

## Thermodynamics of Electrochemical Systems

Javier Garrido\*

*Departamento de Termodinámica, Universitat de Valencia, E-46100 Burjassot, Valencia, Spain*

*Received: February 18, 2004; In Final Form: September 11, 2004*

A discussion of the fundamentals of thermodynamic theory describing electrochemical systems is presented. The basic relationships are deduced as properties of the electrochemical potential. The theory introduces an observable electric potential that is defined at every position within the electrochemical system as the potential of a reversible electrode placed there. To provide a good test of the formalism, five systems have been studied including equilibrium and nonequilibrium. The formalism emphasizes the advantages of the electric current density in order to characterize one of the degrees of irreversibility and the electrical equilibrium. Finally, the electrostatic potential is discussed within the framework of this theory.

### Introduction

One of the most essential characteristics of electrochemical systems is their ability to conduct electric currents. No matter whether they are ionic or electronic conductors, neutral components are always used in their construction, and the electrical conductivity is possible due to the decomposition of some of them in mobile charged species (i.e., ions, electrons, etc.). Electric conduction is intimately related to the concept of electric potential. The spatial distribution of this quantity has long been used to help in understanding the processes taking place inside the electrochemical systems, but its definition requires extra-thermodynamic assumptions. This may lead to conceptual difficulties, particularly in relation to its nonobservable character and the validity of the local electroneutrality assumption. On the contrary, the emf of electrochemical cells (i.e., the cell potential) can be measured and defined from rigorous thermodynamic equations. The problem, however, arises when defining the distribution of the electric potential inside the cell. It may be solved by introducing the local electric potential at a given point as the electric potential of the terminal of a reversible electrode or probe placed there. Differences in this potential are always observable quantities that can be measured by potentiometers or voltmeters.

During the last years several, nonequilibrium electrochemical systems have been studied using the electric potential measured at the electrode terminals.<sup>1–4</sup> These studies have been developed within the theoretical framework of the thermodynamics of irreversible processes.<sup>5</sup> The new transport equations have the generality of thermodynamic theory and do not require that the system be modeled. But a discussion on their basis is needed: they have been accepted without being thermodynamically criticized. We refer to the concept of electrochemical potential and its relations with the electrolyte chemical potential and with the electric potential that are derived from the properties of partial molar functions. Then the theory is applied to five case studies, including equilibrium and nonequilibrium systems. For the sake of simplicity, this analysis is restricted to binary systems at constant temperature and pressure.

One of the advantages of the thermodynamic formalism is the right characterization of the different degrees of irreversibility in electrochemical systems. The thermodynamic theory

emphasizes the electric current density for describing the electrical equilibrium condition. When this one is zero, the electrochemical system is in electrical equilibrium and behaves as a nonelectrochemical system. Transport equations in systems with two nonequilibrium conditions are studied; in these cases, the electrical irreversibility is combined with either concentration, temperature, or pressure gradients.

Although the present thermodynamic theory satisfactorily describes the electrochemical systems, traditionally the electrochemical studies make use of the electric potential from electrostatics. In the last section, this electric potential is evaluated for the case studies and different conventions.

### Fundamental Equations

Consider a binary solution consisting of an un-ionized solvent and an electrolyte  $A_{\nu+}B_{\nu-}$ , which are denoted by subscripts 1 and 2, respectively. The electrolyte can dissociate into the ion constituents  $A^{z+}$  and  $B^{z-}$  denoted by subscripts + and –, respectively. The stoichiometric coefficients  $\nu_i$  and the charge numbers  $z_i$  ( $i = +, -$ ) are related by

$$\nu_+ z_+ + \nu_- z_- = 0 \quad (1)$$

The equilibrium states are characterized by the temperature  $T$ , the pressure  $p$ , and the amount  $n_i$  of constituent  $i$  ( $i = 1, +, -$ ). Although the deviation from the local electroneutrality condition involves extremely small and nonmeasurable<sup>2</sup> values of the quantity  $n_+ z_+ + n_- z_-$ , the present treatment does not require it to vanish.

Following the 1973 IUPAC recommendations,<sup>6</sup> the electrochemical potential  $\tilde{\mu}_i$  of species  $i$  is defined as its partial molar Gibbs function

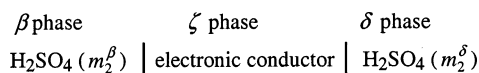
$$\tilde{\mu}_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_1,n_j} \quad i \neq j = +, - \quad (2)$$

We formulate now three fundamental equations required for the thermodynamic description of electrochemical systems. First we note that when species  $i$  ( $i = +, -$ ) can partition between two phases (‘ and ’’) in contact the condition for its distribution equilibrium is

$$\tilde{\mu}'_i = \tilde{\mu}''_i \quad (3)$$

\* E-mail: garridoa@uv.es. Fax: +34-963543385.

## SCHEME 1



The second equation is the relation between the chemical potential  $\mu_2$  of the electrolyte and the electrochemical potentials  $\tilde{\mu}_+$  and  $\tilde{\mu}_-$ , that is,

$$\mu_2 = \nu_+ \tilde{\mu}_+ + \nu_- \tilde{\mu}_- \quad (4)$$

This equation can be deduced by equating the expressions  $dG = \mu_2 dn_2$  and  $dG = \tilde{\mu}_+ dn_+ + \tilde{\mu}_- dn_-$  that describe the elemental change in the Gibbs function when a quantity of electrolyte  $dn_2 = dn_+/ \nu_+ = dn_- / \nu_-$  is added to the system at constant  $T$ ,  $p$ , and  $n_1$ . We point out that this result can be applied to systems that do not satisfy the local electroneutrality condition.

The third property is the relationship between the electrical potential and the electrochemical potential of the electron  $\tilde{\mu}_e$  in an electronic conductor. Consider an electrochemical cell in equilibrium where  $\Delta_\alpha^\omega \psi \equiv \psi^\omega - \psi^\alpha$  is the potential difference measured by a potentiometer between terminals  $\alpha$  and  $\omega$ . This cell reversibly drives electrical charges through an electric device. When a small number of electrons  $dn_e$  circulate, the nonexpansion reversible (NER) work done by the cell is

$$dW_{\text{NER}} = -\Delta_\alpha^\omega \psi F dn_e \quad (5)$$

where  $F$  is the Faraday constant. By evaluating the Gibbs function change in each phase of the cell, the total Gibbs function change is given by

$$dG = (\tilde{\mu}_e^\alpha - \tilde{\mu}_e^\omega) dn_e \quad (6)$$

Because  $dG = -dW_{\text{NER}}$ , we conclude that

$$\Delta_\alpha^\omega \tilde{\mu}_e = -F \Delta_\alpha^\omega \psi \quad (7)$$

Equations 3, 4, and 7 constitute the basis of the thermodynamic theory of electrochemical systems; eqs 4 and 7 are usually postulated rather than derived.<sup>7–10</sup> In this study, we define the electric potential  $\psi$  at a given point as that of the terminal of a reversible electrode or probe placed there. Equation 7 allows us to relate the local variables to the electrical potential. This theory is applied in the following sections to five case studies to show its most interesting characteristics.

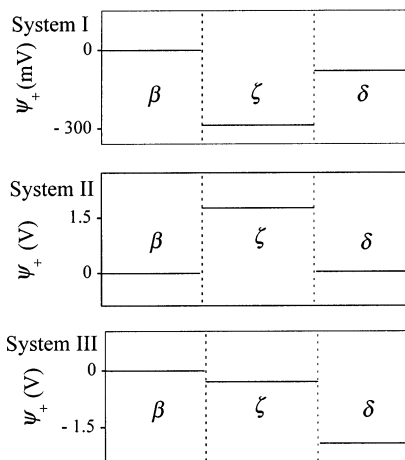
## Equilibrium Systems

Consider the equilibrium systems following Scheme 1, where two sulfuric acid solutions of stoichiometric molalities  $m_2^\beta$  and  $m_2^\delta$  are connected through an electronic conductor, which is denoted as phase  $\zeta$ . Three cases are considered for phase  $\zeta$ : (I) Pb, (II) PbO<sub>2</sub>, and (III) Pb|PbO<sub>2</sub>.

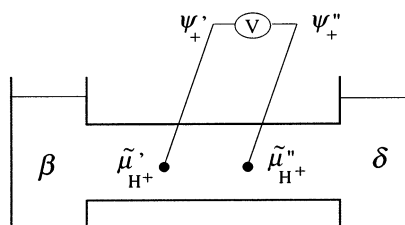
To measure the electric potential, we dipped hydrogen electrodes into phases  $\beta$  and  $\delta$  and attached a copper probe to phase  $\zeta$ . This potential is denoted by  $\psi_+$ ; the plus subindex expresses the fact that electrodes reversible to the H<sup>+</sup> ion are used. The potential difference in volts between electrode or probe terminals  $\Delta_\beta^\zeta \psi_+$  at 298 K is given by<sup>9</sup>

$$\Delta_\beta^\zeta \psi_+ = -0.374 - 0.0385 \ln(m_2^\beta \gamma_\pm^\beta) \quad \text{system I} \quad (8a)$$

$$\Delta_\beta^\zeta \psi_+ = 1.703 + 0.0385 \ln(m_2^\beta \gamma_\pm^\beta) - \ln a_1^\beta \quad \text{system II} \quad (8b)$$



**Figure 1.** Spatial distribution of the electric potential  $\psi_+$  in systems I, II, and III with  $m_2^\beta = 1.0 \text{ mol kg}^{-1}$ ,  $m_2^\delta = 0.10 \text{ mol kg}^{-1}$ , and  $T = 298.15 \text{ K}$ . The constituents of phase  $\zeta$  are Pb for system I, PbO<sub>2</sub> for system II, and Pb|PbO<sub>2</sub> for system III. Data are from ref 11.



**Figure 2.** Sketch of the liquid junction between solutions  $\beta$  and  $\delta$  of sulfuric acid of different concentrations,  $m_2^\beta \neq m_2^\delta$ . The voltmeter  $V$  measures the difference in electric potential  $\Delta\psi_+ = \psi_+'' - \psi_+'$  between the terminals of two electrodes reversible to H<sup>+</sup>. Thus, the gradient in the electrochemical potential  $\nabla\tilde{\mu}_+$  may be evaluated.

where  $\gamma_\pm$  is the mean activity coefficient of the sulfuric acid and  $a_1$  is the solvent activity.

Figure 1 shows the electric potential profile in systems I, II, and III for  $m_2^\beta = 1.0 \text{ mol kg}^{-1}$  and  $m_2^\delta = 0.10 \text{ mol kg}^{-1}$ . The reference value  $\psi_+ = 0$  has been given to the electric potential in phase  $\beta$ . The values of the solvent activity and the mean activity coefficient of the sulfuric acid have been taken from Tables 13-10-1 and 13-11-1 in ref 11. Note that region  $\zeta$  in system III has a uniform electric potential because the electrochemical potential  $\tilde{\mu}_e^\zeta$  has a constant value throughout; therefore, the electric potential difference  $\Delta_\beta^\zeta \psi_+$  does not depend on the location of the copper probe either in Pb or in PbO<sub>2</sub>,

## Nonequilibrium Systems

Consider now two nonequilibrium systems following Scheme 1, where phase  $\zeta$  is one of the following ionic conductors: (IV) a liquid junction (i.e., an aqueous solution in which the sulfuric acid of stoichiometric concentration  $m_2$  varies continuously from  $m_2^\beta$  to  $m_2^\delta < m_2^\beta$ ) or (V) a Nafion-120 membrane. Electrodes reversible to the H<sup>+</sup> ion are used to measure the electric potential  $\psi_+$  as shown schematically in Figure 2, and hence the value of  $\psi_+$  at position  $x$  is interpreted as the potential in the terminal of one such electrode located there. The gradient of the electrochemical potential  $\tilde{\mu}_+$  is given by<sup>1,2</sup>

$$\nabla\tilde{\mu}_+ = z_+ F \nabla\psi_+ \quad (9)$$

The phenomenological transport equations that are deduced from nonequilibrium thermodynamics can be formulated in

**TABLE 1: Electric Potential Differences  $\Delta_{\beta}^{\delta}\psi_{+}$  of Systems IV and V at 298 K Calculated for  $m_2^{\beta} = 1.0 \text{ mol kg}^{-1}$  and Different Molalities  $m_2^{\delta a}$** 

$m_2^{\delta}$ (mol kg <sup>-1</sup> )	$(\Delta_{\beta}^{\delta}\psi_{+})_{\text{IV}}$ (mV)	$(\Delta_{\beta}^{\delta}\psi_{+})_{\text{V}}$ (mV)
0.0005	29.6	
0.01	11.5	
0.05	7.14	
0.10	5.78	6.78
0.50	1.41	4.64

<sup>a</sup> Data are from refs 11 and 15.

terms of this electric potential as follows. The dissipation function  $T\sigma$  is given by<sup>5</sup>

$$-T\sigma = \vec{j}_{+} \nabla \tilde{\mu}_{+} + \vec{j}_{-} \nabla \tilde{\mu}_{-} \quad (10)$$

where  $\vec{j}_i$  is the flow density of matter of ion constituent  $i$  in a solvent-fixed frame of reference. From eqs 4 and 9, we can obtain<sup>1,2</sup>

$$-T\sigma = \frac{1}{\nu_{-}} \vec{j}_{-} \nabla \mu_2 + \vec{j} \nabla \psi_{+} \quad (11)$$

where  $\vec{j}$  is the electric current density. Among the four quantities  $\vec{j}_{-}$ ,  $\vec{j}$ ,  $\nabla \mu_2$  and  $\nabla \psi_{+}$  only two are independent. To characterize the local irreversibilities, we choose the pair  $(\nabla \mu_2, \vec{j})$ . Then the transport equations are expressed by

$$\frac{1}{\nu_{-}} \vec{j}_{-} = -\frac{D_2}{\partial \mu_2 / \partial c_2} \nabla \mu_2 + \frac{t_{-}}{\nu_{-} z_{-} F} \vec{j} \quad (12a)$$

$$-\nabla \psi_{+} = \frac{t_{-}}{\nu_{-} z_{-} F} \nabla \mu_2 + \rho \vec{j} \quad (12b)$$

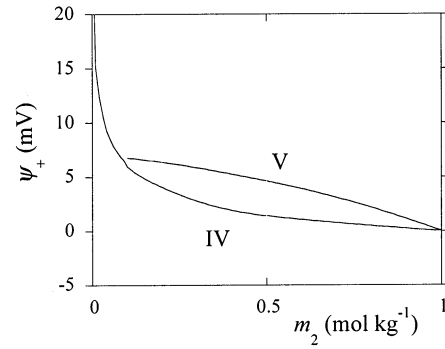
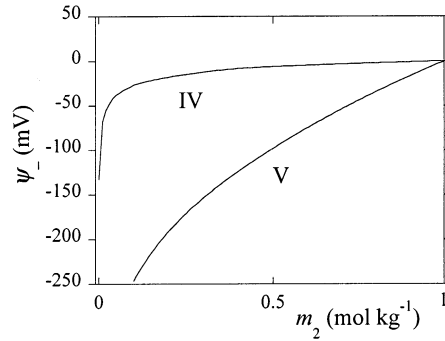
where  $D_2$  is the electrolyte diffusion coefficient in the solvent-fixed reference frame,  $c_2$  is the electrolyte molarity (mol dm<sup>-3</sup>),  $t_{-}$  is the Hittorf transference number of the anion, and  $\rho$  is the electric resistivity.

Because the electric current density  $\vec{j}$  is zero in systems IV and V, the potential difference can be calculated as

$$\Delta_{\beta}^{\delta}\psi_{+} = \frac{1}{2F} \int_{\beta}^{\delta} t_{-} d\mu_2 \quad (13)$$

When applying eq 13 to system V, it is implicitly assumed that<sup>12-14</sup> (a) the sulfuric acid solution fills the membrane pores and the electrolyte molality  $m_2$  varies over the range  $m_2^{\beta} > m_2 > m_2^{\delta}$ ; (b) the solvent and solute chemical potentials depend exclusively on  $m_2$ ; and (c) the transport number  $t_{-}$  in the membrane pores can have different values from those in the bathing solutions. Table 1 shows the values of the potential difference  $\Delta_{\beta}^{\delta}\psi_{+}$  calculated for  $m_2^{\beta} = 1.0 \text{ mol kg}^{-1}$  and several molalities  $m_2^{\delta}$ . The transference number of the sulfate anion in water has been calculated from Table 13-14-1A in ref 11. The anion transference number in Nafion-120 equilibrated with sulfuric acid in water can be calculated from ref 15.

The variation of the electric potential along the liquid junction (system IV) and the membrane pore (system V) may be evaluated by substituting the upper limit  $\delta$  in eq 13 by an intermediate position where the electrolyte molality is  $m_2 > m_2^{\delta}$ . Figure 3 shows these profiles as a function of the local molality  $m_2$ . In both cases,  $m_2^{\beta} = 1.0 \text{ mol kg}^{-1}$  and  $T = 298 \text{ K}$ , and the molality  $m_2^{\delta}$  is  $0.0005 \text{ mol kg}^{-1}$  in system IV and  $0.10 \text{ mol kg}^{-1}$  in system V.

**Figure 3.** Variation of the electric potential  $\psi_{+}$  in the liquid junction (IV) and in the Nafion-120 membrane (V) with local concentration  $m_2$ . In both cases,  $m_2^{\beta} = 1.0 \text{ mol kg}^{-1}$  and  $T = 298 \text{ K}$ , and the molality  $m_2^{\delta}$  is  $0.0005 \text{ mol kg}^{-1}$  in system IV and  $0.10 \text{ mol kg}^{-1}$  in system V. Data are from refs 11 and 15.**Figure 4.** Variation of the electric potential  $\psi_{-}$  in the liquid junction (IV) and in the Nafion-120 membrane (V) with local concentration  $m_2$ . In both cases,  $m_2^{\beta} = 1.0 \text{ mol kg}^{-1}$  and  $T = 298 \text{ K}$ , and the molality  $m_2^{\delta}$  is  $0.0005 \text{ mol kg}^{-1}$  in system IV and  $0.10 \text{ mol kg}^{-1}$  in system V. Data are from refs 11 and 15.

In the previous equations, the potential  $\psi_{+}$  has been defined with respect to electrodes reversible to the  $\text{H}^{+}$  cation. Alternatively, if electrodes reversible to the anion were used, then the theory would include a different electric potential  $\psi_{-}$  such that  $\nabla \psi_{-} = \nabla \tilde{\mu}_{-} / z_{-} F$ . Then, eq 12b would be transformed to

$$-\nabla \psi_{-} = \frac{t_{+}}{\nu_{+} z_{+} F} \nabla \mu_2 + \rho \vec{j} \quad (14)$$

The distribution of this potential when  $\vec{j} = 0$  could be obtained from the integration of

$$d\psi_{-} = -\frac{1}{2F} t_{+} d\mu_2 \quad (15)$$

Figure 4 shows the profiles obtained in this way for systems IV and V. One of the strengths of this theoretical framework is that the transport processes can be described satisfactorily for any choice of the reversible electrodes used.

### Electrical Equilibrium

The distribution equilibrium for a charged species  $i$  in an electrochemical system requires that the electrochemical potential of this species is uniform throughout the system. In the case of mobile species, this statement of the absence of a driving force for the transport of species  $i$  is equivalent to the condition of vanishing flux density (in a solvent-fixed reference frame). Although the electrical charge is always bound to some charged species in the system and has no separate entity in itself, it is reasonable to think that, in addition to the thermal, mechanical, and matter distribution equilibrium conditions, the equilibrium

electrochemical systems must also hold an electrical equilibrium condition. In principle, two possible statements for this condition could be the absence of an electrical potential gradient and the absence of electric current density. It is evident from Figure 1 that the electrical potential is not necessarily uniform in an equilibrium electrochemical system; therefore, the electrical equilibrium condition must be stated as the absence of electric current density. This criterion for electrical equilibrium is emphasized when the transport equations derived within the present thermodynamic theory are considered. This is studied in detail next in the three systems where we consider only two nonequilibrium conditions: one of them is the electrical nonequilibrium, and the other is the matter distribution nonequilibrium, or the thermal nonequilibrium, or the mechanical nonequilibrium, successively.

Equations 12a and 12b describe the transport processes in an electrochemical system with an electrolyte concentration gradient and electrical nonequilibrium. The system has two irreversibility degrees characterized by the quantities  $\nabla\mu_2$  and  $\vec{J}$ . When  $\vec{J} = 0$ , the system is in electrical equilibrium; then the two ions diffuse as a whole, and the electrolyte flux density is  $\vec{J}_2 = \vec{J}_-/\nu_- = \vec{J}_+/\nu_+$  as it occurs in a nonelectrochemical system.

Electrochemical systems with temperature gradients have been considered in ref 3. An electronic conductor X is studied through probes R; the electric potential in the terminals of these probes is denoted by  $\psi$ . The transport equations deduced within this thermodynamic theory are<sup>3</sup>

$$\vec{J}_S = -\frac{\kappa}{T}\nabla T - S_R\vec{J} \quad (16a)$$

$$-\nabla\psi = (S_R - S_X)\nabla T + \rho\vec{J} \quad (16b)$$

where  $\vec{J}_S$  is the entropy flux density,  $\kappa$  is the thermal conductivity, and  $S_i$  is the thermoelectric power of material  $i = X, R$ ; note that  $S_R$  and  $S_X$  are nonmeasurable quantities but the difference  $S_R - S_X$  can be measured. The system has two degrees of irreversibility characterized by the quantities  $\nabla T$  and  $\vec{J}$ . When  $\vec{J} = 0$ , the system is in electrical equilibrium; then heat flux can be described by the Fourier law as in nonelectrochemical systems.

Finally, the thermodynamic theory of electrochemical systems with pressure gradients have been studied in ref 4; a Nafion-120 membrane with a 0.010 mol dm<sup>-3</sup> NaCl solution is considered. Ag|AgCl electrodes are used. The transport equations are

$$q = L_p\Delta p + L_JJ \quad (17a)$$

$$\Delta\psi_- = -L_J\Delta p + R_\psi J \quad (17b)$$

where  $q$  is the volume flux measured in one of the subsystems,  $\Delta p$  is the difference in pressure between the subsystems,  $\Delta\psi_-$  is the electric potential difference between the two electrodes,  $J$  is the electric current, and  $L_p$ ,  $L_J$ , and  $R_\psi$  are phenomenological coefficients. The process is characterized by the quantities  $\Delta p$  and  $J$ . When  $J = 0$ , the system is in electrical equilibrium; then Poiseuille flow is observed as in a nonelectrochemical system.

From the above comments, we can conclude that electrochemical systems in electrical equilibrium evolve similarly to nonelectrochemical systems. Nevertheless these systems have a very interesting property that the nonelectrochemical systems do not have. Effectively in electrochemical systems in electrical equilibrium, electric potential differences can be measured, and either electrolyte concentration, temperature, or pressure differences can be evaluated by eqs 12b, 16b, and 17b. Note also

that when the electric current density is zero the flux is not affected by the electric driving force; eqs 12a, 16a, and 17a determine that the system behaves as a nonelectrochemical system.

### Electrostatic Potential

As we have just seen, the present thermodynamic theory satisfactorily describes the electrochemical systems. The spatial distribution of the electric potential is related to the thermodynamic properties of the system. In equilibrium systems, as those that follow the Scheme 1, the electric potential  $\psi$  depends on electrolyte concentrations, and in nonequilibrium systems, the electric potential  $\psi$  is related to electrolyte concentration, temperature, and pressure gradients and electric current density through measurable transport coefficients. However, the electric potential  $\psi$  is seldom used in the literature. Traditionally, electrochemical studies make use of the electric potential  $\phi$  from electrostatics. At first there was more interest in the electric potential  $\phi$  because it directly refers to the system without interposing foreign elements such as electrodes or probes. Nevertheless, this potential has an important disadvantage: the potentiometers or voltmeters that can always measure differences in the electric potential  $\psi$  can measure differences in the electric potential  $\phi$  only between points of the same chemical composition, temperature, and pressure. To overcome the strong restriction in the potential  $\phi$ , we could resort to electromagnetic theory. The Poisson equation of electrostatics relates the electric potential  $\phi$  to the distribution of electric charge. Unfortunately, this theory does not help to solve the problem because the distribution of electric charge is a nonmeasurable quantity in electrochemical systems.<sup>2</sup>

To use the electric potential  $\phi$  in electrochemistry, it is widely accepted that the ionic electrochemical potential can be split into two contributions

$$\tilde{\mu}_i = \mu_i + z_i F \phi \quad i = +, - \quad (18)$$

The term  $\mu_i$  is named the chemical potential although its definition as a partial molar Gibbs function cannot be applied. This quantity is expressed in the form

$$\mu_i = \mu_i^\circ + RT \ln(m_i \gamma_i) \quad (19)$$

where  $\mu_i^\circ$  is the standard chemical potential,  $m_i = \nu_i m_2$  is the molality of the ionic species ( $i = +, -$ ), and  $\gamma_i$  is the ionic activity coefficient. The activity coefficient is a nonmeasurable quantity, and different conventions have been established for its evaluation.<sup>16</sup> Most of them are based on the Debye–Hückel convention where the two ionic activity coefficients are related to the mean activity coefficient in a symmetrical way:

$$(\gamma_+)^{\nu_+} = (\gamma_\pm)^{\nu_-} \quad (20a)$$

$$(\gamma_-)^{\nu_-} = (\gamma_\pm)^{\nu_+} \quad (20b)$$

We can now evaluate the electric potential  $\phi$  for the above systems studied. In the case of system I, we have

$$\Delta^\delta \phi = \Delta^\delta \psi_+ - \frac{RT}{z_+ F} \ln \frac{m_2^\delta \gamma_+^\delta}{m_2^\beta \gamma_+^\beta} \quad (21)$$

and for systems IV and V, from eqs 9, 18, and 19 we deduce

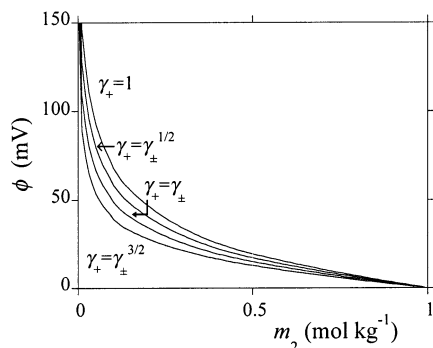
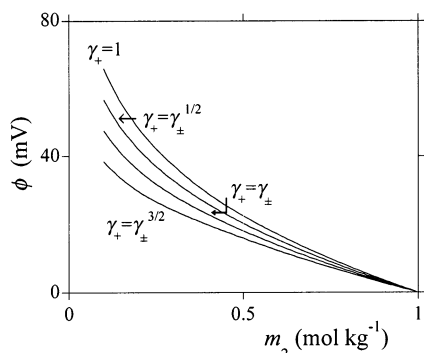
$$d\phi = d\psi_+ - \frac{RT}{z_+ F} d \ln(\nu_+ m_2 \gamma_+) \quad (22)$$



**TABLE 2: Electric Potential Differences  $\Delta_{\beta}\phi$  in System I When  $m_2^{\beta} = 1.0 \text{ mol kg}^{-1}$  and  $m_2^{\delta} = 0.10 \text{ mol kg}^{-1a}$** 

$\gamma_+$	$\Delta_{\beta}u_+/F$ (mV)	$\Delta_{\beta}\phi$ (mV)
1	-59.2	-2.1
$(\gamma_{\pm})^{1/2}$	-50.0	-11.3
$\gamma_{\pm}$	-40.9	-20.4
$(\gamma_{\pm})^{3/2}$	-31.7	-29.6

<sup>a</sup> Four conventions for the ionic activity coefficient  $\gamma_+$  have been used. The constituent of phase  $\zeta$  is Pb. Electrodes reversible to the  $\text{H}^+$  ion are used; the value of potential difference  $\Delta_{\beta}\psi_+ = -61 \text{ V}$ . The chemical potential difference is evaluated by  $\Delta_{\beta}u_+ = RT \ln(m_2^{\delta}\gamma_+^{\delta}/m_2^{\beta}\gamma_+^{\beta})$ . Data are from ref 11.

**Figure 5.** Variation of the electric potential  $\phi$  in the liquid junction (IV), with  $m_2^{\beta} = 1.0 \text{ mol kg}^{-1}$ ,  $m_2^{\delta} = 0.0005 \text{ mol kg}^{-1}$ , and  $T = 298.15 \text{ K}$ . Four conventions for the ionic activity coefficient  $\gamma_+$  have been used. Data are from ref 11.**Figure 6.** Variation of the electric potential  $\phi$  in the Nafion-120 membrane (V), with  $m_2^{\beta} = 1.0 \text{ mol kg}^{-1}$ ,  $m_2^{\delta} = 0.10 \text{ mol kg}^{-1}$ , and  $T = 298.15 \text{ K}$ . Four conventions for the ionic activity coefficient  $\gamma_+$  have been used. Data are from refs 11 and 15.

We need also to postulate the ionic activity coefficient  $\gamma_+ = \gamma_+(T, p, m_2)$ ; we propose the following expressions:

$$\gamma_+ = 1 \quad (23a)$$

$$\gamma_+ = (\gamma_{\pm})^{1/2} \quad \text{Debye-Hückel convention} \quad (23b)$$

$$\gamma_+ = \gamma_{\pm} \quad (23c)$$

$$\gamma_+ = (\gamma_{\pm})^{3/2} \quad (23d)$$

Table 2 shows the values of the electric potential  $\phi$  in system I, and Figures 5 and 6 show the variations of the electric potential  $\phi$  along the liquid junction and in the Nafion

membrane. The dispersion shows that the electric potential  $\phi$  depends strongly on the convention used for the ionic activity coefficient.

## Conclusions

The fundamentals of the thermodynamic description of electrochemical systems have been discussed. The essential concept is the electrochemical potential defined as a partial molar Gibbs function. The thermodynamic properties of this magnitude play a key role in the theory. The study has a wide scope and does not make use of the local electroneutrality condition. Relationships among the chemical potential of the electrolyte, the electrochemical potential of the ionic species, and the electrochemical potential of the electron have been deduced.

The local electric potential in the present thermodynamic theory has been applied to five case studies; in all of them, the spatial distribution of the electric potential has been evaluated. Thus, the most interesting characteristics of the formalism have been evidenced. The electric current density is the best way to characterize one of the degrees of irreversibility in nonequilibrium electrochemical systems. When this electric current density is zero, the system is in electrical equilibrium. Under these conditions, the electrochemical systems evolve as nonelectrochemical systems.

However, the electric potential of thermodynamic theory has been seldom used; in turn, the electrostatic potential has been employed. Extrathermodynamic criteria are needed for the evaluation of this nonmeasurable quantity. The variation of this electric potential in several systems has been calculated. In each case, different conventions of the ionic activity coefficients have been used. The dispersion of the results shows that the electrostatic potential depends strongly on the convention used for the ionic activity coefficient.

**Acknowledgment.** This work is part of project no. MAT2002-00646 funded by the Ministerio de Ciencia y Tecnología of Spain and the Fondo Europeo para el Desarrollo Regional of the European Union (FEDER).

## References and Notes

- (1) Garrido, J.; Compañ, V.; López, M. L. *J. Phys. Chem. B* **1994**, *98*, 6003.
- (2) Garrido, J.; Compañ, V.; López, M. L.; Miller, D. G. *J. Phys. Chem. B* **1997**, *101*, 5740.
- (3) Garrido, J. *J. Phys. Chem. B* **2002**, *106*, 10722.
- (4) Garrido, J. *J. Electrochem. Soc.* **2003**, *150*, E 567.
- (5) Haase, R. *Thermodynamics of Irreversible Processes*; Dover: New York, 1990.
- (6) *IUPAC Manual of Symbols and Terminology for Physicochemical Quantities and Units. Appendix III. Electrochemical Nomenclature*; Butterworths: London, 1973; p 501.
- (7) Guggenheim, E. A. *J. Phys. Chem.* **1929**, *33*, 842.
- (8) Guggenheim, E. A. *J. Phys. Chem.* **1930**, *34*, 1540.
- (9) Newman, J. S.; Thomas-Alyea, K. E. *Electrochemical Systems*; Wiley-Interscience: Hoboken, NJ, 2004.
- (10) Alberty, R. A. *J. Phys. Chem. B* **1997**, *101*, 7191.
- (11) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*; Reinhold Publishing Corp.: New York, 1943.
- (12) Garrido, J.; Compañ, V.; López, M. L. *Phys. Rev. E* **2001**, *64*, 16122.
- (13) Garrido, J.; Compañ, V. *J. Phys. Chem.* **1992**, *96*, 2721.
- (14) López, M. L.; Compañ, V.; Garrido, J.; Riande, E.; Acosta, J. L. *J. Electrochem. Soc.* **2001**, *148*, E372.
- (15) Ceynowa, J. *Polymer* **1982**, *23*, 203.
- (16) Morf, W. E. *The Principles of Ion-Selective Electrodes and of Membrane Transport*; Elsevier: Amsterdam, 1981.