Thermodynamics of Reactions Involving Phases at Different Electric Potentials

Robert A. Alberty

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

Received: May 14, 1997; In Final Form: June 27, 1997[⊗]

A chemical or biochemical reaction can drive an ion through a semipermeable membrane and set up an electric potential difference that can cause the transport of a different ion through the membrane against its concentration gradient. This article treats the thermodynamics of a system in which an ionic reaction A + B = C drives C through a membrane permeable only to C. The fundamental equation for the Gibbs energy G leads to a criterion for spontaneous change and equilibrium involving the transferred charge Q as a natural variable. This leads to an extension of the membrane equilibrium equation. It is shown that the number D of natural variables is equal to the number f of independent intensive variables (degrees of freedom) plus the number of phases. Since the charge transferred is not a convenient natural variable from an experimental point of view, a Legendre transform is used to define a transformed Gibbs energy G' that has the potential difference between the phases as a natural variable. This leads to the transformed chemical potential μ_i' that is related to the chemical potential by $\mu_i = \mu_i' + Fz_i\phi_i$. Since the chemical potential, which has the same value in phases at equilibrium, is given by $\mu_i = \mu_i^\circ + RT \ln a_i + Fz_i\phi_i$, the transformed chemical potential for i in a multiphase system with potential differences is given by $\mu_i' = \mu_i^\circ + RT \ln a_i$.

Introduction

A previous article[1] treated a system in which an ionic reaction $A_\alpha + B_\alpha = C_\beta$ occurs in a two-phase system in which there is a difference in electric potentials between phases α and β. The difference in electric potentials was assumed to be established and maintained by external forces. In that case the electric potential difference is not affected by the reaction that occurs in the system, and the electric potentials do not appear in the Gibbs−Duhem equations for the phases because the other intensive properties are independent of the electric potentials.[2] This article is about a different system in which the ionic reaction A + B = C occurs in both phases, but the electric potential difference is not determined by external forces. The phases are separated by a membrane permeable only by C, and the diffusion of C through the membrane produces an electric potential difference between the phases. The maximum potential difference is reached at equilibrium, and this article is concerned with the thermodynamics of this type of reaction system, which in living cells creates a potential difference that drives the transport of other ions through a cell membrane.

In considering the thermodynamics of systems in which there are electric potential differences, the activity a_i of an ion can be defined in terms of its chemical potential μ_i and the electric potential ϕ_i of the phase it is in by[3,4,5]

$$\mu_i = \mu_i^\circ + RT \ln a_i + Fz_i\phi_i \qquad (1)$$

where μ_i° is the standard chemical potential in a phase where the electric potential is 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 here has the same functional dependence on intensive variables in the presence of electric potential differences as in the absence of electric potential differences. When eq 1 is used in a multiphase system, the specification of the standard state for the standard chemical potential μ_i° must include the statement

that μ_i° is the same in the presence of electric potential as in the absence of electric potential. In the previous article[1] $\mu_i'^\circ$ was used in place of μ_i° in eq 1, but it was pointed out that $\mu_i'^\circ$ was independent of the electric potential of a phase.

The fundamental equation for the Gibbs energy for a multiphase system in which an electric potential is set up by the diffusion of an ion contains an electric work term of the form $(\phi_\beta - \phi_\alpha)dQ$, where Q is the charge transferred. This fundamental equation can be used for derivations, but Q is not a convenient natural variable from an experimental point of view. Therefore, it is useful to introduce the electric potential difference as a natural variable by use of a Legendre transform, which defines a transformed Gibbs energy.[6,7] As emphasized by Callen[8] the definition of a new thermodynamic potential requires a new symbol and a new name. The use of a Legendre transform may also require new symbols for the derivatives of the new thermodynamic potential, but they are related to familiar derivatives.

Fundamental Equation for the Gibbs Energy of a One-Phase System

For an open one-phase system that does not involve chemical reactions, the fundamental equation for the Gibbs energy is

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

where S is the entropy, N is the number of different species, and μ_i and n_i are the chemical potential and amount of species i. When there are no additional constraints on this system, the natural variables for G are T, P, $\{n_i\}$, where $\{n_i\}$ is the set of amounts of species, as indicated by the differential terms in eq 2. The natural variables are important because they are used in stating the criterion for spontaneous change and equilibrium based on a particular thermodynamic potential: in this case, $(dG)_{T,P,\{n_i\}} \leq 0$. For a one-phase system without chemical reactions, the entropy of the system and the chemical potentials of species are given by

---

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}} \tag{3}$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq i} \tag{4}$$

These three equations are changed when there are additional constraints of chemical equilibrium and phase equilibrium on the system because the amounts of species are no longer independent variables. Therefore, it is necessary to use amounts of components, which are independent variables.

The natural variables for a system are also 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 calculated by taking partial derivatives, as indicated by eqs 3 and 4. The number of natural variables is equal to the number of conjugate pairs in the fundamental equation, and the specification of natural variables describes the extensive state of the system. In view of the importance of the natural variables, it is useful to have a symbol for the number of natural variables for a system, in the same way that there is a symbol f for the number of independent intensive properties (degrees of freedom) for a system: namely, $f = N - p + 2$ for a system without chemical reactions and $f = N - R - p + 2 = C - p + 2$ for a system with chemical reactions, where N is the number of species, p is the number of phases, R is the number of independent reactions, and $C = N - R$ is the number of components. It is convenient to use the symbol D for the number of natural variables; the symbol D was used by M. Bailyn in correspondence with R. A. Alberty. The number of Legendre transforms of the internal energy of a system is given by $2^D - 1$, and so there are 2^D thermodynamic potentials related by Legendre transforms.[6] One of the Legendre transforms yields the Gibbs−Duhem equation for the system. The number of Maxwell equations for each of these thermodynamic potentials is given[6] by $D(D - 1)/2$.

The relation between D and f can be derived by extending the derivation of the phase rule to include extensive variables. First, consider a system that does not involve chemical reactions. The composition of a phase can be specified by stating $N - 1$ mole fractions, and the compositions of p phases can be specified by stating $p(N - 1)$ mole fractions. The amounts of phases are independent extensive properties, and usually T and P are independent intensive properties. Therefore, the number of properties required to describe the extensive state of a system is equal to $p(N - 1) + p + 2$. The number of relationships between the chemical potentials of a single species between phases is $p - 1$. Since there are N species, there are $N(p - 1)$ equilibrium relationships. The difference D between the number of variables and the number of relationships is given by $D = p(N - 1) + p + 2 - N(p - 1) = N + 2$. Second, consider a system involving chemical reactions. There are R additional constraints, and so $D = N - R + 2 = C + 2$. In both cases, $D = f + p$. Further independent work terms in the fundamental equation increase D and f. The number D of independent extensive variables is unique, but the choice is not. For example, fundamental eq 2 can be written in terms of the total amount $n = \Sigma n_i$ and the mole fractions of $N - 1$ species.

In view of the importance of the number D of natural variables for the multiphase systems discussed later, the following summary of simpler systems can be used as a reference. For a system involving one species and two phases, $f = 1$ and $D = 3$ so that the natural variables for G are T, n_α, and n_β, or P, n_α, and n_β, where n_α and n_β are the amounts of the two phases. For a system involving two species in two phases, $f = 2$ and $D = 4$ so that the natural variables for G are T, P, n_{c1}, and n_{c2}, where $n_{c1} = n_{1\alpha} + n_{1\beta}$ and $n_{c2} = n_{2\alpha} + n_{2\beta}$, or T, P, n_α, and n_β, where $n_\alpha = n_{1\alpha} + n_{2\alpha}$ and $n_\beta = n_{1\beta} + n_{2\beta}$. For a system involving three species in two phases, $f = 3$ and $D = 5$ so that the natural variables for G are T, P, n_{c1}, n_{c2}, and n_{c3}, where $n_{c1} = n_{1\alpha} + n_{1\beta}$, $n_{c2} = n_{2\alpha} + n_{2\beta}$, and $n_{c3} = n_{3\alpha} + n_{3\beta}$, or T, P, n_{c1}/n_{c2}, n_α, and n_β, where $n_\alpha = n_{1\alpha} + n_{2\alpha} + n_{3\alpha}$ and $n_\beta = n_{1\beta} + n_{2\beta} + n_{3\beta}$. The calculation of the number of independent intensive variables in complicated systems is aided by the use of matrix methods.[9]

Fundamental Equation for the Gibbs Energy for a Two-Phase Reaction System with a Semipermeable Membrane

It is assumed that the reaction A + B = C occurs in both phases, but the membrane separating the two aqueous phases is permeable only by ion C. Since C can diffuse through the membrane without counterions, both phases become electrically charged. However, when electric charge is added to a conductor, the charge is concentrated on the surface so that the bulk of the conductor is electrically neutral. Thus the membrane has a negatively-charged layer in the solution on one side and a positively-charged layer in the solution on the other side. These layers are formed in the charge relaxation time of about a nanosecond and have a thickness of the Debye length,[10] which is about 1 nm at an ionic strength of 0.1 M. The amount of charge transfer required to set up a significant electric potential difference is very small. Many biological membranes[10] have capacitances of about 1 μF per cm^2. The charge transfer per square centimeter required to set up a potential difference of 0.1 V is therefore 10^{-12} mol of singly-charged ions.

The membrane becomes polarized by the electric field due to the two charged layers, but we do not need to include the polarization energy of the membrane in the fundamental equation because the fundamental equation is concerned with the work of transferring electric charge from the α phase to the β phase. The membrane and the diffuse layers of charge on either side form a capacitor, and the stored energy U is given by

$$U = \frac{1}{2}Q(\phi_\beta - \phi_\alpha) \tag{5}$$

Since the capacitance is $C = Q/(\phi_\beta - \phi_\alpha)$

$$U = Q^2/2C \tag{6}$$

At constant capacitance, the differential of the stored energy is given by

$$dU = Q\, dQ/C \tag{7}$$

Substituting the expression for the capacitance yields

$$dU = (\phi_\beta - \phi_\alpha)dQ \tag{8}$$

This gives the work of transferring charge, which is independent of the dielectric properties of the membrane.[11]

There is another way to derive the expression for the electric work term, which is based on the work in changing the polarization of a dielectric solid.[12,13] The differential work is given by

$$\text{d}w = V\epsilon_0 \mathbf{E}\, d\mathbf{E} + \mathbf{E}\, d\mathbf{P} \tag{9}$$

where ϵ_0 is the permittivity of vacuum, $\mathbf{E}$ is the electric field strength, and $\mathbf{P}$ is the extensive polarization. The first term is the work required to increase the electric field strength by d$\mathbf{E}$

Reactions Involving Phases at Different Potentials

J. Phys. Chem. B, Vol. 101, No. 36, 1997 **7193**

and would be present if the membrane was replaced by a vacuum, and so this term does not contribute since the transfer of charge through a membrane is accomplished at constant electric field strength. In the second term the electric field strength is given by $(\phi_\alpha - \phi_\beta)/l$, where l is the thickness of the membrane, and the polarization is given by lQ. Thus $\mathbf{E}\, d\mathbf{P} = (\phi_\beta - \phi_\alpha)dQ$ at constant l, in agreement with eq 8.

The fundamental equations for G for the phases on either side of the membrane are

$$dG_\alpha = -S_\alpha\, dT + V_\alpha\, dP + \mu_{A\alpha}\, dn_{A\alpha} + \mu_{B\alpha}\, dn_{B\alpha} + \mu_{C\alpha}\, dn_{C\alpha} + \phi_\alpha\, dQ_\alpha \quad (10)$$

$$dG_\beta = -S_\beta\, dT + V_\beta\, dP + \mu_{A\beta}\, dn_{A\beta} + \mu_{B\beta}\, dn_{B\beta} + \mu_{C\beta}\, dn_{C\beta} + \phi_\beta\, dQ_\beta \quad (11)$$

where $n_{i\alpha}$ is the amount of a species in the α phase. Since $dQ_\alpha = -dQ_\beta = dQ$, the fundamental equation for G for this two-phase system prior to the establishment of phase equilibrium and chemical equilibrium is

$$dG = -S\, dT + V\, dP + \mu_{A\alpha}\, dn_{A\alpha} + \mu_{B\alpha}\, dn_{B\alpha} + \mu_{C\alpha}\, dn_{C\alpha} + \mu_{A\beta}\, dn_{A\beta} + \mu_{B\beta}\, dn_{B\beta} + \mu_{C\beta}\, dn_{C\beta} + (\phi_\beta - \phi_\alpha)dQ \quad (12)$$

The charge transfer involves only C because the membrane is impermeable to the other ions and water. Counterions are present in both phases so that the bulk phases are electrically neutral, but it is not necessary to include counterions or water in the fundamental equation because their amounts do not change. Note that a species that is in more than one phase counts as a different species in each phase, so that there are $N = 6$ species.

Assuming that the chemical reaction occurs in both phases and that C can diffuse through the membrane, there are three independent reactions:

$$A_\alpha + B_\alpha = C_\alpha \quad (13)$$

$$A_\beta + B_\beta = C_\beta \quad (14)$$

$$C_\alpha = C_\beta \quad (15)$$

Note that the phase transfer is treated like a chemical reaction. Dividing up the six chemical terms in eq 12 into three reactions is difficult, and so it is convenient to use eq 12 in matrix notation[9]

$$dG = -S\, dT + V\, dP + \boldsymbol{\mu}'\, d\mathbf{n} + (\phi_\beta - \phi_\alpha)dQ \quad (16)$$

where $\boldsymbol{\mu}'$ is the $1 \times N$ matrix of chemical potentials and $\mathbf{n}$ is the $N \times 1$ matrix of amounts of species. The extent of reaction matrix $\boldsymbol{\xi}$ is defined by

$$\mathbf{n} = \mathbf{n}_0 + \boldsymbol{\nu\xi} \quad (17)$$

where $\boldsymbol{\nu}$ is the $N \times R$ stoichiometric number matrix and $\boldsymbol{\xi}$ is the $R \times 1$ extent of reaction matrix. Substituting $d\mathbf{n} = \boldsymbol{\nu}\, d\boldsymbol{\xi}$ in eq 16 yields

$$dG = -S\, dT + V\, dP + \boldsymbol{\mu\nu}\, d\boldsymbol{\xi} + (\phi_\beta - \phi_\alpha)dQ \quad (18)$$

The stoichiometric number matrix for reactions 13−15 is

		rx 13	rx 14	rx 15
$\nu =$	A_α	-1	0	0
	B_α	-1	0	0
	C_α	1	0	-1
	A_β	0	-1	0
	B_β	0	-1	0
	C_β	0	1	1

$$(19)$$

Carrying out the matrix multiplications in eq 18 yields

$$dG = -S\, dT + V\, dP + (-\mu_{A\alpha} - \mu_{B\alpha} + \mu_{C\alpha})d\xi_{13} + (-\mu_{A\beta} - \mu_{B\beta} + \mu_{C\beta})d\xi_{14} + (-\mu_{C\alpha} + \mu_{C\beta})d\xi_{15} + (\phi_\beta - \phi_\alpha)dQ \quad (20)$$

which shows the equilibrium conditions ($\mu_{A\alpha} + \mu_{B\alpha} = \mu_{C\alpha}$, $\mu_{A\beta} + \mu_{B\beta} = \mu_{C\beta}$, and $\mu_{C\alpha} = \mu_{C\beta}$) for the three reactions. It should be noted that the effect of an electric potential difference between the phases cancels in reactions 13 and 14, but not in reaction 15. In order to state the criterion of spontaneous change and equilibrium for the system, it is necessary to identify a suitable set of components, since the components are independent variables. This is done by substituting the equilibrium conditions for the three reactions into eq 12. When this is done in such a way to eliminate $\mu_{B\alpha}$, $\mu_{B\beta}$, and $\mu_{C\alpha}$ the following fundamental equation is obtained.

$$dG = -S\, dT + V\, dP + \mu_{A\alpha}\, dn_{cA\alpha} + \mu_{A\beta}\, dn_{cA\beta} + \mu_C\, dn_{cC} + (\phi_\beta - \phi_\alpha)dQ \quad (21)$$

where n_c represents the amount of a component. The partial derivative of the Gibbs energy with respect to the amount of a component yields the chemical potential of a species.

$$\left(\frac{\partial G}{\partial n_{cA\alpha}}\right)_{T,P,n_{cA\beta},n_{cC},Q} = \mu_{A\alpha} \quad (22)$$

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

$$n_{cA\alpha} = n_{A\alpha} - n_{B\alpha} \quad (23)$$

$$n_{cA\beta} = n_{A\beta} - n_{B\beta} \quad (24)$$

$$n_{cC} = n_{C\alpha} + n_{C\beta} + n_{B\alpha} + n_{B\beta} \quad (25)$$

Since $\mu_{C\alpha} = \mu_{C\beta}$, these symbols are replaced with μ_C in eq 21. Equation 21 indicates that there are six natural variables, and so $D = 6$. The criterion for equilibrium based on G is

$$(dG)_{T,P,n_{cA\alpha},n_{cA\beta},n_{cC},Q} \leq 0$$

Integration of eq 22 at constant values of the intensive variables yields

$$G = \mu_{A\alpha}n_{cA\alpha} + \mu_{A\beta}n_{cA\beta} + \mu_C n_{cC} + (\phi_\beta - \phi_\alpha)Q \quad (26)$$

To identify a set of independent intensive variables, it is necessary to start with the fundamental equations for the two phases. Introduction of the equilibrium relations into eq 10 and 11 yields

7194 *J. Phys. Chem. B, Vol. 101, No. 36, 1997*

Alberty

$$dG_\alpha = -S_\alpha \, dT + V_\alpha \, dP + \mu_{A\alpha} \, dn_{cA\alpha} + \mu_C \, dn_{cC\alpha} + \phi_\alpha dQ_\alpha \tag{27}$$

$$dG_\beta = -S_\beta \, dT + V_\beta \, dP + \mu_{A\beta} \, dn_{cA\beta} + \mu_C \, dn_{cC\beta} + \phi_\beta \, dQ_\beta \tag{28}$$

Since $dQ_\alpha = -dQ_\beta = dQ$, these two equations add up to eq 21. Now the following Legendre transforms are used to interchange the roles of potentials and amounts:

$$G_\alpha'' = G_\alpha - \mu_{A\alpha}n_{cA\alpha} - \mu_C n_{cC\alpha} - \phi_\alpha Q_\alpha \tag{29}$$

$$G_\beta'' = G_\beta - \mu_{A\beta} \, dn_{cA\beta} - \mu_C \, dn_{cC\beta} - \phi_\beta Q_\beta \tag{30}$$

Since $G_\alpha'' = 0$ and $G_\beta'' = 0$, this yields the Gibbs–Duhem equations for the two phases:

$$0 = -S_\alpha \, dT + V_\alpha \, dP - n_{cA\alpha} \, d\mu_{A\alpha} - n_{cC\alpha} \, d\mu_C - Q_\alpha \, d\phi_\alpha \tag{31}$$

$$0 = -S_\beta \, dT + V_\beta \, dP - n_{cA\beta} \, d\mu_{A\beta} - n_{cC\beta} \, d\mu_C - Q_\beta \, d\phi_\beta \tag{32}$$

It looks like there are seven intensive variables, but this is not true because only the difference between the electric potentials of the phases is important. Therefore, ϕ_α can be taken to be equal to zero. Since there are six variables and two equations, $f = 4$, which can be taken to be T, P, $\mu_{A\alpha}$, and ϕ_β. The number D of natural variables is given by $D = f + p = 4 + 2 = 6$.

There is another way to write the Gibbs–Duhem equations that recognizes the membrane as a phase. The membrane region includes a little more than 1 nm on either side where there is a diffuse charged layer. The membrane plus the electrically-charged regions on either side is electrically neutral, but it is the site of the electric work. The Gibbs–Duhem equations for the three phases are

$$0 = -S_\alpha \, dT + V_\alpha \, dP - n_{cA\alpha} \, d\mu_{A\alpha} - n_{cC\alpha} \, d\mu_C \tag{33}$$

$$0 = -S_\beta \, dT + V_\beta \, dP - n_{cA\beta} \, d\mu_{A\beta} - n_{cC\beta} \, d\mu_C \tag{34}$$

$$0 = -S_m \, dT + V_m \, dP - Q \, d\phi_\beta \tag{35}$$

Since there are six variables and three independent equations, $f = 3$, which can be taken as T, $\mu_{A\alpha}$, and ϕ_β. This is in agreement with $f = C - p + 2 = 4 - 3 + 2 = 3$, where Q is counted as a component. Note that $D = f + p = 3 + 3 = 6$, as expected.

Equation 20 shows that the following three equilibrium constant expressions can be derived:

$$K_\alpha = \frac{a_{C\alpha}}{a_{A\alpha}a_{B\alpha}} = \exp[-(\mu_C° - \mu_A° - \mu_B°)/RT] \tag{36}$$

$$K_\beta = \frac{a_{C\beta}}{a_{A\beta}a_{B\beta}} = \exp[-(\mu_C° - \mu_A° - \mu_B°)/RT] \tag{37}$$

$$K_C = \frac{a_{C\beta}}{a_{C\alpha}} = \exp\left[-\frac{Fz_C\phi_\beta}{RT}\right] \tag{38}$$

Equation 38 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 36 and 37 can be substituted in eq 38 to obtain

$$\frac{a_{A\beta}a_{B\beta}}{a_{A\alpha}a_{B\alpha}} = \exp\left[-\frac{Fz_C\phi_\beta}{RT}\right] \tag{39}$$

or

$$-\frac{RT}{Fz_C} \ln \frac{a_{A\beta}a_{B\beta}}{a_{A\alpha}a_{B\alpha}} = \phi_\beta \tag{40}$$

This membrane potential equation for the reaction system shows how the activities of A and B can drive the electric potential difference to ϕ_β. This is the potential difference that the system will set up by itself, not an applied potential.

The diffusion of C through the membrane does not affect the chemical reactions in the two phases because the amount is very small, as mentioned at the beginning of this section. But this diffusion sets up an electric potential difference that at equilibrium corresponds with that calculated using the membrane potential equation.

Fundamental Equation for the Transformed Gibbs Energy for a Two-Phase System with a Semipermeable Membrane

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

$$G' = G - \phi_\beta Q \tag{41}$$

which defines the transformed Gibbs energy G'. Since

$$dG' = dG - \phi_\beta \, dQ - Q \, d\phi_\beta \tag{42}$$

substituting eq 21 with $\phi_\alpha = 0$ yields

$$dG' = -S \, dT + V \, dP + \mu_{A\alpha} \, dn_{cA\alpha} + \mu_{A\beta} \, dn_{cA\beta} + \mu_C \, dn_{cC} - Q \, d\phi_\beta \tag{43}$$

To learn more about the derivatives of the transformed Gibbs energy, the chemical potentials of species are replaced by use of eq 1 to obtain

$$dG' = -S \, dT + V \, dP + (\mu_A° + RT \ln a_{A\alpha})dn_{cA\alpha} + (\mu_A° + RT \ln a_{A\beta} + Fz_A\phi_\beta)dn_{cA\beta} + (\mu_C° + RT \ln a_{C\alpha})dn_{cC} - Q \, d\phi_\beta \tag{44}$$

Thus

$$\left(\frac{\partial G'}{\partial n_{cA\alpha}}\right)_{T,P,n_{cA\beta},n_{cC},\phi_\beta} = \mu_A° + RT \ln a_{A\alpha} = \mu_{A\alpha}' \tag{45}$$

$$\left(\frac{\partial G'}{\partial n_{cA\beta}}\right)_{T,P,n_{cA\alpha},n_{cC},\phi_\beta} = \mu_A° + RT \ln a_{A\beta} + Fz_A\phi_\beta = \mu_{A\beta}' + Fz_A\phi_\beta \tag{46}$$

$$\left(\frac{\partial G'}{\partial n_{cC}}\right)_{T,P,n_{cA\beta},n_{cA\beta},\phi_\beta} = \mu_C° + RT \ln a_{C\alpha} = \mu_{C\alpha}' \tag{47}$$

where $\mu_{A\alpha}'$ is referred to as the transformed chemical potential of A in the α phase. This corresponds with writing eq 1 as

$$\mu_i = \mu_i' + Fz_i\phi_i \tag{48}$$

Reactions Involving Phases at Different Potentials

J. Phys. Chem. B, Vol. 101, No. 36, 1997 **7195**

Thus μ_i' is equal to the chemical potential of i in a phase where $\phi_i = 0$. When the differential of G' is taken with respect to n_{cC}, $\mu_{C\alpha}' = \mu_C^\circ + RT \ln a_{C\alpha} = \mu_{C\beta} = \mu_C^\circ + RT \ln a_{C\beta} + Fz_C\phi_\beta = \mu_{C\beta}' + Fz_C\phi_\beta = \mu_C$ is obtained. Thus $(\partial G'/\partial n_i) = \mu_i'$ only in phases where the electric potential is zero.

Equation 43 indicates that the number of natural variables for the system is six; $D = 6$. Thus the number D of natural variables is the same for G and G', as expected, since the Legendre transform interchanges conjugate variables. The criterion for equilibrium is $(dG')_{T,P,n_{cA\alpha},n_{cA\beta},n_{cC},\phi_\beta} \leq 0$. The Gibbs–Duhem equations are the same as eqs 31 and 32 or eqs 33–35, and so the number of independent intensive variables is not changed. Equations 36–40 can also be derived from eq 43.

The integration of eq 43 at constant values of the intensive variables yields

$$G' = \mu_{A\alpha}n_{cA\alpha} + \mu_{A\beta}n_{cA\beta} + \mu_C n_{cC} \tag{49}$$

which agrees with eqs 26 and 41.

Determination of Molar Entropies and Enthalpies of Species

The fundamental equation for G for a two-phase system with a potential difference can be written

$$dG = -S\,dT + V\,dP + \sum \mu_{i\alpha}\,dn_{i\alpha} + \sum \mu_{i\beta}\,dn_{i\beta} + \phi_\beta\,dQ \tag{50}$$

where $\phi_\alpha = 0$. Integration at constant values of intensive variables yields

$$G = \sum \mu_{i\alpha}n_{i\alpha} + \sum \mu_{i\beta}n_{i\beta} + \phi_\beta Q \tag{51}$$

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

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,\{n_{i\alpha}\},\{n_{i\beta}\},Q} \tag{52}$$

Taking this derivative of G yields

$$S = \sum n_{i\alpha}\bar{S}_{i\alpha} + \sum n_{i\beta}\bar{S}_{i\beta} \tag{53}$$

where $\bar{S}_i$ is the molar entropy of i, since ϕ_β is determined by Q, which is held constant. Substituting eq 48 in eq 51 yields

$$G = \sum \mu_{i\alpha}'n_{i\alpha} + \sum \mu_{i\beta}'n_{i\beta} + F\phi_\beta \sum z_i n_{i\beta} + \phi_\beta Q \tag{54}$$

Taking the derivative in eq 52 yields

$$S = \sum n_{i\alpha}\bar{S}_{i\alpha}' + \sum n_{i\beta}\bar{S}_{i\beta}' \tag{55}$$

where $\bar{S}_i'$ is the transformed molar entropy of i. Comparing this equation with eq 53 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 51 and 54 yields

$$H = \sum n_{i\alpha}\bar{H}_{i\alpha} + \sum n_{i\beta}\bar{H}_{i\beta} + \phi_\beta Q \tag{56}$$

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

$$H = \sum n_{i\alpha}\bar{H}_{i\alpha}' + \sum n_{i\beta}\bar{H}_{i\beta}' + F\phi_\beta \sum z_i n_i + \phi_\beta Q \tag{57}$$

where $\bar{H}_i'$ is the transformed molar enthalpy. Comparing eqs 56 and 57 shows that

$$\bar{H}_i = \bar{H}_i' + Fz_i\phi_\beta \tag{58}$$

Thus the molar enthalpy of an ion is affected by the electric potential of the phase in the same way as the chemical potential.

Discussion

The fundamental equations for the Gibbs energy G and the transformed Gibbs energy G' for a two-phase system involving a membrane permeable only by C have been discussed for a system involving the reaction $A + B = C$ in both phases. The fundamental equation for G involves an electric work term with the differential of the charge Q, but the charge can be replaced with the electric potential difference ϕ_β as a natural variable by use of a Legendre transform to define a transformed Gibbs energy G'. The use of the transformed Gibbs energy has the advantage that ϕ_β is a more convenient natural variable than Q from an experimental point of view. This illustrates how a Legendre transform can be used to invent a thermodynamic potential that is more convenient for the experimenter.

In this treatment the identification of natural variables has been emphasized because they are used in the criterion for spontaneous change and equilibrium. It is important to distinguish between the number of natural variables for a system before and after application of equilibrium conditions. It is shown that the number D of natural variables is equal to the sum of the number f of independent intensive variables, given by the phase rule, and the number p of phases; thus, $D = f + p$.

The use of Legendre transforms introduces nomenclature problems because each Legendre transform leads to a new thermodynamic potential. The partial derivatives of this new thermodynamic potential may also require new symbols, such as the transformed chemical potential and the transformed molar enthalpy. Callen[8] suggested a nomenclature that provides a unique symbol for any possible thermodynamic potential, but G', S', and H' are used here because these thermodynamic potentials have properties similar to G, S, and H. The use of G' to introduce the electric potential of a phase as a natural variable leads to the transformed chemical potential μ_i', which is $\mu_i^\circ + RT \ln a_i$ in a phase in which the electric potential is zero. The chemical potential μ_i, which is the same for i in all of the phases of the system at equilibrium, is given by

$$\mu_i = \mu_i' + Fz_i\phi_i \tag{59}$$

where ϕ_i is the electric potential of the phase that species i is in.

In 1974 IUPAC[14] recommended that the electrochemical potential $\tilde{\mu}_i$ be defined by

$$\tilde{\mu}_i = \mu_i + Fz_i\phi \tag{60}$$

where μ_i was referred to as the chemical potential. There are several problems with this recommendation. The electrochemical potential is actually the chemical potential defined by eq 4 or eq 22. The quantity represented by μ_i on the right-hand side of eq 60 is the transformed chemical potential μ_i' defined by eq 48. According to the equations presented here, the chemical potential for an ion should be defined by eq 4 or eq 22, rather than eq 60.

Appendix. Symbols and Nomenclature

$a_{i\alpha}$ = activity of i in the α phase (dimensionless)

C = number of components (dimensionless)

C = capacitance (F = C V^{-1})

D = number of natural variables for a system, $D = f + p$ (dimensionless) (has different values before and after application of equilibrium conditions)

$\mathbf{E}$ = electric field strength (V = J C^{-1})

f = number of independent intensive variables for a system (degrees of freedom) (dimensionless)

F = Faraday constant (C mol^{-1})

G = Gibbs energy of a system (J)

G' = transformed Gibbs energy of a system (J)

G'' = complete Legendre transform of a system (equal to zero) (J)

$\Delta_r G$ = reaction Gibbs energy (J mol^{-1})

$\Delta_r G°$ = standard reaction Gibbs energy (J mol^{-1})

H = enthalpy of a system (J)

$\bar{H}_i$ = molar enthalpy of species i (J mol^{-1})

H_i' = molar transformed enthalpy of species i (J mol^{-1})

$\Delta_r H$ = reaction enthalpy (J mol^{-1})

K = equilibrium constant (dimensionless)

l = thickness of membrane (m)

N = number of species in a system (dimensionless)

$n_{i\alpha}$ = amount of i in phase α (mol)

$n_{ci\alpha}$ = amount of component i in phase α (mol)

n_{ci} = amount of component i in a system (mol)

p = number of phases in a system (dimensionless)

P = pressure (bar)

$\mathbf{P}$ = polarization (C m)

Q = electric charge transferred between phases (C)

S = entropy of a system (J K^{-1})

S_α = entropy of phase α (J K^{-1})

$\bar{S}_i$ = molar entropy of species i (J K^{-1} mol^{-1})

$\bar{S}_i'$ = molar transformed entropy (J K^{-1} mol^{-1})

$\Delta_r S$ = reaction entropy (J K^{-1} mol^{-1})

R = gas constant (J K^{-1} mol^{-1})

R = number of independent reactions in a system (dimensionless)

T = temperature (K)

U = internal energy of a system (J)

V_α = volume of phase α (m^3)

w = work (J)

z_i = charge number of an ion (dimensionless)

ϵ_0 = permittitivity of vacuum (C^2 N^{-1} m^{-2})

ϕ_α = electric potential of phase α (V)

$\mu_{i\alpha}$ = chemical potential of species i in phase α (J mol^{-1})

$\mu_i°$ = standard chemical potential of i (J mol^{-1})

μ_i' = transformed chemical potential of i (J mol^{-1})

$\mu_{i\alpha}'$ = transformed chemical potential of i in phase α (J mol^{-1})

$\boldsymbol{\mu}$ = matrix of chemical potentials of species $(1 \times N)$ (J mol^{-1})

$\boldsymbol{\nu}$ = stoichiometric number matrix $(N \times R)$ (J mol^{-1})

$\boldsymbol{\xi}$ = extent of reaction matrix $(R \times 1)$ (mol)

ξ = extent of reaction (mol)

References and Notes

(1) Alberty, R. A. *J. Electrochem. Soc.* **1995**, *142*, 120−124.

(2) Bailyn, M. *A Survey of Thermodynamics*; American Institute of Physics: New York, 1994.

(3) Guggenheim, E. A. *Thermodynamics*; North-Holland Publishing Co.: Amsterdam, 1967.

(4) Newman, J. S. *Electrochemical Systems*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1991.

(5) Rieger, P. H. *Electrochemistry*, 2nd ed.; Chapman and Hall: New York, 1994.

(6) Beattie, J. A.; Oppenheim, I. *Principles of Thermodynamics*; Elsevier: Amsterdam, 1979.

(7) Alberty, R. A. *Chem. Rev.* **1994**, *94*, 1457−1482.

(8) Callen, H. B. *Thermodynamics*; John Wiley: New York, 1961.

(9) Alberty, R. A. *J. Phys. Chem.* **1992**, *96*, 9614.

(10) Weiss, T. F. *Cellular Biophysics*; MIT Press: Cambridge, MA, 1996; Vol. 1.

(11) Ohanian, H. C. *Physics*; Norton and Co., New York, 1989.

(12) Kirkwood, J. G.; Oppenheim, I. *Chemical Thermodynamics*; McGraw-Hill: New York, 1961.

(13) Zemansky, M. W.; Dittman, R. H. *Heat and Thermodynamics*; McGraw-Hill Book Co.: New York, 1981.

(14) Parsons, R. *Pure Appl. Chem.* **1974**, *37*, 499.