix notation:

$$dG = -SdT + VdP + \boldsymbol{\mu}_c d\mathbf{n}_c = \boldsymbol{\mu}_c \mathbf{A} d\mathbf{n} \quad (2.1-14)$$

where $\boldsymbol{\mu}_c$ is the $1 \times C$ chemical potential matrix for the components and \mathbf{n}_c is the $C \times 1$ amount matrix for components. The second form is obtained by use of eq. 2.1-12. Note that \mathbf{A} is a transformation matrix for the transformation from a set of N species to a set of C components. For a reaction system, the number of degrees of freedom is given by $f = N - R - p + 2 = C - p + 2$, so that the intensive state for a one-phase system is specified by $f = C + 1$ intensive variables. Since $D = f + p = C + 2$, the natural variables for a one-phase reaction system can be chosen to be T , P , and $\{n_{ci}\}$.

For a reaction system, it may be useful to choose the chemical potential of a species to be an independent variable. Some of the amounts of components can be replaced as natural variables by the chemical potentials of the corresponding species by use of a Legendre transforms to define a transformed Gibbs energy, as explained in Sections 2.2 and 2.3. It is evident from $(dG)_{T,P,\{n_{ci}\}} \leq 0$ that only $C - 1$ amounts of components can be replaced by specified chemical potentials because the description of the state of the system must include at least one extensive variable.

2.2 Gas reactions

Under certain circumstances it is of interest to consider chemical equilibrium in a gaseous reaction system when the chemical potential of a reacting species, represented here as B, is held constant. The cri-

terion for spontaneous change and equilibrium at specified T , P , and chemical potential of a species can be derived by defining a new thermodynamic potential by using a Legendre transform in which a product of conjugate variables is subtracted from the Gibbs energy. The conjugate variable to the chemical potential of a species is the amount of the component corresponding with that species. The chemical potential of species B can be introduced as a natural variable by making a Legendre transform of the Gibbs energy of the form [21–23]

$$G' = G - n_{\text{cB}}\mu_{\text{B}} \quad (2.2-1)$$

where n_{cB} is the amount of component B in the system. The amount of component B in the system can be expressed in terms of the amounts of B in the various species by

$$n_{\text{cB}} = \sum_{i=1}^N N_{\text{B}i}n_i \quad (2.2-2)$$

where N is the number of species in the system and $N_{\text{B}i}$ is the number of component molecules of B in a species molecule of i . Equation 2.2-2 gives the amount of the B component, and it is this amount that has to be used in the Legendre transform because at chemical equilibrium, it is only the amounts of components that are independent variables (see eq. 1.5-1). Substituting $G = \sum \mu_i n_i$ and 2.2-2 in eq. 2.2-1 yields

$$G' = \sum_{i=1}^N (\mu_i - N_{\text{B}i}\mu_{\text{B}})n_i = \sum_{i=1}^N \mu'_i n_i \quad (2.2-3)$$

where the transformed chemical potential μ'_i of species i is defined by

$$\mu'_i = \mu_i - N_{\text{B}i}\mu_{\text{B}} \quad (2.2-4)$$

When the chemical potential of B is specified, the contributions of other species to the transformed Gibbs energy of the system are additive in their transformed chemical potentials μ'_i , as shown by eq. 2.2-3.

Eliminating μ_i between eqs. 2.2-4 and 2.1-2 yields

$$dG = -SdT + VdP + \mu_{\text{B}}dn_{\text{cB}} + \sum_{i=1}^{N-1} \mu'_i dn_i \quad (2.2-5)$$

Note that there is no longer a separate term for species B in the summation. Since the B component is in a separate term, we can use the Legendre transform (2.2-1) to make μ_{B} a natural variable. The differential of G' in eq. 2.2-1 is taken, and eq. 2.2-5 is substituted to obtain

$$dG' = -SdT + VdP - n_{\text{cB}}d\mu_{\text{B}} + \sum_{i=1}^{N-1} \mu'_i dn_i \quad (2.2-6)$$

When the chemical potential of B is specified, species that differ only in the number of B molecules that they contain become pseudoisomers, and they have the same transformed chemical potential at equilibrium, just as isomers have the same chemical potential at equilibrium. The amounts of pseudoisomers can be summed to yield n'_i , the amount of species in the pseudoisomer group; $n'_i = \sum n_i$. Thus, the specification of the chemical potential of a species leads to a reconceptualization of the equilibrium calculation in terms of amounts n'_i of pseudoisomer groups, rather than amounts n_i species. This may lead to a considerable simplification of the fundamental equation because the number N' of pseudoisomer groups may be considerably less than the number N of species. Thus, eq. 2.2-6 can be written

$$dG' = -SdT + VdP - n_{\text{cB}}d\mu_{\text{B}} + \sum_{i=1}^{N'} \mu'_i dn'_i \quad (2.2-7)$$

For example, when the partial pressure of ethylene is specified, the successive isomer groups in an entire homologous series become pseudoisomers and are represented by one term in the summation in eq. 2.2-7.

Up to this point, the treatment has been completely general, but now we assume that the gases are ideal so that

$$\mu_i = \mu_i^0 + RT \ln(P_i/P^0) \quad (2.2-8)$$

where P^0 is the standard state pressure (1 bar = 0.1 MPa). In order to use P_B as an independent variable in the fundamental equation rather than μ_B , $d\mu_B$ in eq. 2.2-7 is replaced with the expression for the total differential:

$$d\mu_B = \left(\frac{\partial \mu_B}{\partial T} \right)_{P_B} dT + \left(\frac{\partial \mu_B}{\partial P_B} \right)_T dP_B \quad (2.2-9)$$

When the derivatives of μ_B are taken and eq. 2.2-9 is substituted in eq. 2.2-7, we obtain

$$dG' = -S'dT + VdP' - (n_{cB}RT/P_B)dP_B + \sum_{i=1}^{N'} \mu_i' dn_i' \quad (2.2-10)$$

where N' is the number of pseudoisomer groups.

The transformed entropy of the system is given by

$$S' = S - n_{cB} \bar{S}_B \quad (2.2-11)$$

where \bar{S}_B is the molar entropy of B and n_{cB} is the total amount of B bound in the system. In eq. 2.2-10, P' is the sum of the partial pressures of species other than B

$$n_{cB} = \sum_{i=1}^{N'} \bar{N}_B(i) n_i' \quad (2.2-12)$$

Here $\bar{N}_B(i)$ is the average number of B molecules in i and n_i' is the sum of the amounts of species that differ only with respect to the number of B molecules that they contain. Thus, the natural variables of G' before applying the equilibrium constraints are represented by $G'(T, P', P_B, \{n_i'\})$, where n_i' is the amount of pseudoisomer group i . After applying the equilibrium constraints, the criterion for equilibrium is $(dG')_{T, P', P_B, \{n_{ci}\}} \leq 0$. Note that eq. 2.2-10 shows that the transformed chemical potential of species i is defined by

$$\mu_i' = \left(\frac{\partial G'}{\partial n_i'} \right)_{T, P', P_B, n_j'} \quad (2.2-13)$$

before chemical constraints are applied.

Equation 2.2-4 shows how to calculate the transformed chemical potential of a species. Substituting eq. 2.2-8 in eq. 2.2-4 yields

$$\begin{aligned} \mu_i' &= \mu_i^0 + RT \ln(P_i/P^0) - N_{Bi} \mu_B \\ &= \mu_i'^0 + RT \ln(P_i/P^0) \end{aligned} \quad (2.2-14)$$

where $\mu_i'^0 = \mu_i^0 - N_{Bi} \mu_B$. For an actual calculation, eq. 2.2-14 for species i can be written in terms of transformed Gibbs energies of formation.

$$\Delta_i G_i' = \Delta_i G_i'^0 + RT \ln(P_i/P^0) \quad (2.2-15)$$

where

$$\Delta_f G_i'^{\circ} = \Delta_f G_i^{\circ} - N_{B_i} [\Delta_f G_B^{\circ} + RT \ln(P_B/P^{\circ})] \quad (2.2-16)$$

At chemical equilibrium, the various species binding B are pseudoisomers, and so the standard transformed Gibbs energy of the isomer group can be calculated with the equation for isomer groups [17].

$$\Delta_f G'^{\circ}(\text{pseudoisomer group}) = -RT \ln\{\sum \exp[-\Delta_f G_i'^{\circ}/RT]\} \quad (2.2-17)$$

where the summation includes all of the pseudoisomers in a group. It is important to note that the standard transformed Gibbs energy of the pseudoisomer group is not a weighted average of the standard transformed Gibbs energies of formation of the pseudoisomers in the group because there is an entropy of mixing term. It will always be more negative than any one of them; in other words, the pseudoisomer group is more stable than any of the pseudoisomers. The mole fraction r_i of the i -th pseudoisomers in the pseudoisomer group is given by [24]

$$r_i = \exp\{[\Delta_f G'^{\circ}(\text{pseudoisomer group}) - \Delta_f G_i'^{\circ}]/RT\} \quad (2.2-18)$$

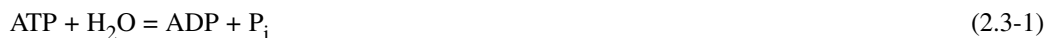
The standard transformed enthalpy of formation of the pseudoisomer group is a mole fraction weighted average and is given by

$$\Delta_f H'^{\circ}(\text{pseudoisomer group}) = \sum r_i \Delta_f H_i'^{\circ} \quad (2.2-19)$$

This discussion has been based on making the chemical potential of one species a natural variable, but it may be possible to make a Legendre transform involving more than one species. For example, for a system of benzenoid polycyclic aromatic hydrocarbons, acetylene, and molecular hydrogen, which has three components, it is possible to specify $P(\text{C}_2\text{H}_2)$ and $P(\text{H}_2)$ [22]. If hydrogen atoms are included in the system as a reactant ($C = 4$), it is possible to specify $P(\text{C}_2\text{H}_2)$, $P(\text{H}_2)$, and $P(\text{H})$. In other words, if species that are specified can be interconverted, it is not necessary that they be at equilibrium.

2.3 Biochemical reactions

This method of using a Legendre transformed Gibbs energy G' is especially useful in biochemistry where it is convenient to study systems at a specified pH, and, in some cases, at a specified free concentration of Mg^{2+} or other cation that is bound by reactants. When the pH and pMg are specified, it is as if the biochemical reaction was carried out in a reaction chamber connected to pH and pMg reservoirs through semipermeable membranes. In this case, the Gibbs energy G of the contents of the reaction chamber is not minimized at equilibrium because the concentrations of certain species are held constant. Hydrogen and magnesium are not conserved in the reaction chamber. This is the reason why biochemical reactions are written in terms of sums of species, as in the hydrolysis of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) and inorganic phosphate (P_i), which is represented by the biochemical equation



with apparent equilibrium constant K' defined by

$$K' = \frac{[\text{ADP}][\text{P}_i]}{[\text{ATP}]c^{\circ}} \quad (2.3-2)$$

where ATP, ADP, and P_i represent sums of species and c° is the standard state concentration. This value of K' depends on T , P , pH, pMg, and I (ionic strength). Note that K' and other thermodynamic properties like G , H , and μ_i are taken to be functions of ionic strength so that concentrations can be used in eq. 2.3-2. This means that $\text{pH} = -\lg[\text{H}^+]$ and $\text{pMg} = -\lg[\text{Mg}^{2+}]$ because activity coefficients are incorporated in the thermodynamic properties.

The chemical potentials of hydrogen ion and the magnesium ion are introduced as natural variables by use of the Legendre transform [25–27].

$$G' = G - n_c(\text{H})\mu(\text{H}^+) - n_c(\text{Mg})\mu(\text{Mg}^{2+}) \quad (2.3-3)$$

The amount of the hydrogen component in the reaction chamber is given by

$$n_c(\text{H}) = \sum_{i=1}^N N_{\text{H}}(i)n_i \quad (2.3-4)$$

where $N_{\text{H}}(i)$ 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

$$n_c(\text{Mg}) = \sum_{i=1}^N N_{\text{Mg}}(i)n_i \quad (2.3-5)$$

where $N_{\text{Mg}}(i)$ is the number of magnesium atoms in species i . The Gibbs energy of the material in the reaction chamber is given by $G = \sum \mu_i n_i$. Substituting this and eqs. 2.3-4 and 2.3-5 in eq. 2.3-3 yields $G' = \sum \mu'_i n_i$, where the transformed chemical potential of species i is given by

$$\mu'_i = \mu_i - N_{\text{H}}(i)\mu(\text{H}^+) - N_{\text{Mg}}(i)\mu(\text{Mg}^{2+}) \quad (2.3-6)$$

Taking the differential of G' that is defined in eq. 2.3-3 and substituting eq. 1.1-16 leads to

$$dG' = -S'dT + VdP + n_c(\text{H})RT \ln(10)dp\text{H} + n_c(\text{Mg})RT \ln(10)dp\text{Mg} + \sum_{i=1}^{N'} \mu'_i dn'_i \quad (2.3-7)$$

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). Some of the steps in the introduction of p H and p Mg have been omitted, but they are discussed elsewhere [27]. The transformed entropy S' of the system is defined by

$$S' = S - n_c(\text{H})\bar{S}(\text{H}^+) - n_c(\text{Mg})\bar{S}(\text{Mg}^{2+}) \quad (2.3-8)$$

This equation can be used to show that

$$S' = \sum n'_i \bar{S}'_i \quad (2.3-9)$$

where

$$\bar{S}'_i = \bar{S}_i - N_{\text{H}}(i)\bar{S}(\text{H}^+) - N_{\text{Mg}}(i)\bar{S}(\text{Mg}^{2+}) \quad (2.3-10)$$

Since $H' = G' + TS'$,

$$H' = H - n_c(\text{H})\bar{H}(\text{H}^+) - n_c(\text{Mg})\bar{H}(\text{Mg}^{2+}) \quad (2.3-11)$$

This equation can be used to show that

$$H' = \sum n'_i \bar{H}'_i \quad (2.3-12)$$

where

$$\bar{H}'_i = \bar{H}_i - N_{\text{H}}(i)\bar{H}(\text{H}^+) - N_{\text{Mg}}(i)\bar{H}(\text{Mg}^{2+}) \quad (2.3-13)$$

The natural variables for G' are T , P , p H , p Mg , and $\{n'_i\}$, and the criterion for equilibrium is $(dG')_{T,P,p\text{H},p\text{Mg},\{n'_i\}} \leq 0$. Equation 2.3-7 gives rise to many useful Maxwell equations.

Equation 2.3-7 can be used to derive eq. 2.3-2 for K' at specified T , P , p H , and p Mg . The ionic strength also has an effect on K' , but the ionic strength is not an independent variable in the same sense as the other four. It is important to specify the ionic strength, just like it is important to specify the solvent. The standard transformed Gibbs energy of reaction can be calculated using

$$\Delta_r G'^{\circ} = -RT \ln K' \quad (2.3-14)$$

Other thermodynamic properties can be obtained by taking derivatives of this equation. Tables of standard transformed Gibbs energies of formation at a specified pH and pMg and standard transformed enthalpies of formation can be prepared and used like the usual tables of standard thermodynamic properties [28].

The Panel on Biochemical Thermodynamics of the IUBMB–IUPAC Joint Commission on Biochemical Nomenclature has published *Recommendations for Nomenclature and Tables in Biochemical Thermodynamics* [29]. Standard transformed formation properties of carbon dioxide in aqueous solution at specified pH have been calculated [30,31]. Legendre transformed thermodynamic potentials are also used in the study of binding and linkage by macromolecules [32,33].

3. FUNDAMENTAL EQUATIONS OF THERMODYNAMICS FOR SYSTEMS WITH GRAVITATIONAL WORK AND ELECTRIC WORK

3.1 Systems with gravitational work

The effect of the gravitational potential ψ has been discussed earlier [34,35]. As shown in Table 1, gravitational work adds a term $\psi dm = \sum ghM_i dn_i$ to the fundamental equation for U and the fundamental equation for G , where g is the gravitational acceleration and h is the height above the surface of the earth. However, this term does not change the natural variables for G , which are T , P , and $\{n_i\}$. Therefore, the fundamental equation for G (eq. 1.1-16) is unchanged. In order to bring in the gravitational potential ψ , which is an external variable that is not affected by what happens in the system, the chemical potential of a species in the system is taken as

$$\mu_i = \mu_i^{\circ} + RT \ln a_i + ghM_i \quad (3.1-1)$$

This is the definition of the activity a_i of a species i in a system in which gravitational work is important. In such a system, the definition of the standard chemical potential μ_i° has to include a statement that μ_i° is the value at unit activity at the surface of the earth ($h = 0$). For a given activity, the chemical potential μ_i is a linear function of the height above the earth's surface. The fundamental equation for G is

$$dG = -SdT + VdP + \sum (\mu_i^{\circ} + RT \ln a_i + ghM_i) dn_i \quad (3.1-2)$$

Note that although the height above the surface of the earth is involved, the fundamental equation does not give the derivative of G with respect to h . At equilibrium in an isothermal atmosphere, the chemical potential of each species is independent of height, and this leads to the barometric formula for an ideal gas.

The height h can be introduced as a natural variable by use of the Legendre transform to define a transformed Gibbs energy.

$$G' = G - \sum ghM_i n_i \quad (3.1-3)$$

Taking the differential of G' and substituting eq. 3.1-2 yields

$$dG' = -SdT + VdP + \sum (\mu_i^{\circ} + RT \ln a_i) dn_i - \sum gM_i n_i dh \quad (3.1-4)$$

This indicates that it is reasonable to define a transformed chemical potential μ_i' by

$$\mu_i' = \left(\frac{\partial G'}{\partial n_i} \right)_{T,P,h,n_j} = \mu_i^{\circ} + RT \ln a_i \quad (3.1-5)$$

where $j \neq i$. Thus, eq. 3.1-1 can be written

$$\mu_i = \mu_i' + ghM_i \quad (3.1-6)$$

Since μ_i is constant throughout an equilibrium system with changing gravitational potential, μ_i' varies throughout the system. Other transformed thermodynamic properties of species i can be obtained by taking derivatives of eq. 3.1-5. Since $\sum M_i v_i = 0$, where v_i is the stoichiometric number for i , for a chemical reaction, there is no effect of a gravitational potential on the equilibrium constant for a chemical reaction.

The potential ψ in a centrifugal field is given by [34]

$$\psi = -\frac{1}{\omega^2 r^2} \quad (3.1-7)$$

where ω is the angular velocity and r is the distance from the axis of rotation.

3.2 Systems with electric work

3.2a Fundamental equation for the Gibbs energy of a multiphase system with electric work

In considering the thermodynamics of systems in which there are electric potential differences, the activity a_i of an ion is defined in terms of its chemical potential μ_i and the electric potential ϕ_i of the phase the ion is in [35–38]:

$$\mu_i = \mu_i^\circ + RT \ln a_i + z_i F \phi_i \quad (3.2a-1)$$

where μ_i° is the standard chemical potential of ion i in a phase with an electric potential of zero, F is the Faraday constant, and z_i is the charge number. The purpose of this definition is to introduce the activity a_i , which is more convenient than μ_i in discussing experimental data. This shows that the chemical potential of an ion is a function of ϕ_i as well as a_i . The activity has the same functional dependence on intensive properties in the presence of electric potential differences as in their absence. The description of the state for the standard chemical potential μ_i° of species i has to include the statement that μ_i° is the same in the presence of an electric potential as in its absence.

The symbol $\tilde{\mu}_i$ has been used in electrochemistry to describe ionic properties that depend on electric potential. It has the same physical meaning as μ_i on the left-hand side of eq. 3.2a-1 and has been referred to by electrochemists as the electrochemical potential. Thus, $\mu_i^\circ + RT \ln a_i$ can be considered to be the contribution to μ_i or $\tilde{\mu}_i$ independent of the electrical state of the phase in question. However, $\tilde{\mu}_i$ or μ_i in eq. 3.2a-1 is really the chemical potential in the sense of Gibbs in that it is a quantity that is independent of phase at equilibrium.

The form of the fundamental equation for a system involving phases at different electric potentials depends on the system. There is a fundamental equation for each phase, and the fundamental equation for the system is the sum of the fundamental equations for the various phases. This is illustrated here by a system consisting of two aqueous phases separated by a semipermeable membrane. The two phases contain ions A, B, and C, which are involved in the reaction $A + B = C$ in each phase. The membrane is permeable only by ion C. This system has been discussed by Alberty [39]. Since C can diffuse through the membrane without counter ions, the membrane becomes polarized. When electric charge is added to a conductor, as in this case when C diffuses through the membrane, the charge is concentrated on the surface of the conductor so that the bulk phases remain electrically neutral. If C is a cation and some of it has diffused from the α side of the membrane to the β side of the membrane, the membrane has a positively charged layer in the solution on the β side and a negatively charged layer of solution on the α side. These layers are formed in the charge relaxation time of about a nanosecond and have a thickness of the Debye length [40], which is about 1 nm at an ionic strength I of 0.1 M. Many biological membranes have capacitances of about $1 \mu\text{F cm}^{-2}$, and in this case, the charge transfer per square centimeter required to set up a potential difference of 0.1 V is 10^{-12} mol of singly charged ions.

As C diffuses through the membrane a difference in electric potential is set up that opposes the transfer of more C ions, and so an equilibrium difference in electric potential across the membrane is reached.

Since the bulk phases remain electrically neutral, even though they are at different electric potentials, it is convenient to think of this system as having three phases, α , β , and a membrane phase consisting of the membrane and thin layers of solution on either side with thickness of the order of 10 nm (10 Debye lengths). When ion C diffuses through the membrane, these ions can be considered to come from the thin layer on one side of the membrane and to go into the thin layer on the other side. This transfer of the order of 10^{-12} mol of C per cm^2 from one side to the other involves only a small fraction of the C ions in the thin layers. Thus, the amounts of C in phases α and β are not altered by this transfer, which leads to a large electric effect.

The fundamental equations for G for the three phases are

$$dG_{\alpha} = -S_{\alpha}dT + V_{\alpha}dP + \mu_{A\alpha}dn_{A\alpha} + \mu_{B\alpha}dn_{B\alpha} + \mu_{C\alpha}dn_{C\alpha} \quad (3.2a-2)$$

$$dG_{\beta} = -S_{\beta}dT + V_{\beta}dP + \mu_{A\beta}dn_{A\beta} + \mu_{B\beta}dn_{B\beta} + \mu_{C\beta}dn_{C\beta} \quad (3.2a-3)$$

$$dG_{\text{mb}} = (\phi_{\beta} - \phi_{\alpha})dQ \quad (3.2a-4)$$

where G_{mb} is the Gibbs energy of the membrane including the thin layers of solution with diffuse ionic gradients. The fundamental equation for the membrane is written in terms of the charge Q transferred from the α side of the membrane to the β side; it could be written in terms of amounts of C in the thin layers on either side of the membrane, but Q is used to emphasize that this quantity is independent of $n_{C\alpha}$ and $n_{C\beta}$. In subsequent equations, ϕ_{α} is taken as zero as a simplification. In writing eq. 3.2a-4, the contribution of the entropy and volume of the membrane phase to the entropy and volume of the whole system is neglected.

When ionic species are involved, there must be counter ions so that the bulk phases will be electrically neutral. The inclusion of the counter ion in the fundamental equation for a phase increases the number of species by one, but this brings in the electroneutrality condition so that the number of natural variables is not changed. In making equilibrium calculations, it is simpler to omit the counter ions and the electroneutrality condition because the same equilibrium composition is obtained either way. It has to be understood that when ions are involved, there are counter ions to make each of the bulk phases electrically neutral. The membrane phase is an electrically neutral dipolar layer. Water is omitted in writing the fundamental equations because its amounts in the three phases do not change.

The fundamental equation for G for the system is the sum of eqs. 3.2a-2 to 3.2a-4, which is

$$dG = -SdT + VdP + \mu_{A\alpha}dn_{A\alpha} + \mu_{B\alpha}dn_{B\alpha} + \mu_{C\alpha}dn_{C\alpha} + \mu_{A\beta}dn_{A\beta} + \mu_{B\beta}dn_{B\beta} + \mu_{C\beta}dn_{C\beta} + \phi_{\beta}dQ \quad (3.2a-5)$$

where $S = S_{\alpha} + S_{\beta}$ and $V = V_{\alpha} + V_{\beta}$. Because of the reaction in each phase, $dn_{A\alpha} = dn_{B\alpha} = -dn_{C\alpha}$ and $dn_{A\beta} = dn_{B\beta} = -dn_{C\beta}$. This leads to the equilibrium conditions

$$\mu_{A\alpha} + \mu_{B\alpha} = \mu_{C\alpha} \quad (3.2a-6)$$

$$\mu_{A\beta} + \mu_{B\beta} = \mu_{C\beta} \quad (3.2a-7)$$

for the reactions in the two bulk phases:



The transfer of electric charge from the thin layer on the α side of the membrane to the thin layer on the β side leads to the following equilibrium condition

$$\mu_{C\alpha} = \mu_{C\beta} \quad (3.2a-10)$$

because the electric potential difference ϕ_β reaches the value at equilibrium that is required to make $\mu_{C\beta}$ equal to $\mu_{C\alpha}$ at the specified values of $a_{C\alpha}$ and $a_{C\beta}$. This condition corresponds with the reaction

$$C_\alpha = C_\beta \quad (3.2a-11)$$

In other words, the equilibration of C between the phases is accomplished by changing the electric potential of the β phase, rather than changing the amount of C in the β phase.

The equilibrium conditions 3.2a-6, 3.2a-7, and 3.2a-10 can be used to derive the following three equilibrium constant expressions by inserting equation 3.2a-1:

$$K_\alpha = \frac{a_{C\alpha}}{a_{A\alpha}a_{B\alpha}} = \exp\left[-(\mu_C^\circ - \mu_A^\circ - \mu_B^\circ)/RT\right] \quad (3.2a-12)$$

$$K_\beta = \frac{a_{C\beta}}{a_{A\beta}a_{B\beta}} = \exp\left[-(\mu_C^\circ - \mu_A^\circ - \mu_B^\circ)/RT\right] \quad (3.2a-13)$$

$$K_C = \frac{a_{C\beta}}{a_{C\alpha}} = \exp\left[-\frac{Fz_C\phi_\beta}{RT}\right] \quad (3.2a-14)$$

Equation 3.2a-14 is the familiar relation for the membrane potential equation [3,10], except that $a_{C\alpha}$ and $a_{C\beta}$ are not independent variables. Note that the effect of the electric potential cancels in the derivation of the expressions for K_α and K_β and that $K_\alpha = K_\beta$. The equilibrium concentrations of C from eqs. 3.2a-12 and 3.2a-13 can be substituted in eq. 3.2a-14 to obtain

$$\frac{a_{A\beta}a_{B\beta}}{a_{A\alpha}a_{B\alpha}} = \exp\left[-\frac{Fz_C\phi_\beta}{RT}\right] \quad (3.2a-15)$$

or

$$-\frac{RT}{Fz_C} \ln \frac{a_{A\beta}a_{B\beta}}{a_{A\alpha}a_{B\alpha}} = \phi_\beta \quad (3.2a-16)$$

This shows how a reaction between ions can produce a difference in electric potentials between phases at equilibrium.

Substitution of the equilibrium conditions for the three reactions in the fundamental eq. 3.2a-5 yields

$$dG = -SdT + VdP + \mu_{A\alpha}dn_{cA\alpha} + \mu_{A\beta}dn_{cA\beta} + \mu_{C\alpha}dn_{cC} + \phi_\beta dQ \quad (3.2a-17)$$

where $n_{cA\alpha} = n_{A\alpha} - n_{B\alpha}$, $n_{cA\beta} = n_{A\beta} - n_{B\beta}$, $n_{cC\alpha} = n_{C\alpha} + n_{B\alpha}$, $n_{cC\beta} = n_{C\beta} + n_{B\beta}$, and $n_{cC} = n_{cC\alpha} + n_{cC\beta}$. The use of n_{c_i} to represent the amount of a component has been discussed in Section 1.5. Equation 3.2-17 indicates that there are six natural variables; $D = 6$. The criterion for spontaneous change and equilibrium for the system is

$$(dG)_{T,P,n_{cA\alpha},n_{cA\beta},n_{cC},Q} \leq 0 \quad (3.2a-18)$$

The chemical potential of A in the α phase is given by

$$\mu_{A\alpha} = \left(\frac{\partial G}{\partial n_{cA\alpha}}\right)_{T,P,n_{cA\beta},n_{cC},Q} \quad (3.2a-19)$$

3.2b Fundamental equation for the transformed Gibbs energy of a multiphase system with electric work

The equilibrium relations of the preceding section were derived on the assumption that the charge transferred Q can be held constant, but that is not really practical from an experimental point of view. It is better to consider the potential difference between the phases to be a natural variable. That is accomplished by use of the Legendre transform

$$G' = G - \phi_{\beta}Q \quad (3.2b-1)$$

which defines the transformed Gibbs energy G' . Since

$$dG' = dG - \phi_{\beta}dQ - Qd\phi_{\beta} \quad (3.2b-2)$$

substituting eq. 3.2a-17 yields

$$dG' = -SdT + VdP + \mu_{A\alpha}dn_{cA\alpha} + \mu_{A\beta}dn_{cA\beta} + \mu_{cC}dn_{cC} - Qd\phi_{\beta} \quad (3.2b-3)$$

This indicates that there are six natural variables for the transformed Gibbs energy, the same as for the Gibbs energy (eq. 3.2a-17). The criterion for spontaneous change and equilibrium is given by

$$(dG')_{T,P,n_{cA\alpha},n_{cA\beta},n_{cC},\phi_{\beta}} \leq 0 \quad (3.2b-4)$$

This can be used to derive eqs. 3.2a-12 to 3.2a-16. To learn more about the derivatives of the transformed Gibbs energy, the chemical potentials of species are replaced by use of eq. 3.2a-1 to obtain

$$dG' = -SdT + VdP + (\mu_{A}^{\circ} + RT \ln a_{A\alpha})dn_{cA\alpha} + (\mu_{A}^{\circ} + RT \ln a_{A\beta})dn_{cA\beta} \\ + (\mu_{cC}^{\circ} + RT \ln a_{cC\alpha})dn_{cC\alpha} - Qd\phi_{\beta} \quad (3.2b-5)$$

Thus,

$$\left(\frac{\partial G'}{\partial n_{cA\alpha}} \right)_{T,P,n_{cA\beta},n_{cC},\phi_{\beta}} = \mu_{A}^{\circ} + RT \ln a_{A\alpha} = \mu_{A\alpha}' \quad (3.2b-6)$$

This derivative is referred to as the transformed chemical potential of A in the α phase. Substituting this relation in eq. 3.2a-1 yields

$$\mu_i = \mu_i' + z_i F \phi_i \quad (3.2b-7)$$

which shows the relationship between the chemical potential and the transformed chemical potential.

Since this three-phase system has six natural variables at equilibrium ($D = 6$), the number of intensive degrees of freedom f is given by $f = D - p = 6 - 3 = 3$, where p is the number of phases. This is in accord with $f = C - p + 3 = 3 - 3 + 3 = 3$, where the electric potential is considered to be an independent natural variable like T and P .

3.2c Thermodynamic properties of an ion in phases with different electric potentials

Equation 3.2a-5 can be written in a more general way as

$$dG = -SdT + VdP + \sum \mu_{i\alpha}dn_{i\alpha} + \sum \mu_{i\beta}dn_{i\beta} + \phi_{\beta}dQ \quad (3.2c-1)$$

Integration at constant values of the intensive variables yields

$$G = \sum \mu_{i\alpha}n_{i\alpha} + \sum \mu_{i\beta}n_{i\beta} + \phi_{\beta}Q \quad (3.2c-2)$$

The entropy of the system can be obtained by use of the following derivative:

$$S = - \left(\frac{\partial G}{\partial T} \right)_{P, \{n_{i\alpha}\}, \{n_{i\beta}\}, Q} \quad (3.2c-3)$$

where $\{n_{i\alpha}\}$ represents the set of amounts of species in the α phase. Taking this derivative of G yields

$$S = \sum n_{i\alpha} \bar{S}_{i\alpha} + \sum n_{i\beta} \bar{S}_{i\beta} \quad (3.2c-4)$$

where $\bar{S}_{i\alpha}$ is the partial molar entropy of i , since ϕ_β is determined by Q , which is held constant. Substituting eq. 3.2b-7 in eq. 3.2c-2 yields

$$G = \sum \mu'_{i\alpha} n_{i\alpha} + \sum \mu'_{i\beta} n_{i\beta} + F\phi_\beta \sum z_i n_{i\beta} + \phi_\beta Q \quad (3.2c-5)$$

Taking the derivative in eq. 3.2c-3 yields

$$S = \sum n_{i\alpha} S'_{i\alpha} + \sum n_{i\beta} \bar{S}'_{i\beta} \quad (3.2c-6)$$

where $\bar{S}'_{i\alpha}$ is the transformed molar entropy of i in the α phase. Comparing this equation with eq. 3.2c-4 shows that the molar entropy of a species is not affected by the electric potential of a phase: thus, $\bar{S}_i = \bar{S}'_i$ and $S = S'$.

The corresponding molar enthalpy is obtained by use of the Gibbs–Helmholtz equation: $H = -T^2 [\partial(G/T)/\partial T]_P$. Applying this to eqs. 3.2c-1 and 3.2c-2 yields

$$H = \sum n_{i\alpha} \bar{H}_{i\alpha} + \sum n_{i\beta} \bar{H}_{i\beta} + \phi_\beta Q \quad (3.2c-7)$$

where \bar{H}_i is the molar enthalpy of i , and

$$H = \sum n_{i\alpha} \bar{H}'_{i\alpha} + \sum n_{i\beta} \bar{H}'_{i\beta} + F\phi_\beta \sum z_i n_i + \phi_\beta Q \quad (3.2c-8)$$

where \bar{H}'_i is the transformed molar enthalpy. Comparing eqs. 3.2c-7 and 3.2c-8 shows that

$$\bar{H}_i = \bar{H}'_i + Fz_i\phi_\beta \quad (3.2c-9)$$

Thus, the molar enthalpy of an ion is affected by the electric potential of the phase in the same way as the chemical potential (see eq. 3.2b-7).

3.2d Nomenclature of the electrochemical potential

A number of different treatments have been given of multiphase systems with electric potential differences between the phases, starting with Gibbs [1]. An early treatment was made by Guggenheim [41] in which he used μ and referred to it as the electrochemical potential. Later in his textbook, *Thermodynamics* [35], he used the equivalent of eq. 3.2a-1 with $\tilde{\mu}_i$, and he referred to it as the electrochemical potential. In making recommendations about thermodynamic nomenclature for such systems, IUPAC [42–44] has used $\tilde{\mu}_i$ and referred to it as the electrochemical potential. The IUPAC Recommendations for Quantities, Units, and Symbols in Physical Chemistry [45] has recommended $\tilde{\mu}_i$, and this will continue in the next edition with the electrochemical potential defined as

$$\tilde{\mu}_i = \mu_i^0 + RT \ln a_i + z_i F \phi_i \quad (3.2d-1)$$

While the symbol $\tilde{\mu}_i$ has been used widely in electrochemistry, the symbol μ_i (as defined in eq. 3.2a-1) has been used in the preceding three sections. The two symbols have the same meaning. The important point is that this physical quantity is independent of phase at equilibrium. This aspect is particularly important when the effects of temperature and pressure are being discussed and when other kinds of work, e.g., chemical and surface, are also involved. Since both conventions are currently used, it is important to check which convention is being followed.

4. FUNDAMENTAL EQUATIONS OF THERMODYNAMICS FOR SYSTEMS WITH OTHER KINDS OF WORK

4.1 Systems with surface work

A number of treatments of the thermodynamics of systems with interfaces are available [34,35,47,48]. As an example of a system involving surface work, consider a binary liquid solution in contact with its vapor or two immiscible binary solutions at equilibrium with variable surface area between the phases. The fundamental equation for the Gibbs energy of the whole three-phase system is [49]

$$dG = -SdT + VdP + \mu_1^\alpha dn_1^\alpha + \mu_2^\alpha dn_2^\alpha + \mu_1^\beta dn_1^\beta + \mu_2^\beta dn_2^\beta + \mu_1^\sigma dn_1^\sigma + \mu_2^\sigma dn_2^\sigma + \gamma dA_s \quad (4.1-1)$$

Here, γ is the interfacial tension, and A_s is the interfacial area. The superscripts α and β indicate the two bulk liquid phases, and the σ superscript indicates a property of the surface phase. If the three phases are at equilibrium, the values of the chemical potentials are restricted by the following equilibrium conditions: $\mu_1^\alpha = \mu_1^\sigma$, $\mu_1^\alpha = \mu_1^\beta$, $\mu_2^\alpha = \mu_2^\sigma$, and $\mu_2^\alpha = \mu_2^\beta$. In writing these conditions, the phase equilibria are treated like chemical reactions. Since $\mu_1^\alpha = \mu_1^\beta = \mu_1^\sigma = \mu_1$ and $\mu_2^\alpha = \mu_2^\beta = \mu_2^\sigma = \mu_2$, the superscripts on the chemical potentials can be dropped when the system is at equilibrium. Thus, eq. 4.1-1 can be written as

$$dG = -SdT + VdP + \mu_1(dn_1^\alpha + dn_1^\beta + dn_1^\sigma) + \mu_2(dn_2^\alpha + dn_2^\beta + dn_2^\sigma) + \gamma dA_s = -SdT + VdP + \mu_1 dn_{c1} + \mu_2 dn_{c2} + \gamma dA_s \quad (4.1-2)$$

where the amounts of the two components are represented by n_{c1} and n_{c2} :

$$n_{c1} = n_1^\alpha + n_1^\beta + n_1^\sigma \quad (4.1-3)$$

$$n_{c2} = n_2^\alpha + n_2^\beta + n_2^\sigma \quad (4.1-4)$$

At equilibrium, the natural variables for G are indicated by $G(T, P, n_{c1}, n_{c2}, A_s)$. The amounts of components are independent variables because they are the amounts added to the system, but the amounts of species in a phase are not independent variables because they are determined by the equilibrium. Integration of eq. 4.1-2 at constant T, P , and composition yields

$$G = \mu_1 n_{c1} + \mu_2 n_{c2} + \gamma A_s \quad (4.1-5)$$

There is a Gibbs–Duhem equation for each phase, including the interfacial phase, and the sum of these three equations is the Gibbs–Duhem equation for the system, which can be obtained by making the following Legendre transform to define a transformed Gibbs energy G' that has T, P, μ_1, μ_2 , and γ as its natural variables.

$$G' = G - \mu_1 n_{c1} - \mu_2 n_{c2} - \gamma A_s = 0 \quad (4.1-6)$$

It is important that this equation contain n_{c1} and n_{c2} , rather than $n_1^\alpha, n_2^\alpha, n_1^\beta, n_2^\beta, n_1^\sigma$, and n_2^σ , because n_{c1} and n_{c2} are independent variables for the equilibrium system. Taking the differential of G' and substituting eq. 4.1-2 yields

$$0 = -SdT + VdP - n_{c1} d\mu_1 - n_{c2} d\mu_2 - A_s d\gamma \quad (4.1-7)$$

This Gibbs–Duhem equation can be used to derive the Gibbs adsorption equation for a liquid–liquid interface or a liquid–vapor interface. The equation for the system with a liquid–liquid interface is quite complicated, but it reduces to the Gibbs adsorption derived by Bett, Rowlinson, and Saville [47] for a liquid–vapor interface. This equation is

$$d\gamma = -\left[(S^\sigma/A_s) - \bar{S}_1^\alpha \Gamma_1 - \bar{S}_2^\alpha \Gamma_2\right]dT + (x_1^\alpha \Gamma_2 - x_2^\alpha \Gamma_1) \frac{1}{x_1^\alpha} \left(\frac{\partial \mu_2}{\partial x_1^\alpha}\right)_T dx_2^\alpha \quad (4.1-8)$$

where S^σ is the interfacial entropy, the adsorptions of the components are given by $\Gamma_1 = n_1^\sigma / A_s$ and $\Gamma_2 = n_2^\sigma / A_s$, and x_1^α and x_2^α are the mole fractions of species 1 and 2 in the liquid phase. This indicates that two derivatives can be determined experimentally.

$$\left(\frac{\partial \gamma}{\partial T}\right)_{P, x_2^\alpha} = -\left[(S^\sigma/A_s) - \bar{S}_1^\alpha \Gamma_1 - \bar{S}_2^\alpha \Gamma_2\right] \quad (4.1-9)$$

and

$$\left(\frac{\partial \gamma}{\partial x_2^\alpha}\right)_{T, P} = (x_1^\alpha \Gamma_2 - x_2^\alpha \Gamma_1) \frac{1}{x_1^\alpha} \left(\frac{\partial \mu_2}{\partial x_1^\alpha}\right)_T \quad (4.1-10)$$

Thus,

$$\Gamma = x_1^\alpha \Gamma_2 - x_2^\alpha \Gamma_1 \quad (4.1-11)$$

can be determined from measurements of the surface tension as a function of x_1^α .

The IUPAC recommendations on the thermodynamic properties of surfaces [50] are based on Legendre transforms, but they do not follow all of the conventions recommended here.

4.2 Systems with mechanical work

The thermodynamics of crystals is discussed very thoroughly by Wallace [51]. He shows that the fundamental equation for the Helmholtz energy of a crystal under stress is given by

$$dA = -SdT + V \sum_{ij} \tau_{ij} d\eta_{ij} \quad (4.2-1)$$

where τ_{ij} is the tensor representing the applied stress and η_{ij} is the Lagrangian strain parameter. The applied stress is assumed to be uniform (i.e., constant on a given crystal surface), and the resulting strain is homogeneous (i.e., uniform throughout the crystal).

Rather than going into the details of this subject here, we simply observe that the length L of a solid subjected to a force f of extension is an extensive property, which is a natural variable of U , H , A , and G . The fundamental equations for U and A can be written

$$dU = TdS + fdL \quad (4.2-2)$$

$$dA = -SdT + fdL \quad (4.2-3)$$

if PV work is negligible. This application of thermodynamics is of special interest to chemists in connection with the properties of high polymers. For rubber, the tension is primarily an entropy effect. In making stress-strain measurements, the change in the force f with temperature can be measured, but it may be more convenient to hold the force constant and measure the length. In this case, it is convenient to make the force a natural variable by making the Legendre transform

$$A' = A - fL = 0 \quad (4.2-4)$$

This is a complete Legendre transform. Taking the differential of this equation and substituting eq. 4.2-3 yields

$$0 = -SdT - Ldf \quad (4.2-5)$$

which is a Gibbs–Duhem equation. This yields the Maxwell equation

$$\left(\frac{\partial S}{\partial f}\right)_T = \left(\frac{\partial L}{\partial T}\right)_f \quad (4.2-6)$$

Chemical work is coupled with mechanical work in muscle contraction.

4.3 Systems with work of electric polarization

The effect of work of electric transport on thermodynamics has been discussed in Section 3.2, but here we are concerned with the work of producing electric polarization in a nonconductor by an electric field. This topic has been discussed in a number of books [14,34]. In treating electric polarization, it is of interest to consider electrically polarizable systems involving elongation work, but no PV work. The fundamental equation for U for such a system is

$$dU = TdS + fdL + \mathbf{E} \cdot d\mathbf{p} \quad (4.3-1)$$

where \mathbf{E} is the electric field strength and \mathbf{p} is the dipole moment of the system. When it is not necessary to consider pressure as a natural variable, we use the Helmholtz energy A , rather than the Gibbs energy. The fundamental equation for A is

$$dA = -SdT + fdL + \mathbf{E} \cdot d\mathbf{p} \quad (4.3-2)$$

In discussions of thermoelectric, pyroelectric, and piezoelectric effects, it is advantageous to use the transformed Helmholtz energy obtained with the Legendre transform

$$A' = A - fL - \mathbf{E} \cdot \mathbf{p} = 0 \quad (4.3-3)$$

This is a complete Legendre transform and yields a Gibbs–Duhem equation. Taking the differential of A' and substituting 4.3-2 yields

$$0 = -SdT + VdP - Ldf - \mathbf{p} \cdot d\mathbf{E} \text{ or } 0 = -SdT + VdP - Ldf - pdE \quad (4.3-4)$$

where the last form applies to an isotropic system. This Gibbs–Duhem equation yields three Maxwell equations [14]:

thermoelastic:

$$\left(\frac{\partial S}{\partial f}\right)_{E,T} = \left(\frac{\partial L}{\partial T}\right)_{f,E} \quad (4.3-5)$$

pyroelectric:

$$\left(\frac{\partial S}{\partial E}\right)_{T,f} = \left(\frac{\partial p}{\partial T}\right)_{f,E} \quad (4.3-6)$$

piezoelectric:

$$\left(\frac{\partial L}{\partial E}\right)_{T,f} = \left(\frac{\partial p}{\partial f}\right)_{T,E} \quad (4.3-7)$$

Note that Gibbs–Duhem equations are especially useful for obtaining Maxwell equations in which the derivatives are with respect to intensive variables and the variables held constant are all intensive variables.

4.4 Systems with work of magnetic polarization

The effects of magnetic polarization on thermodynamics are discussed in several places in the literature [14,34,52,53]. The fundamental equation for U for a system involving magnetic polarization is

$$dU = TdS + \mathbf{B} \cdot d\mathbf{m} \quad (4.4-1)$$

where \mathbf{B} is the magnetic flux density and \mathbf{m} is the magnetic moment of the system. It is assumed that PV work is negligible. The corresponding fundamental equation for the Helmholtz energy is

$$dA = -SdT + \mathbf{B} \cdot d\mathbf{m} \text{ or } dA = -SdT + Bdm \quad (4.4-2)$$

In order to treat adiabatic demagnetization, it is advantageous to use the magnetic flux density as an intensive variable. A transformed Helmholtz energy is defined by

$$A' = A - \mathbf{B} \cdot \mathbf{m} = 0 \quad (4.4-3)$$

This is the complete Legendre transform, and it yields the Gibbs–Duhem equation.

$$0 = -SdT - \mathbf{m} \cdot d\mathbf{B} \text{ or } 0 = -SdT - mdB \quad (4.4-4)$$

where the last form applies to an isotropic system. This yields the Maxwell equation

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial m}{\partial T}\right)_B \quad (4.4-5)$$

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

5. RECOMMENDATIONS

1. These recommendations are based on the following definitions of the enthalpy H , Helmholtz energy A , and Gibbs energy G : $H = U + PV$, $A = U - TS$, and $G = U + PV - TS$. We recommend that these definitions not be altered. If the fundamental equation for U involves terms for work in addition to PV work, they should be of the form (intensive property)d(extensive property). Thus, the fundamental equations for U , H , A , and G involve the same non- PV work terms, which involve the differentials of extensive properties.
2. Natural variables are important because if a thermodynamic potential can be determined as a function of its natural variables, all of the other thermodynamic properties of the system can be calculated by taking partial derivatives. Natural variables are also important because they are held constant in the criterion for spontaneous change and equilibrium. It is important to distinguish between natural variables before and after the application of constraints resulting from phase equilibrium and chemical equilibrium. The criterion for equilibrium is stated in terms of the natural variables after all the constraints have been applied.
3. The chemical potential of species i is defined by

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j,X_i} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j,X_i} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j,X_i} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j,X_i} \quad (5-1)$$

where $j \neq i$ and X_i represent all of the independent extensive variables in non- PV and non-chemical 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 and have different pressures or different electric potentials. When phase equilibrium and chemical equilibrium are involved, these derivatives can be written in terms of components rather than 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 Legendre transforms are of the form, $U' = U - \Sigma$ (extensive property)(conjugate intensive property), and so the transformed thermodynamic potential U' can always be represented by Callen's nomenclature as $U[P_i]$, where the P_i are the intensive properties introduced as natural

variables by the Legendre transform. This nomenclature can be extended by making Legendre transforms of H , A , and G , and representing the transformed thermodynamic potentials by $H[P_i]$, $A[P_i]$, and $G[P_i]$, where the P_i are the intensive properties introduced as natural variables in addition to the intensive variables that have been introduced by the definitions of these thermodynamic potentials. Examples are $G[\text{pH}, \text{pMg}]$, $G[\phi]$, $A[f]$, $G[r]$, and $U[E]$. 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 when this notation is used.

5. The transformed chemical potential of species i is defined by

$$\begin{aligned} \mu'_i &= \left(\frac{\partial U'}{\partial n_i} \right)_{S, V, n_j, X_i, P_j} = \left(\frac{\partial H'}{\partial n_i} \right)_{S, P, n_j, X_i, P_j} \\ &= \left(\frac{\partial A'}{\partial n_i} \right)_{T, V, n_j, X_i, P_j} = \left(\frac{\partial G'}{\partial n_i} \right)_{T, P, n_j, X_i, P_j} \end{aligned} \quad (5-2)$$

where $j \neq i$ and 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 variables X_i . When phase equilibrium and chemical equilibrium are involved, these derivatives can be written in terms of components rather than species.

6. The properties subscripted on partial derivatives are always natural variables. It is important to be sure that natural variables are independent. The number D of natural variables is given by $f + p$, where f is the number of independent intensive variables given by the phase rule and p is the number of phases.

6. APPENDIX: FIELDS AND DENSITIES

The variables in a fundamental equation are often classified as intensive variables and extensive variables, but there is a problem because a fundamental equation can be divided by volume, mass, or total amount. When this is done, the fundamental equation is expressed entirely in terms of intensive variables. When a fundamental equation is written in this way, it is important to make a distinction between two types of intensive variables because some of the intensive variables are uniform throughout a system at equilibrium and others are not. Griffiths and Wheeler [54] recommended that a distinction be made by referring to T , P , μ_i , electric field strength, and magnetic field strength as “fields” and referring to extensive variables divided by volume, mass, or amount as “densities”. The important feature of fields is that they have uniform values in a system at equilibrium. The pressure is an exception to this statement when there are curved surfaces or when there are semipermeable membranes that lead to an osmotic pressure at equilibrium. When fundamental equations are written for U , H , S , A , G , etc., some of the variables are fields and others are extensive variables. When fundamental equations are divided by volume, mass, or amount, some of the variables are fields and the others are densities.

7. NOMENCLATURE

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

a_i	activity of species i (dimensionless)
A	Helmholtz energy (J)
A'	transformed Helmholtz energy (J)

A_s	surface area (m^2)
A	conservation matrix ($C \times N$) (dimensionless)
B	magnetic flux density (T)
B	magnitude of the magnetic flux density, $B = \mathbf{B} $ (T)
C	number of components ($C = N - R$) (dimensionless)
c°	standard state concentration (mol L^{-1})
D	number of natural variables (dimensionless)
E	electric field strength (V m^{-1})
E	magnitude of the electric field strength, $E = \mathbf{E} $ (V m^{-1})
f	force (N)
f	number of independent intensive variables (degrees of freedom) (dimensionless)
F	Faraday (96 485 C mol^{-1})
g	acceleration of gravity (m s^{-2})
G	Gibbs energy (J)
G'	transformed Gibbs energy (J)
$\Delta_f G_i^\circ$	standard Gibbs energy of formation of species i (kJ mol^{-1})
$\Delta_f G_i'^{\circ}$	standard transformed Gibbs energy of formation of reactant i (kJ mol^{-1})
$\Delta_r G^\circ$	standard Gibbs energy of reaction (J mol^{-1})
$\Delta_r G'^{\circ}$	standard transformed Gibbs energy of reaction at a specified pressure or concentration of a species (J mol^{-1})
$\Delta_r G$	Gibbs energy of reaction (J mol^{-1})
$\Delta_r G'$	transformed Gibbs energy of reaction at a specified pressure or concentration of a species (J mol^{-1})
h	height above the surface of the earth (m)
H	enthalpy (J)
H'	transformed enthalpy (J)
$\Delta_r H$	reaction enthalpy (J mol^{-1})
\bar{H}_i	partial molar enthalpy of i (J mol^{-1})
\bar{H}_i'	partial molar transformed enthalpy of i (J mol^{-1})
$\bar{H}_i'^{\circ}$	standard partial molar transformed enthalpy of i (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 at specified concentration of a species (dimensionless)
L	elongation (m)
m	mass (kg)
\mathbf{m}	magnetic dipole moment of the system (J T^{-1})
m	magnitude of the magnetic moment of the system (J T^{-1})
M_i	molar mass of species i (kg mol^{-1})
n_i	amount of species i (mol)
n_{ci}	amount of component i (mol)

n	amount of species matrix ($N \times 1$) (mol)
n_c	amount of component matrix ($C \times 1$) (mol)
n_i'	amount of reactant i (sum of species) (mol)
n_i^σ	interfacial amount of species i (mol)
n_{cB}	amount of B component (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 (pseudoisomer groups) (dimensionless)
$N_H(i)$	number of hydrogen atoms in a molecule of i (dimensionless)
$N_{Mg}(i)$	number of magnesium atoms in a molecule of i (dimensionless)
$\bar{N}_B(i)$	average number of B bound by a molecule of i (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_j	intensive variable in Callen's nomenclature (varies)
p	electric dipole moment of the system (C m)
p	magnitude of the dipole moment of the system (C m)
p	number of phases (dimensionless)
pH	$-\lg([H^+]/c^\circ)$ (dimensionless)
pMg	$-\lg([Mg^{2+}]/c^\circ)$ (dimensionless)
Q	canonical ensemble partition function (dimensionless)
Q_i	electric charge transferred (C)
r_i	equilibrium mole fraction of i within an isomer group or pseudoisomer group (dimensionless)
R	gas constant ($8.314\ 472\ \text{J K}^{-1}\ \text{mol}^{-1}$)
R	number of independent reactions (dimensionless)
S	entropy (J K^{-1})
$\Delta_r S$	entropy of reaction ($\text{J K}^{-1}\ \text{mol}^{-1}$)
$\Delta_r S'$	transformed entropy of reaction ($\text{J K}^{-1}\ \text{mol}^{-1}$)
\bar{S}_i	partial molar entropy of i ($\text{J K}^{-1}\ \text{mol}^{-1}$)
\bar{S}_i'	partial molar transformed entropy of i ($\text{J K}^{-1}\ \text{mol}^{-1}$)
\bar{S}_i°	standard partial molar transformed entropy of i ($\text{J K}^{-1}\ \text{mol}^{-1}$)
S'	transformed entropy (J K^{-1})
T	temperature (K)
U	internal energy (J)
U'	transformed internal energy (J)
$U[P_j]$	Callen's nomenclature for the transformed internal energy that has intensive variable P_j as a natural variable (J)
V	volume (m^3)
X_k	extensive variable in Callen's nomenclature (varies)
x_i	mole fraction of i (dimensionless)
z_i	number of protonic charges on ion i (dimensionless)
γ	surface tension (N m^{-1})

Γ_i	adsorption of component i (n_i^σ/A_s) (mol m^{-2})
Δ	isothermal-isobaric partition function (dimensionless)
η_{ij}	Lagrangian strain parameter
μ_i	chemical potential of species i (J mol^{-1})
μ_i^0	standard chemical potential of species i (J mol^{-1})
μ_i'	transformed chemical potential of reactant i (J mol^{-1})
$\boldsymbol{\mu}$	chemical potential matrix ($1 \times N$)(J mol^{-1})
$\boldsymbol{\mu}_c$	component chemical potential matrix ($1 \times C$)(J mol^{-1})
$\tilde{\mu}_i$	electrochemical potential of i defined by eq. 3.2d-1 (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)
$\boldsymbol{\tau}_{ij}$	applied stress tensor
ξ_j	extent of reaction (mol)
Ξ	ground canonical partition functional (dimensionless)
ϕ_i	electric potential of the phase containing species i (V, J C^{-1})
ψ	gravitational potential (J kg^{-1})

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