4.0 INTRODUCTORY COMMENTS

In this chapter, the thermodynamic properties of ionic solutions will be investigated. Since the interaction forces between charged species are quite strong and of long range, it is important at the outset to take account of deviations from ideality. Hence, considerable use will be made of the machinery set up in the first half of Chapter 3, in which the concept of activity and activity coefficients plays an important part. Heavy reliance is also placed on the Debye-Hückel Theory: Since the requisite derivations are based on microscopic properties of matter, the final results are quoted without any attempt to provide a deeper understanding of their microscopic significance. The latter portion of the present chapter deals with the properties and characteristics of galvanic cells. Here, again, the emphasis is on fundamentals; for the myriad applications, special uses, or refined specializations of the general approach, the reader is referred to monographs and review papers in the field.

4.1 ACTIVITIES OF STRONG ELECTROLYTES

In 1887 Svante Arrhenius advanced the then very revolutionary hypothesis that many salts dissolved in aqueous solutions ionize partially or completely. Such a process may be
represented by an 'equation' of the form $M_{\nu^+}A_{\nu^-} = \nu^+M^{z^+} + \nu^-A^{z^-}$, where $M$ and $A$ represent the cationic and anionic constituents of the compound, $z^+$ and $z^-$ are their appropriate ionic charges, and $\nu^+$ and $\nu^-$, the stoichiometry numbers. The ionization process symbolized as above requires that $M_{\nu^+}A_{\nu^-}$ itself be considered either as a dissolved species or as an undissolved pure compound present as a separate phase. One may define a corresponding differential free energy change for the ionization by

$$\Delta G_d = \sum \nu_i \mu_i - \nu^+\mu^+ + \nu^-\mu^- - \mu,$$

(4.1.1)

where $\mu$ is the chemical potential of the undissolved salt or undissociated compound $M_{\nu^+}A_{\nu^-}$. At chemical equilibrium Eq. (4.1.1) vanishes, so that

$$\mu = \nu^+\mu^+ + \nu^-\mu^-.$$

(4.1.2)

It is now appropriate to introduce the conventional equation $\mu_i = \mu^*_i(T,1) + RT \ln a_i(T,P,q_i)$ set up in Eq. (3.6.2), with $q_i = x_i, c_i, m_i$. Then Eq. (4.1.2) becomes

$$\mu = \mu^* + RT \ln a - (\nu^+\mu^*_+ + \nu^-\mu^*_-) + RT (\nu^+ \ln a^+ + \nu^- \ln a^-),$$

(4.1.3a)

where the subscript $i$ has been temporarily dropped to avoid proliferation of symbols. Equation (4.1.3a) now assumes the conventional form

$$\mu = \mu^* + RT \ln [a^+a^-],$$

(4.1.3b)

which suggests that one should define the standard chemical potential in solution by the relation

$$\mu^* = \nu^+\mu^*_+ + \nu^-\mu^*_-, $$

(4.1.4)

and a mean relative activity by
Equations (4.1.3)-(4.1.5) imply more than meets the eye. First, one must always satisfy the Law of Electroneutrality, according to which

\[ \nu_z z_+ + \nu_- z_- = \nu_z z_+ - \nu_- |z_-| = 0. \]  

(4.1.6a)

We recognize that \( z_- < 0 \); hence, we have introduced the absolute value, \(|z_-|\). Second, there is no possibility of separately determining either \( a_+ \) or \( a_- \). For, by definition, \( \mu_+ = (\partial G/\partial n_+)_{T,P,n_-} \); that is, the determination of \( \mu_+ \) requires addition of just positive ions to the solution, while holding the concentration of anions fixed. However, this step cannot be carried out operationally because it involves a violation of the Law of Electroneutrality. Consequently, one should not attempt to deal with individual ionic activities; rather, as Eq. (4.1.3b) shows, the ionic activities occur in such a manner that only their product or their logarithmic sum is involved. Third, since thermodynamic descriptions must be confined to measurable properties we may regard the quantity \( \mu^* + RT \ln a \) on the left of Eq. (4.1.3a) as an 'effective chemical potential' that is to be used to represent the behavior of the electrolytes. On the other hand, one does not wish to ignore the ionic nature of the solution; hence it is customary to set

\[ \mu = \mu^* + RT \ln a^\nu, \]  

(4.1.6b)

which is in consonance with (4.1.5).

Fourth, we must refer the activity \( a \) or \( a^\nu \) to a measurable quantity in an ideal solution. For this purpose we set up relations analogous to (4.1.5), namely,
We next adapt the arguments of Section 3.5 to the present situation by defining the mole fraction for the \(i\)th positively charged species in solution by \(x_{i+} = \frac{n_{i+}}{\sum_{s} \nu_{s} n_{s}} = \frac{m_{i+}}{\sum_{s} \nu_{s} m_{s}}\). Here a new notation has been adopted: The index \(s\) runs over all distinct chemical compounds added to the aqueous phase, not over the ionic species \(i\) present in the solution; the dissociation process of these compounds in water is attended to by insertion of the sum \(\nu_{s} = \nu_{s+} + \nu_{s-}\). Here \(\nu_{s+}\) or \(\nu_{s-}\) are the number of cations or anions derived from the complete dissociation of the \(s\)th species \(M_{\nu+}A_{\nu-}\) into the \(\nu_{s+}\) positive and \(\nu_{s-}\) negative ions, \(M^{z+}\) and \(A^{z-}\). Thus, each mole of the compound \(M_{\nu+}A_{\nu-}\) yields \((\nu_{+} + \nu_{-}) = \nu\) moles of ions in solution. We assume that the solvent \((s = 1)\) remains un-ionized and that complete solute ionization occurs; the case of incomplete ionization is handled later. For nonionic species \(\nu_{s} = 1\); moreover, for the solvent, \(m_{1} = 1000/M_{1}\); see Eq. (3.5.2). Thus,

\[
x_{i+} = \frac{m_{i+}}{1000/M_{1} + \nu_{2} m_{2} + \nu_{3} m_{3} + \ldots}^{-1},
\]

and therefore,

\[
x_{1} = \frac{m_{1}}{\sum_{s} \nu_{s} m_{s}} = \left[1 + \nu_{2} m_{2} M_{1}/1000 + \nu_{3} m_{3} M_{1}/1000 \ldots\right]^{-1}.
\]

Accordingly, when one introduces (4.1.7) and (4.1.8), one obtains

\[
\frac{m_{i+}}{x_{i+}} = \frac{m_{i-}}{x_{i-}} = \frac{m_{i\pm}}{x_{i\pm}} = \frac{1000}{M_{1}} \left[1 + \frac{\nu_{2} m_{2} M_{1}}{1000} + \frac{\nu_{3} m_{3} M_{1}}{1000} + \ldots\right] = \frac{1000}{M_{1} x_{1}}.
\] (4.1.9)

Next, we determine \(c_{i+}/m_{i+}\) utilizing the fact that \(m_{i+} = 1000 n_{i+}/M_{i} n_{1}\), \(c_{i+} = n_{i+} 1000/V\), where \(V\) is specified in \(\text{cm}^{3}\). Thus,
ci+/mi+ = (ci+/ni+)(ni+/mi+) = M_inl/V. When eliminating $V$ in terms of the mass of solution we sum over all component species $s$ from which the final mixture was made up, ignoring the fact that many of the components ionize in going into solution. Thus, $ci+/mi+ = M_{1n_1p}/\sum_s M_{s_1n_s} = M_{1m_1p}/\sum_s M_{s_1m_s}$, and since $M_{1m_1} = 1000$,

$$\frac{c_{i+}}{m_{i+}} = \frac{c_{i-}}{m_{i-}} = \frac{c_{i\pm}}{m_{i\pm}} = \frac{\rho}{1 + \frac{M_{2m_2}}{1000} + \frac{M_{3m_3}}{1000} + \ldots}. \quad (4.1.10)$$

Multiplication of (4.1.10) with (4.1.9), followed by (4.1.8b), yields

$$\frac{c_{i+}}{x_{i+}} = \frac{c_{i-}}{x_{i-}} = \frac{c_{i\pm}}{x_{i\pm}} = \frac{1000 \rho}{M_{1x_1} \left[ 1 + \frac{m_{2m_2}}{1000} + \frac{m_{3m_3}}{1000} + \ldots \right]} \quad (4.1.11)$$

In the limit of very dilute solutions for which $x_1 \to 1$ and $M_{s_1m_s}/1000 << 1$, one obtains

$$(m_{i\pm}/x_{i\pm})_{x_1=1} = 1000/M_1 \quad (4.1.12a)$$

$$(c_{i\pm}/x_{i\pm})_{x_1=1} = 1000\rho_1/M_1 \quad (4.1.12b)$$

$$(c_{i\pm}/m_{i\pm})_{x_1=1} = \rho_1. \quad (4.1.12c)$$

We now introduce mean activity coefficients

$$(\gamma_1)_z^{\nu_1} = (\gamma_1)_z^{\nu_1+} (\gamma_1)_z^{\nu_1-}, \quad (4.1.13)$$

in strict analogy with Eq. (4.1.5a); here $\gamma_z = \gamma_z(T, P, q_z); q = x, c, m$.

It should then be clear that the relation between activity and activity coefficient which supplants Eq. (3.6.3) now reads (omitting subscripts $i$ for simplicity)
in which \( q = x, c, m \). Here \( a_\alpha^q(T,P) \) refers to the species under consideration in pure (undissociated and undissolved) form, and \( q_\alpha^* \) is the concentration of the pure (undissociated and undissolved) species; as usual, \( x^* = 1 \); also, \( a_\alpha^*(T,P) \) is ordinarily close to unity in value. Further, in the interest of consistency we have introduced the definitions \( [a_\alpha^*(T,P)]^\nu = a^*(T,P) \), \( [q_\alpha^*(T,P)]^\nu = q^*(T,P) \), and \( \nu = \nu_+ + \nu_- \).

In attempting to interrelate the various \( \gamma_\alpha(T,P,q) \) we note that the \( q_\alpha^* \) are related in the same manner as \( x^* (= 1) \), \( c^* \), \( m^* \) are. Further, according to Eqs. (3.5.17) and (3.5.20),

\[
a_\alpha^x(T,P) = [\gamma_1^x(T,P)]^{1/\nu} a_\alpha^x(T,P)/[\gamma_{11}(T,P,c_1^*)]^{1/\nu}
\]

while according to (3.5.8) and (3.5.10),

\[
\gamma_{i\alpha}(T,P,c_{i\alpha}) = \gamma_{i\alpha}(T,P,x_{i\alpha}) \left[ \frac{\rho_i^*(T,P)}{\rho(T,P)} \frac{\sum_n M_n}{M_i \sum_n} \right]^{1/\nu} \gamma_{i1}(T,P,c_i^*)^{1/\nu}
\]

\[
\gamma_{i\alpha}(T,P,m_{i\alpha}) = \gamma_{i\alpha}(T,P,x_{i\alpha}) \left[ x_i M_i / M_{i1} \right]^{1/\nu} \gamma_{i1}(T,P,m_i^*)^{1/\nu},
\]

where the summation over \( s \) again serves as an explicit reminder that one sums over all chemical species added to the solution, not over the individual ionic species.

Lastly, the \( q_\alpha \) are interrelated as shown in Section 3.5, after replacing \( q \) by \( q_\alpha^\nu \).

EXERCISES

4.1.1 Carefully relate \( \gamma_\alpha \) to \( \gamma \) and \( q_\alpha^* \) to \( q^* \) and prove that Eq. (4.1.14) is consistent with (3.5.3).

4.1.2 Carefully verify that (4.1.9) and (4.1.10) hold
for the ratios $m_{i\pm}/x_{i\pm}$ or $c_{i\pm}/x_{i\pm}$ as well as for $m_{i+}/x_{i+}$, etc., individually.

4.2 THEORETICAL DETERMINATION OF ACTIVITIES IN ELECTROLYTE SOLUTIONS; THE DEBYE–HÜCKEL EQUATION

Having defined various activities and activity coefficients in solutions made up from strong electrolytes we now turn to the determination of $\gamma_x$. For this purpose we briefly discuss some aspects of the Debye–Hückel Theory.

We first call attention to the concept of ionic strength introduced by Lewis and Randall in 1921. This quantity is defined as

$$S = \frac{1}{2} \sum_j c_j z_j^2,$$

(4.2.1)

in which $c_j$ ($= c_+ \text{ or } c_-$ for every ion $j$) is the molarity of the $j$th ionic species in solution and $z_j$ is the formal charge on the corresponding ion. The summation is to be carried out over all ionic species present in solution, not just over the species of interest.

What renders this concept useful is the experimental fact that in dilute solutions the activity coefficient of any strong electrolyte is the same in all solutions of the same ionic strength, regardless of the chemical nature of the dissolved ions.

In discussing the theory of Debye and Hückel (1923) we shall skip entirely the derivation of the final results, on the basis that these steps transcend the methodology of classical thermodynamics. As a purist one is forced to take the view that the expressions listed below represent excellent limiting laws that are known empirically to represent a very large body of experimental data. This obviously obscures the fact that a detailed understanding is available on the basis of statistical thermodynamics and electrodynamics for dealing with ionic interactions in solutions.
The Debye–Hückel limiting laws specify the following relations: For the individual ionic species, the activity coefficient is given by

\[ \ln \gamma_+ = -z_+^2 C_1 \sqrt{\frac{\varepsilon}{S}} \left(1 + \frac{C_2}{\sqrt{S}}\right) \]  
\[ \ln \gamma_- = -z_-^2 C_1 \sqrt{\frac{\varepsilon}{S}} \left(1 + \frac{C_2}{\sqrt{S}}\right), \]  

whereas the mean molar activity coefficient, which is the experimentally more meaningful quantity, is given by

\[ \ln \gamma_z = -\frac{z_+ z_- |C_1 \sqrt{\varepsilon}}{1 + C_2 \sqrt{\varepsilon}}, \]  

in which, according to the methods of statistical mechanics,

\[ C_1 = \frac{e^3 N^2}{(\varepsilon RT)^{3/2}} \left[ \frac{2\pi}{1000} \right]^{1/2} \]  
\[ C_2 = \left[ \frac{8\pi e^2 \varepsilon N^2}{1000 \varepsilon RT} \right]^{1/2}. \]

In the above \( e \) is the electronic charge, \( a \) the average ionic diameter, \( N \) Avogadro's number, \( \varepsilon \) the dielectric constant, and \( R \) the gas constant. Usually, \( C_2 \sqrt{\varepsilon} \) is small relative to unity; one then deals with the extreme limiting law:

\[ \ln \gamma_z = -z_+ z_- |C_1 \sqrt{\varepsilon}|. \]

On switching from natural to common logarithms and inserting numerical values for \( C_1 \) and \( C_2 \) one obtains the following result, valid for aqueous solutions at room temperature:

\[ \log \gamma_z = -\frac{0.5092 z_+ z_- \sqrt{\varepsilon}}{1 + \sqrt{\varepsilon}}, \]

where \( a \) in Eq. (4.2.3c) has been set at 3.1 Å. As already
noted in conjunction with Eq. (4.2.3d), the denominator is ordinarily ignored, since under conditions where the theory is applicable $\sqrt{S} \ll 1$. If the constants $C_1$ and $C_2$ are to be computed at other temperatures one must take into account not only the $T^{-3/2}$ factor in Eq. (4.2.3b) but also the variation of $\varepsilon$ with $T$, which is substantial for water.

One should note the following: (i) Eq. (4.2.3a) applies to any aqueous electrolyte solution at room temperature, but (ii) with limits of applicability generally restricted to solutions of molarity $10^{-2}$ or less. (It is generally stated that the Debye–Hückel Law applies only to slightly contaminated distilled water.) (iii) The activity coefficients for different solutions of the same ionic strength and for the same valencies are the same. (iv) A plot of $\log \gamma_e$ versus $\sqrt{S}$ for extremely dilute solutions should yield a straight line of limiting slope $-0.5092 \frac{z_+ z_-}{2}$ in aqueous solution at room temperature. Extensive testing over a long period of time has confirmed the correctness of this prediction. (v) It has been established by use of different solvents that in the limiting case of dilute solutions, $- \log \gamma_e \sim \varepsilon^{-3/2}$.

From the context of the current discussion, it should be evident that the mean activity coefficient cited above is related to molarity. On the other hand, as is to be proved in Exercise 4.2.2, the definition of $S$ remains virtually unaltered by switching from molarity to molality in aqueous solutions at ordinary conditions of temperature and pressure. Thus, the quantity specified by Eq. (4.2.3a) may be considered to represent either $\gamma_e(T,P,c) = \gamma_e^{(c)}$ or $\gamma_e(T,P,m) = \gamma_e^{(m)}$. However, for very precise work, or when nonaqueous solvents are employed, or whenever $T$ and $P$ deviate greatly from standard conditions, the two preceding quantities cannot be used interchangeably; Eq. (4.2.3a) specifies $\gamma_e^{(c)}$.

As has repeatedly been stressed, the Debye–Hückel relation, even in the form (4.2.3a), is of only limited applicability. There have been many attempts to extend the range over which it remains useful; one of the most widely used versions reads
\[
\ln \gamma_z = - \frac{z_+|z_-|C_z \sqrt{S}}{1 + C_{2z} \sqrt{S}} + \frac{2\nu_+\nu_-}{\nu} C_3 m_z, \quad \nu = \nu_+ + \nu_-, \quad (4.2.5)
\]

in which \( C_3 \) is a purely empirical constant whose value must be determined by experiment. One method for accomplishing this is explained in Section 4.10. Equation (4.2.5) is sometimes termed the extended Debye–Hückel equation.

**EXERCISES**

4.2.1 Verify that Eqs. (4.2.2a) and (4.2.2b) may indeed be combined to yield Eq. (4.2.3a).

4.2.2 Prove that for aqueous solutions under ordinary temperature and pressure Eq. (4.2.1) may be replaced by the relation \( S \approx \frac{1}{2} \Sigma_{(i)} m_j z_j^2 \).

4.2.3 Determine the mean molal activity coefficient at 25°C for \( Al_2(SO_4)_3 \) present at \( 2 \times 10^{-4} \) m concentration in a solution also containing a \( 10^{-4} \) m \( Na_3PO_4 \).

4.2.4 By rewriting the Debye–Hückel law as

\[
- \frac{C_z z_+ |z_-| \sqrt{S}}{1 + c_{a} \sqrt{S}} = 1 + c_{a} \sqrt{S}
\]

\((c_a = C_2)\), suggest a method for determining the appropriate value for \( a \), the average distance of closest approach for ions.

4.2.5 Hückel has suggested a further modification of the Debye–Hückel equation which takes the form

\[
\ln \gamma_z = - \frac{z_+|z_-|C_z \sqrt{S}}{1 + C_{2z} \sqrt{S}} + C_3 S.
\]

Expand the denominator and retain only powers up to \( \sqrt{S} \). Suggest ways of determining numerical values for \( C_3 \). Note that this equation holds for molarities up to the order of unity.

4.2.6 Define \( S_a = (1/2) \Sigma_{(j)} m_j z_j^2 \) and \( S_c = (1/2) \Sigma_{(i)} C_i z_i^2 \). What is the interrelation between \( S_c \) and \( S_a \) in nondilute or nonaqueous solutions?

**4.3 EXPERIMENTAL DETERMINATION OF ACTIVITIES AND ACTIVITY COEFFICIENTS OF STRONG ELECTROLYTES**

Since the determination by theoretical methods of activities or activity coefficients for strong electrolytes is limited to
very dilute solutions, experimental methods must be invoked to find $\gamma_2$ for $m > 10^{-2}$ molal. We shall briefly describe some of the methods in use; here the discussion is closely patterned after Sections 3.11-3.12. The use of emf methods for the same purpose is described in Section 4.10, after proper background material has been developed. Once again, the choice of $P - 1$ atm serves as the standard pressure; in this case the activities $\gamma_1$ and $\Gamma_1$ introduced in Sec. 3.4 are identical.

(a) Vapor pressure measurements may be used to determine the activity of the solvent. Equation (3.11.4b) may be taken over without change:

$$\gamma_1^{(x)} \approx \frac{P_1}{P_1^*} x_1,$$

(4.3.1)

where $P_1^*$ is the vapor pressure of pure solvent and $P_1$ is the vapor pressure of the solvent in the presence of the electrolyte.

(b) The Gibbs-Duhem relation may be used in conjunction with the foregoing to determine the molar activity in a binary solution as follows: Since $d\ln a_2^{(x)} = d\ln a_2^{(m)}$, we use the form (T and P constant)

$$\frac{1000}{M_1} d\ln a_1^{(m)} + m_2 \frac{d\ln a_2^{(m)}}{M_1 m_2} = 0,$$

(4.3.2)

wherein $a_2^{(m)} = (a_2^{(m)})_x^{\nu_2}$, $m_2 = (m_2)_x^{\nu_2}$, $\nu_{2+} + \nu_{2-} = \nu_2$. Integration coupled with the use of (3.11.4a), yields

$$\int d\ln a_2^{(m)} = - \int \frac{1000}{M_1 m_2} d\ln a_1^{(m)} \approx - \int \frac{1000}{M_1 m_2} d\ln \left(\frac{P_1}{P_1^*}\right).$$

(4.3.3)

Thus, plots of $1000/M_1 m_2$ versus $\ln \left(\frac{P_1}{P_1^*}\right)$ yield a value of the integral on the right for molalities between the lower and upper limits $m_i \leq m_2 \leq m_u$; the left hand is given by
\( \ln[a_2(T,1,m_u)/a_2(T,1,m_1)] \). The problem with this approach is that changes in the vapor pressure cannot be measured with sufficient accuracy in very dilute solution. One must therefore employ this procedure in conjunction with the Debye–Hückel limiting law, which holds for \( m_2 < m_1 \approx 10^{-2} \).

(c) Freezing point depression measurements furnish another convenient approach to the determination of the activity of the solvent. Here Eq. (3.12.1) may be taken over without change. Notice that up to this point in the present section we have not had occasion to refer to the ionic dissociation process.

(d) For the determination of the activity of the ionic solute in a binary solution we modify Eq. (3.12.9) by writing \( m_2 = m; \nu = \nu_+ \nu_- \) for the compound \( M_\nu A_{\nu-} \)

\[
\frac{d\ln a_\pm^{(m)}}{(1/\nu)d\ln a_\pm^{(m)}} = \frac{d\theta}{\nu \lambda m} + \frac{c}{\nu m} d\theta, \quad (4.3.4)
\]

and in place of (3.12.10) we introduce

\[
j = 1 - \frac{\theta}{\nu \lambda m}. \quad (4.3.5)
\]

It should be verified that instead of (3.12.12) we obtain

\[
d\theta/\nu \lambda m = (1 - j)d\ln m - dj. \quad (4.3.6)
\]

Next, we set \( a^{1/\nu}_\pm = a_\pm, \nu_+ = \nu_+ \nu_-, \nu_- = \nu_- m \), so that \( m_\pm = m (\nu_+ \nu_-)^{-1/\nu} \). It follows from (4.1.14) with \( P = 1 \) atm, and with \( a_\pm \) replaced by \( a_\pm \), that

\[
d\ln \frac{\Gamma_\pm^{(m)}}{m (\nu_+ \nu_-)^{1/\nu}} = d\ln \left( \frac{a_\pm^{(m)}}{m} \right) = d\ln \left( \frac{a_\pm^{(m)}}{m} \right). \quad (4.3.7)
\]

Thus, in place of (3.12.13b) we find from (4.3.4)–(4.3.7)

\[
d\ln \Gamma_\pm^{(m)} = d\ln a_\pm^{(m)} - d\ln m = - j d\ln m - dj + \frac{c}{\nu m} d\theta, \quad (4.3.8)
\]
whose integration yields the analogue of (3.12.14), namely, the quantity

$$\ln \Gamma_1^{(m)}(T_f) = - j - \int_0^m (j/m) dm + (c/\nu) \int_0^m (\theta/m) d\theta.$$  \hspace{1cm} (4.3.9)

Here it is advisable to replace the central term by its equivalent $2\int_0^m (j/m^{1/2}) dm^{1/2}$, since for strong electrolytes $j/m^{1/2}$ remains finite as $m \to 0$.

Finally, it is to be checked out in Exercise 4.3.1 that at any temperature other than $T_f$ one obtains the analogue of Eq. (3.12.19), namely,

$$\ln \Gamma_1^{(m)}(T) = \ln \Gamma_1^{(m)}(T_f) - (b_1/\nu) \int_0^m (1/m) dy,$$  \hspace{1cm} (4.3.10)

in which $b_1 = 1000/m$.

(e) Frequently, solubility measurements may be used in mixed electrolytes to obtain mean molar activity coefficients. This method hinges on the use of an electrolyte solution which is saturated with respect to any particular salt, so that the equilibrium $M^{\nu+}_νA^{\nu-}_ν(s) = ν_νM^{\nu+} + ν_νA^{\nu-}$ prevails.

This situation may be characterized by (among others) use of the equilibrium constant $K_m$ specified by Eq. (3.7.8b). It is conventional either to ignore the product term $\int_s [a_m(T,P)]ν_ν$ as being equal to (at unit pressure) or close to unity, or to absorb this constant factor into the equilibrium constant as well. This then gives rise to the expression

$$K_m = a_+^{ν+}a_-^{ν-}/a_+^{ν_ν}a_-^{ν_ν}.$$  \hspace{1cm} (4.3.11a)

Since the activity of pure $M^{\nu+}_νA^{\nu-}_ν$ is a constant, it, too, may be absorbed into the equilibrium constant; this step finally yields

$$K_s = a_+^{ν+}a_-^{ν-} = a^ν_+ = (m_νγ_2^{(m)}) ν.$$  \hspace{1cm} (4.3.11b)

Inversion of this relation leads to
The procedure now consists in adding other strong electrolytes to the solution. Since $K_s$ remains unaffected by this step while $\gamma_z^{(m)}$ of the electrolyte of interest necessarily changes, $m_z$ will change in the opposite direction. One thus measures $m_z$ from the observed solubilities of the salt $M_{\nu+}A_{\nu-}$ in the presence of other salts added in varying amounts. The results may then be extrapolated to infinite dilution on a plot of $m_z$ versus $\sqrt{S}$. This permits an extrapolation to zero molarity where $\gamma_z^{(m)} = 1$. The mean molarity obtained from this extrapolation thus yields $K_s^{1/\nu}$. Measuring $m_z$ for any other value of $S$ then yields the desired $\gamma_z^{(m)}$.

Two additional observations should be made. First, the methods used here treat each of the ionic types as a separate species that influences the thermodynamic properties of solutions very strongly by virtue of its associated charge. Second, it is instructive to examine the dependence of the mean molal activity coefficient for several different electrolytes as a function of the molality. Representative examples are shown in Fig. 4.3.1. One sees at first a very steep drop in $\gamma_z$ as $m$ is increased, and then either a gradual or a very sharp

\[ \gamma_z^{(m)} = K_s^{1/\nu}/m_z. \] (4.3.12)
rise in $\gamma_\pm$ as $m$ is increased beyond 0.5. The greater the value $z_+ z_-^1$ the sharper is the initial dropoff. [Explain why!].

EXERCISES

4.3.1 Derive Eq. (4.3.10), referring to Section 3.12 where necessary.

4.3.2 For NaCl in the range $0.01 < m < 0.5$, the following information has been provided: $j/2.303 - 0.1465 m^{1/2} - 0.2180 m + 0.1321 m^{3/2}$. Determine $\gamma_\pm(m)$ for $m = 0.01, 0.033, 0.1, \text{ and } 0.33$.

4.3.3 For moderately dilute solutions, one may usually represent the quantity $j$ by setting $j = A m^{1/2} - B m$, where $A$ and $B$ are constants. Obtain the functional dependence of $\gamma_\pm(m)$ on $m$ for this case.

4.3.4 In conjunction with Eq. (4.3.9) Randall and White introduced an auxiliary function $h = 1 + (b_1/\nu m) \ln \alpha_1$. Prove that the use of this function leads to the relation $\ln \gamma_\pm(m) = -h - 2 \int_m^\infty (h/m^{1/2}) dm^{1/2}$. Explain the advantages of this function over the function $j$ used in the text.

4.3.5 The following data pertain to the lowering of the freezing point of aqueous KCl solutions:

<table>
<thead>
<tr>
<th>$c(M)$</th>
<th>$\theta(\deg)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5.06 \times 10^{-3}$</td>
<td>0.0184</td>
</tr>
<tr>
<td>$9.63 \times 10^{-3}$</td>
<td>0.0348</td>
</tr>
<tr>
<td>$1.648 \times 10^{-2}$</td>
<td>0.0590</td>
</tr>
<tr>
<td>$3.170 \times 10^{-2}$</td>
<td>0.1122</td>
</tr>
<tr>
<td>$5.818 \times 10^{-2}$</td>
<td>0.2031</td>
</tr>
<tr>
<td>$1.1679 \times 10^{-1}$</td>
<td>0.4014</td>
</tr>
</tbody>
</table>

4.3.6 The solubility of AgI03 at 25°C in aqueous solutions containing different concentrations of KNO3 is shown by the following data:

<table>
<thead>
<tr>
<th>$c$(KNO3)</th>
<th>$c$(AgI03)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-2}$ mol/liter</td>
<td>$10^{-4}$ mol/liter</td>
</tr>
<tr>
<td>0.1301</td>
<td>1.823</td>
</tr>
<tr>
<td>0.3252</td>
<td>1.870</td>
</tr>
<tr>
<td>0.6503</td>
<td>1.914</td>
</tr>
<tr>
<td>1.410</td>
<td>1.999</td>
</tr>
<tr>
<td>7.050</td>
<td>2.301</td>
</tr>
<tr>
<td>19.98</td>
<td>2.665</td>
</tr>
</tbody>
</table>

Determine the mean activity coefficient with respect to
molarity of AgIO₃ in 0.5 x 10⁻² and 20 x 10⁻² molar solution of KNO₃.

4.3.7 The following data have been collected concerning the freezing point for HCl in aqueous solutions:

<table>
<thead>
<tr>
<th>m molal</th>
<th>θ deg</th>
<th>H₁ - H₀I cal/mol</th>
<th>θP₁ - θ₀P cal/deg-mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.003675</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.002</td>
<td>0.007318</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>0.018152</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.010</td>
<td>0.036027</td>
<td>-0.0042</td>
<td>-0</td>
</tr>
<tr>
<td>0.020</td>
<td>0.07143</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.040</td>
<td></td>
<td>-0.031</td>
<td>-0</td>
</tr>
<tr>
<td>0.050</td>
<td>0.17666</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.100</td>
<td>0.35209</td>
<td>-0.111</td>
<td>-0</td>
</tr>
<tr>
<td>0.200</td>
<td>0.7064</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.250</td>
<td></td>
<td>-0.44</td>
<td>-0.0056</td>
</tr>
<tr>
<td>0.300</td>
<td>1.0689</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.500</td>
<td>1.8225</td>
<td>-1.28</td>
<td>-0.0159</td>
</tr>
<tr>
<td>0.700</td>
<td>2.5801</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.750</td>
<td></td>
<td>-2.60</td>
<td>-0.0293</td>
</tr>
<tr>
<td>1.000</td>
<td>3.5172</td>
<td>-4.16</td>
<td>-0.450</td>
</tr>
</tbody>
</table>

Determine γₓ(m) both at the freezing point and at 25°C for m = 0.020, 0.100, and 1.000. Estimate roughly for what m the discrepancy of γₓ(m) as calculated above and from the Debye-Hückel Law at the two temperatures first exceeds 10%.

4.3.8 The following data are reported for the solubility of AgCl in various concentrations of KNO₃ at 25°C:

<table>
<thead>
<tr>
<th>c(KNO₃) mol/liter</th>
<th>c(AgCl) 10⁻⁵ mol/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.273</td>
</tr>
<tr>
<td>1.3695</td>
<td>1.453</td>
</tr>
<tr>
<td>1.6431</td>
<td>1.469</td>
</tr>
<tr>
<td>2.0064</td>
<td>1.488</td>
</tr>
<tr>
<td>2.7376</td>
<td>1.516</td>
</tr>
<tr>
<td>3.3760</td>
<td>1.537</td>
</tr>
<tr>
<td>4.0144</td>
<td>1.552</td>
</tr>
</tbody>
</table>
4.3.9 The freezing point depression of water containing LiCl is as follows:

<table>
<thead>
<tr>
<th>(c(\text{LiCl})) (x 10^{-3} \text{ mol/liter})</th>
<th>(\theta_f) (x 10^{-3} \text{ deg})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.815</td>
<td>2.99</td>
</tr>
<tr>
<td>1.000</td>
<td>3.58</td>
</tr>
<tr>
<td>1.388</td>
<td>5.03</td>
</tr>
<tr>
<td>1.889</td>
<td>6.87</td>
</tr>
<tr>
<td>3.350</td>
<td>12.12</td>
</tr>
<tr>
<td>3.706</td>
<td>13.45</td>
</tr>
<tr>
<td>5.982</td>
<td>21.64</td>
</tr>
<tr>
<td>10.810</td>
<td>38.82</td>
</tr>
</tbody>
</table>

Determine the mean molal activity coefficient for LiCl at the concentrations \(c = 10^{-2}, 3.3 \times 10^{-2}, 10^{-1} \text{ mol/liter}\).

4.3.10 Show how a measurement of the boiling point elevation may be used to determine the activity coefficients of solvent and of ionic species in solution.

4.4 EQUILIBRIUM PROPERTIES OF WEAK ELECTROLYTES

Weak electrolytes are characterized by the equilibration of undissociated \(M_{\nu+}A_{\nu^-}\) with its ions in solution according to the schematic reaction \(M_{\nu+}A_{\nu^-} \rightarrow \nu^+M^{\nu+} + \nu^-A^{\nu^-}\).

There are many different ways of characterizing equilibrium conditions. Here we shall adopt Eq. (3.7.8) for the specification of the equilibrium constant; when \(M_{\nu+}A_{\nu^-}\) represents a pure phase we find:

\[
K_q = \frac{a^{\nu^+}a^{-\nu^-}}{a_{M_{\nu+}A_{\nu^-}}}.
\]  

The reader should refer back to Section 3.7 for a discussion of the standard states which have been adopted in the specification of \(K_q\). In the event that undissociated \(M_{\nu+}A_{\nu^-}\) is present in a pure condensed state, its relative activity is equal to unity under standard conditions. So long as the pressure is not enormously different from standard conditions, \(a\) does not deviate significantly from unity; see Section 3.7(e). In either case, this factor may then be dropped, so that the equilibrium constant now reads
Equation (4.4.2) may be rewritten in terms of activity coefficients as indicated by Eq. (4.1.14), omitting $q^*$ while also converting from $a$ to $a$. With $q = x, c, m$ one finds

$$K_q = [q_x \gamma_x(T,P,q_x) a_x(T,P)]^\nu_{eq},$$  \hspace{1cm} (4.4.3)$$

where $[a_x(T,P)]^\nu = [a_x(T,P)]^\nu [a_x(T,P)]^\nu = a_x(T,P)$, and $a^*$ is determined as in Section 3.7(e). In the above, $K_q$ is termed the solubility product constant; under standard conditions, where $a^* = 1$,

$$K_s = [q_x \gamma_x(T,1,q)]^\nu_{eq}. \hspace{1cm} (4.4.4)$$

If, on the other hand, $M_{\nu_x}A_{\nu_-}$ represents a dissolved but un-ionized species one then deals with the partial dissociation of a weak electrolyte. The discussion that follows will be restricted to solutions subjected to a pressure of one atmosphere, in which case $a^*(T,1) = 1$ for all species. The dissociation of a weak electrolyte is then characterized by an equilibrium constant in the form

$$K_{q}^\prime = [\prod_i (q_i + \gamma_i+)^{\nu_i+}_{eq} / (q_0 \gamma_0)^{\nu_0}_{eq}] \prod_j (q_j - \gamma_j-)^{\nu_j-}_{eq} / (q_0 \gamma_0)^{\nu_0}_{eq}$$

$$- [\prod [q_x \gamma_x(T,1,q_x)]^\nu_{eq} / (q_0 \gamma_0)^{\nu_0}_{eq}], \hspace{1cm} (4.4.5)$$

in which the subscript zero refers to the undissociated species; since the latter is electrically neutral, deviations from ideality are often neglected for these components, by setting $\gamma_0 = 1$.

In what follows, general principles are illustrated by specific examples.

(a) The case of water is well known: here one deals with the equilibrium $H_2O(l) = H^+ + OH^-$, which leads to the equilibrium constant
\[ K_w = \frac{a_{H^+}a_{OH^-}}{a_{H_2O}}. \]  

(4.4.6)

It is customary to take \( a_{H_2O} = 1 \); as discussed elsewhere, this step is strictly correct only if \( P = 1 \) atm and if no other dissolved species are present.

\( K_w \) has been measured carefully as a function of temperature over a considerable temperature interval; for each temperature \( K_w \) may be determined from conductivity or from emf measurements, the latter technique being described in Section 4.13(d). The heat of ionization per unit advancement of the ionization reaction may be determined according to Eq. (3.7.4) in conjunction with van't Hoff's Law. This requires a knowledge of the manner in which \( \gamma_z \) changes with \( T \). Details, based on Section 3.10, are to be handled in Exercise 4.4.1, which the reader is advised to work out in detail.

(b) Another elementary case of considerable interest pertains to the ionization of acetic acid, which is representative of a whole class of materials that dissociate only weakly. Here one deals with the equilibrium \( HA = H^+ + A^- \) which is characterized by the equilibrium constant

\[ K_A = \frac{a_{H^+}a_{A^-}}{a_{HA}} = \frac{\gamma_{H^+}\gamma_{A^-}c_{H^+}c_{A^-}}{\gamma_{HA}c_{HA}}, \]  

(4.4.7)

where \( A^- \) represents the acetate ion. Strictly speaking, one should not neglect the water dissociation equilibrium which provides the common ion \( H^+ \), but in practice this contribution is usually negligible compared to the \( H^+ \) ion concentration generated from \( HA \).

Since \( HA \) is neutral no significant error is made in setting \( \gamma_{HA} = 1 \). If we write \( \gamma_z = (\gamma_{H^+}\gamma_{A^-})^{1/2} \) we obtain from (4.4.7)

\[ \log \frac{c_{H^+}c_{A^-}}{c_{HA}} = \log K_A - 2 \log \gamma_z, \]  

(4.4.8)

and on using the Debye–Hückel equation (4.2.3a), we obtain the result
Next, introduce the degree of dissociation, $\alpha$, whereby $c_{H^+} = c_{A^-} = \alpha c$, $c_{HA} = (1 - \alpha)c$, $c$ being the starting concentration of $HA$. We now find

$$\log \frac{\alpha^2}{1 - \alpha} = \log K_A + \frac{2(2.303) C_1 \sqrt{S}}{1 + C_2 \sqrt{S}}, \quad (4.4.10)$$

in both of which $C_2 \approx 1$ at room temperature. Equation (4.4.10) involves the ionic strength and is applicable if the solution contains other strong electrolytes with no ions in common with $H^+$ or $A^-$; one can still replace the left-hand side by $\log \left[ \frac{\alpha^2}{1 - \alpha} \right]$ but the $\sqrt{S}$ form must be used if other electrolytes are added to the solution. Equations (4.4.9) and (4.4.10) serve to show the extent to which the quantity $\left( c_{H^+} c_{A^-} / c_{HA} \right)$ differs from $K_A$.

(c) We turn next to hydrolysis reactions, typified by the interaction with water of the salt $BA$ formed from a strong base $BOH$ and a weak acid $HA$: $A^- + H_2O \rightarrow HA + OH^-$. Correspondingly,

$$K_H = \frac{a_{OH^-} a_{HA}}{a_{A^-} a_{H_2O}}. \quad (4.4.11)$$

If again we set $a_{H_2O} = 1$, and $a_{HA} = c_{HA},$

$$K_H = \gamma_{OH^-} c_{OH^-} c_{HA} / \gamma_{A^-} c_{A^-}. \quad (4.4.12)$$

If $BA$ is the salt of a weak base and strong acid, the relevant hydrolysis reaction reads $B^+ + H_2O = BOH + H^+$, which leads to the expression

$$K_H = a_{B^+} a_{H_2O} / a_{BOH} a_{H^+}. \quad (4.4.13)$$
If BA is the salt of the weak base BOH and the weak acid HA, the relevant reaction is written as $B^+ + A^- + H_2O = BOH + HA$. Correspondingly, the equilibrium constant assumes the following form:

$$K_a = \frac{a_{BOH}a_{HA}}{a_{B}a_{A}a_{H_2O}}.$$  \[4.4.14\]

(d) Next, we turn briefly to the case in which a pure solid A(s) is in equilibrium with undissociated A in solution, which in turn is in equilibrium with $A_+$ and $A_-$ according to the schematic equation $A(s) = A = \nu_A A_+ + \nu_A^-$. The equilibrium situation is characterized by

$$\mu_s = \mu_A = \nu_A \mu_+ + \nu_A^- \mu_-. \tag{4.4.15}$$

In the event there is no undissociated A, we obtain the relation

$$a_\nu^+ a^-_\nu = K, \tag{4.4.16}$$

where K is termed the activity product, which may be compared with three solubility products:

$$L_x = x_\nu^+ x^-_\nu, \quad L_c = c_\nu^+ c^-_\nu, \quad L_m = m_\nu^+ m^-_\nu. \tag{4.4.17}$$

Thus, in each case one obtains an interrelation of the type

$$K^{1/\nu} = L^{1/\nu} \gamma_x. \tag{4.4.18}$$

EXERCISES

4.4.1 Write out in detail the expressions relating to the heat of ionization of water; discuss the experimental quantities required as input parameters.

4.4.2 Let $K_m$ be the equilibrium constant relative to molalities for a sparingly soluble salt. (a) Prove that
\[ \Delta H^\circ = \nu RT \left[ \frac{\partial \ln m}{\partial T} \right]_p + \left( \frac{\partial \ln \gamma^\circ}{\partial T} \right)_{T,P} \left( \frac{\partial \ln m}{\partial T} \right)_p + \left( \frac{\partial \ln \gamma^\circ}{\partial T} \right)_{m,P}. \]

(b) Rewrite this expression by introducing the Debye-Hückel formulation. (c) Show that in the limit of very low dissociation
\[ \Delta H^\circ = \left( \frac{1 + \gamma^\circ}{2} \right) \frac{\nu RT_2 T_1}{T_2 - T_1} \ln \left( \frac{m_2}{m_1} \right), \]

where \( m_1 \) and \( m_2 \) are the equilibrium molalities of the ionic species at temperatures \( T_1 \) and \( T_2 \), respectively.

4.4.3 The dissociation constant of weak acids may be fitted to an equation of the form \( \log K_d = -\frac{A}{T} + B - CT \), where \( A, B, \) and \( C \) are constants. Determine \( \Delta G^\circ, \Delta F^\circ, \Delta H^\circ, \Delta S^\circ, \) and \( \Delta C_P^\circ \) in terms of these parameters.

4.4.4 For acetic acid (HA) and for the two dissociation steps of carbonic acid in water, one has the following parameters relating to the quantities introduced in Exercise 4.4.3:

\[
\begin{array}{ccc}
 & A & B \\
HA & 1.17048 \times 10^3 & 3.1649 & 1.3399 \times 10^{-2} \\
H_2CO_3^- & 3.40471 \times 10^3 & 14.8435 & 3.2786 \times 10^{-2} \\
HCO_3^- & 2.90239 \times 10^3 & 6.4980 & 2.3790 \times 10^{-2} \\
\end{array}
\]

(a) Determine \( \Delta G^\circ, \Delta H^\circ, \Delta S^\circ \) and \( \Delta C_P^\circ \) for the appropriate dissociation process at 30°C. (b) Determine the degree of dissociation for acetic acid in water at 25°C using the Debye-Hückel limiting law to estimate activity coefficients relative to concentrations. (c) Determine the concentrations of \( H_2CO_3, HCO_3^-, CO_3^{2-}, H^+, \) and \( OH^- \) in an aqueous solution at 25°C, using the Debye-Hückel law to estimate activity coefficients.

4.4.5 (a) Determine the pH of a solution at 25°C that is composed of 0.01N NH₄OH and 0.01N NH₄Cl; \( K_B = 1.8 \times 10^{-5} \) and \( \gamma^\circ = 0.9 \) for univalent ions. (b) Determine the degree of hydrolysis at 25°C in an aqueous solution that contains 1 N, 0.1 N, and 0.01 N KCN; \( K_A = 7.2 \times 10^{-10} \). (c) At 25°C aniline hydrochloride is hydrolyzed to an extent of 1.56%; determine \( K_H \) and \( K_B \). (d) Calculate the degree of hydrolysis in a 0.1 N aniline hydrochloride solution containing 0.01 N HCl.

4.4.6 The degree of dissociation of AgCl in water at 9.97°C and 25.86°C is 8.9 \times 10^{-7} \) and 1.94 \times 10^{-7} \), respectively; determine the enthalpy of solution per mole of AgCl.

4.4.7 For the reaction AgBr(s) = Ag⁺(aq) + Br⁻(aq), \( \Delta G^- = 70.04 \) kJ at 298 K. (a) Determine the concentration of either ion and determine the error made in neglecting deviations from ideal behavior. (b) Determine the concentration of Ag⁺ in a solution saturated with respect to AgBr and containing 0.02 M NaBr. (c) Repeat (b) when the solution contains 0.01 M NaNO₃. Note the effect in each case.
4.4.8 For the dissociation \( HA = H^+ + A^- \), \( K_A = 1.76 \times 10^{-5} \) at 25°C: (a) Determine the pH of a 10\(^{-2}\) M solution of acetic acid. (b) Then determine the pOH of a 10\(^{-1}\) M solution of sodium acetate. (c) Determine the pH for a solution containing 10\(^{-3}\) mol of acetic acid and sodium acetate in a total volume of 1 liter.

4.4.9 (a) Using the method of successive approximations, determine the calcium ion concentration in a solution saturated with respect to \( CaCO_3 \); \( \Delta G_{298^\circ} = 47.20 \) kJ/mol. (b) Repeat the calculation when the solution also contains (i) 0.02 M \( Na_2CO_3 \), (ii) 0.02 M \( NaN_3 \).

4.4.10 For the dissociation of \( NH_4OH \), \( K_B = 1.79 \times 10^{-5} \) at 25°C: (a) Determine the pH of a 0.1 M ammonia solution, taking nonideality into consideration. (b) Repeat the calculation for a 10\(^{-1}\) M solution of ammonia containing 10\(^{-3}\) mol of \( NaOH \) per liter of solution.

4.4.11 The solubility of \( PbI_2 \) in water at 20°C is 1.37 \times 10\(^{-3}\) molal; for this temperature the numerical value of 0.5092 must be replaced with 0.5071. (a) Determine the solubility product constant at 20°C. Determine the solubility of \( PbI_2 \) in a 0.30 molal solution of \( KI \) in water.

4.5 THE ELECTROCHEMICAL POTENTIAL

The work performed on a charge \( ze \) that is moved from infinity under the influence of an electrostatic field to a point where the electrostatic potential is \( \phi \), is given by

\[
W = -ze\phi. \tag{4.5.1}
\]

The energy change required in having \( dn_i \) moles of species \( i \) and charge \( z_iF \) per mole participate in this process is thus given by \( -z_iF\phi dn_i \), and the energy change for the entire system of charges reads

\[
dU = dE + \sum_i z_iF\phi dn_i = TdS - PdV + \sum_i (\mu_i + z_iF\phi)dn_i, \tag{4.5.2}
\]

where \( dE \) is the energy differential for the system in the absence of the electrostatic potential. Proceeding by the usual set of Legendre transforms one obtains for the differential of the Gibbs free energy the expression
\[
\frac{dG}{d} = -SdT + VdP + \sum_i (\mu_i + z_iF\phi)dn_i.
\]

This suggests that we define an electrochemical potential as
\[
\zeta_i = \mu_i + z_iF\phi,
\]
so that in the presence of an electric field
\[
\zeta_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P}.
\]

Equations (4.5.4) and (4.5.5) are useful where equilibrium is established for two or more phases in contact. As was shown in Section 2.1, a necessary and sufficient condition for equilibrium is the equality of the chemical potential \(\mu_i\) for each component \(i\) distributed among the phases. Whenever electrostatic effects are relevant it is necessary also to demand that the quantity \(z_i F\phi\) involving the electrostatic potential be the same for all phases in contact; otherwise, ions or electrons will move under the influence of an electrostatic field. Both requirements may be met simultaneously by demanding that the electrochemical potential for each of the species distributed among different phases be the same.

The splitting of \(\zeta_i\) into an electrical and a chemical component is quite arbitrary, as is discussed in some detail by Guggenheim\(^1\) and in a different context, by Harman and Honig\(^2\). What is in fact physically measurable is only a difference in electrochemical potential, not a difference in electrostatic potential. However, it turns out that for two phases at identical chemical composition, temperature, pressure, and mechanical condition, \(\Delta\zeta/e = (\zeta' - \zeta'')/e\) is equal


to $\Delta \phi_+ = \phi' - \phi''$ for positively charged particles.

4.6 GALVANIC AND ELECTROLYSIS CELLS: GENERAL DISCUSSION

(a) The operation of galvanic and of electrolysis cells has been intensively studied for well over 150 years; as an elementary example we consider the Daniell cell depicted in Fig. 4.6.1. Basically, it consists of a strip of copper metal immersed in a saturated $\text{CuSO}_4$ solution located in one compartment. A second compartment, separated from the first by a salt bridge or porous wall, contains a saturated $\text{ZnSO}_4$ solution into which a strip of zinc metal is immersed. When the two compartments are electrically connected there is set up a difference in electrochemical potential that activates a current flow whenever these electrodes are linked by a wire.

![Spontaneous electron flow diagram](image)

FIGURE 4.6.1 A Daniell cell. The rectangular box labeled P represents a potentiometer. Anode and cathode are shown for spontaneous operation of the cell, wherein Zn enters the solution and Cu is deposited on the right-hand electrode. The cell operates as shown when the potentiometer emf is slightly below the emf of the cell. If the opposing potentiometer emf exceeds that of the Daniell cell, the cell operation is reversed.
Alternatively, a potentiometer connected across the open circuit is found to register a potential difference that renders the Cu electrode positive relative to the Zn electrode; the magnitude of the open-circuit electrochemical potential difference, which later will be shown to be identical with the electromotive force (emf), symbolized by $\mathcal{E}$, is approximately 1.1 volts.

If the potentiometer is readjusted so that its own emf, $\mathcal{E}_p$, is less than that generated by the Daniell cell, electric current is found to flow through the external circuit. Conventionally, one states that positive current passes from the Cu to the Zn electrode; in actuality, electrons pass from the Zn to the Cu terminal.

The electron flow is governed by the requirement that electroneutrality must everywhere be strictly preserved: Electrons are furnished to the external circuit by the oxidative process $\text{Zn} - \text{Zn}^{2+} + 2e^{-}$; the electrode where oxidation occurs is termed the anode. The electron concentration in the wire is exactly neutralized by the positive ion cores of the constituent atoms making up the wire. Electrons entering the circuit at A displace a corresponding number onto the electrode at C, where a reductive process $\text{Cu}^{2+} + 2e^{-} = \text{Cu}$ acts as a sink for electron removal. The electrode where reduction occurs is known as the cathode. Accompanying these processes is the accumulation of $\text{Zn}^{2+}$ in the anode compartment and the depletion of $\text{Cu}^{2+}$ in the cathode compartment. Electroneutrality is maintained by migration of $\text{SO}_4^{2-}$ from right to left. The deposition of $\text{Cu}^{2+}$ as Cu and migration of $\text{SO}_4^{2-}$ away from the cathode region is compensated for by dissolution of an appropriate quantity of $\text{CuSO}_4$ crystals. The generation of $\text{Zn}^{2+}$ resulting from the oxidation and the arrival of $\text{SO}_4^{2-}$ in the anode region results in deposition of appropriate amounts of $\text{ZnSO}_4$ crystals. The net result of all these processes may be represented schematically by the equation $\text{Zn} + \text{CuSO}_4 = \text{Cu} + \text{ZnSO}_4$; clearly, the actual intermediate processes are vastly more complex. Finally, the potentiometer acts essentially as a passive, nonreactive element in the external circuit; if
replaced by a resistor, the cell is found to do useful work by the passage of current through the resistor. One sees that the Daniell cell functions because the tendency of Zn to give up electrons and thus, to undergo oxidation, is stronger than that of Cu to do so, forcing a reductive process on Cu$^{2+}$. The current flow is therefore a consequence of the chemical instability of Zn relative to Zn$^{2+}$ under the conditions present in the Daniell cell: Chemical potential has been transformed into electrical energy flow.

Suppose now that the potentiometer is so adjusted that its emf counteracts and exceeds that of the Daniell cell. In this event the potentiometer acts as a battery; electrons are now forcibly transported from the Cu to the Zn terminal. This is accompanied by the forced release of electrons to the Cu terminal according to the oxidative process Cu → Cu$^{2+}$ + 2e$^-$ and by the forced acceptance of electrons at the Zn terminal in the reductive process Zn$^{2+}$ + 2e$^-$ → Zn. The net process inside the cell is representable according to the reaction Cu + ZnSO$_4$ → CuSO$_4$ + Zn. The cell operation has now been reversed; it should be noted that now the Cu electrode becomes the anode and the Zn electrode, the cathode.

An important consequence of the preceding discussion is the element of reversibility: By adjusting the potentiometer emf so that it exactly opposes the cell emf, the entire system is maintained in a static, quiescent condition, even though it may be far removed from the normal equilibrium state. A slight offset in bias permits a chemical process to proceed infinitesimally in either direction. A reversible process can thus be made to occur in this type of cell, and its mode of operation thereby becomes amenable to the methodology of thermodynamics.

In more general terms, one seeks to characterize by thermodynamics the properties of a galvanic cell consisting of (a) two electrolyte solutions usually in separate compartments, (b) in physical contact with metallic electrodes, (c) which are connected to each other through an adjustable potentiometer, and (d) which additionally may interact with reactive gases.
Actually, this situation may be further generalized as shown later. In particular reversible processes that involve any infinitesimal departures from the quiescent condition of the open-circuit conditions, chemical oxidation-reduction processes occur, which keep in step with the electron flow through a closed external circuit.

The preceding discussion and the description in Section 4.5 suggests that one can identify the electrochemical potential as the source of emf in any cell. Let us again use the Daniell cell as an example. For the process $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ at the cathode, the equilibrium process described in Section 4.5 leads to the requirement $\zeta_{\text{Cu}} - \zeta_{\text{Cu}^{2+}} - 2\zeta_{e^-} = 0$. Here $\zeta_{\text{Cu}^{2+}}$, for example, represents the electrochemical potential of Cu$^{2+}$ in the vicinity of the Cu electrode. Similarly, for the process $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$ at the anode one must require $2\zeta_{e^-} + \zeta_{\text{Zn}^{2+}} - \zeta_{\text{Zn}} = 0$. It follows that $2(\zeta_{e^-} - \zeta_{\text{Zn}}) = (\zeta_{\text{Cu}} - \zeta_{\text{Zn}}) - (\zeta_{\text{Cu}^{2+}} - \zeta_{\text{Zn}^{2+}})$. One now defines the electromotive force (emf) $\mathcal{E}$ by $\mathcal{E} = 2(\zeta_{e^-} - \zeta_{\text{Cu}^{2+}})$, where $\mathcal{E}$ is the Faraday (96,487 coulombs, the numerical value of the charge associated with one mole of electrons).

More generally, the emf is related to the difference in the electrochemical potential for electrons that develops under open circuit conditions between the two electrodes of the cell under study. For the example considered here $\mathcal{E} = \frac{1}{2}(\zeta_{\text{Zn}} - \zeta_{\text{Cu}}) + \frac{1}{2}(\zeta_{\text{Cu}^{2+}} - \zeta_{\text{Zn}^{2+}})$. This may be revamped by noting that the solutions also contain $\text{SO}_4^{2-}$ as the common anion in different concentrations. We may set $\frac{1}{2}\zeta_{\text{Zn}^{2+}} = \frac{1}{2}(\zeta_{\text{ZnSO}_4} - \zeta_{\text{SO}_4^{2-}})$ and $\frac{1}{2}\zeta_{\text{Cu}^{2+}} = \frac{1}{2}(\zeta_{\text{CuSO}_4} - \zeta_{\text{SO}_4^{2-}})$. Then $2\mathcal{E} = -(\zeta_{\text{Cu}} - \zeta_{\text{CuSO}_4}) + (\zeta_{\text{Zn}} - \zeta_{\text{ZnSO}_4}) - (\zeta_{\text{SO}_4^{2-}} - \zeta_{\text{SO}_4^{2-}})$. This relation is composed of three terms, involving the electrochemical potential drop at the anode compartment, across the junction of the ZnSO$_4$, CuSO$_4$ solutions, and at the cathode compartment. This division is strongly suggestive and provides insight into the origin of the overall emf. However, it should be recognized that the decomposition of $\mathcal{E}$ into these three terms is quite arbitrary, and that entirely different schemes of analysis can be devised. Nevertheless, in every case, one encounters contributions relating to changes in $\zeta$ at the vicinity of cathode and of the anode, as well as a
contribution representing an electrochemical potential drop across dissimilar solutions. This latter contribution is hard to evaluate but can be rendered small by methods to which we allude later. For the moment we ignore this term, assuming it to be negligible. The emf then arises solely from the two processes of equilibration at the cell electrodes.

In more general terms, the operation of electrochemical cells may be understood on the basis that each electrode represents a medium for the electron interchange concomitant to oxidation-reduction processes. These reactions may involve electron transfer (i) between ions of different valence states in immediate proximity close to the electrode surface, (ii) through the decomposition of the solvent into ionic species, (iii) by species adsorbed on the electrode surface which themselves are in equilibrium with an ambient atmosphere, or (iv) in reactions involving the electrode materials and/or solid or liquid phases by contact with the electrode. The key feature in this scheme is the occurrence of electron-transfer processes at both electrodes, with the transport of electrons through an external circuit and the concomitant set of ionic displacements that preserve electroneutrality everywhere in the system.

(b) The preceding description must now be translated into a proper mathematical analysis of the underlying thermodynamic principles. Consider the schematic cell depicted in Fig. 4.6.2, which is subject to a reversible spontaneous transfer of electrons through the external circuit. For this to happen the left electrode must remain negatively biased with respect to the right electrode. The electric field $E$ then points in the direction of conventional positive current flow, i.e., to the left. The electrostatic potential gradient $\nabla \phi = -E$ is oppositely directed, and points to the right. Given the proposed operational conditions, the electron density, and hence $\ln a_e$ for the electrons, increases from right to left. Thus, the electrochemical potential gradient, $\nabla \mu_e = \nabla \mu_e - \nabla F \phi$
FIGURE 4.6.2 Schematic diagram illustrating the directions of electric field, electrostatic potential gradients, electrochemical potential gradient, and emf for a representative cell under open circuit conditions, and set up in accord with Conventions 1 and 2, developed later.

\[ -RT \ln a_e - \nabla F \phi, \] points to the left and the electrochemical potential itself is governed by the inequality \( \zeta_e(l) > \zeta_e(r) \).

We now modify slightly the approach in Section 2.9, where we had shown that at equilibrium (subject to constant temperature and pressure) \( \Delta G_d = \sum_{i} \nu_i \mu_i = 0 \), corresponding to the schematic chemical reaction \( \sum_{i} \nu_i A_i = 0 \). In our particular case we deal with charged species; we therefore adopt the expression (4.5.3), employing \( \sum_{i} \nu_i \xi_i = 0 \) as the appropriate equilibrium condition, in conformity with the earlier discussion.

As applied to the Daniell cell we again write \( \text{Zn}(s) = \text{Zn}^{2+}(m_L) + 2e^-(l) \) for the oxidation step on the left and \( \text{Cu}^{2+}(m_r) + 2e^-(r) \rightarrow \text{Cu}(s) \) for the reduction step on the right. These are then to be combined into the net reaction schematized by Eq.
4. THERMODYNAMIC PROPERTIES OF ELECTROLYTES

(4.6.1), in which we have also included the compensating anions that preserve electroneutrality in the two compartments: We write

\[ \text{Zn}(s) + \text{Cu}^{2+}(m_r) + \text{SO}_4^{2-}(m_r) + 2e^-(r) \]

\[ = \text{Cu}(s) + \text{Zn}^{2+}(m_l) + \text{SO}_4^{2-}(m_l) + 2e^-(l). \]  

Note that we have not canceled out the important electronic constituents; they are present at different concentrations at the two electrodes. It is precisely this difference that drives the cell operation when the open circuit is closed.

We next apply the condition \( \Sigma_\xi \mu_i \xi_i = 0 \) to Eq. (4.6.1) and note that for uncharged species \( \xi = \mu \). This leads to

\[ \mu_{\text{Cu}(s)} + \mu_{\text{ZnSO}_4(s)} + \text{RT} \ln a_z^2(m_l) + F\phi_{\text{Zn}^{2+}(m_l)} - F\phi_{\text{SO}_4^{2-}(m_l)} + 2\xi_e^-(l) \]

\[ - [\mu_{\text{Zn}(s)} + \mu_{\text{CuSO}_4(s)} + \text{RT} \ln a_z^2(m_r)] \]

\[ + F\phi_{\text{Cu}^{2+}(m_r)} - F\phi_{\text{SO}_4^{2-}(m_r)} + 2\xi_e^-(r)] = 0. \]  

(4.6.2)

The ionic constituents \( \text{Zn}^{2+} \) and \( \text{SO}_4^{2-} \) in the left compartment are at the same electrostatic potential \( \phi(l) \), whence the corresponding terms in \( \phi \) cancel out from Eq. (4.6.2). The same is true of \( \text{Cu}^{2+} \) and of \( \text{SO}_4^{2-} \) on the right. Furthermore, for standard conditions the terms in \( \mu^* \) can be grouped into an equilibrium constant \( \text{RT} \ln K_q \), as in Section 3.7. We can then solve Eq. (4.6.2) for

\[ 2F\mathcal{E} = [\xi_e^-(l) - \xi_e^-(r)] - \text{RT} \ln K_q - \text{RT} \ln \left\{ \frac{a_z^2(m_l)}{a_z^2(m_r)} \right\}. \]  

(4.6.3)

with \( \text{RT} \ln K_q = \mu_{\text{Zn}(s)}^* + \mu_{\text{CuSO}_4}^* - \mu_{\text{Cu}(s)}^* - \mu_{\text{ZnSO}_4}^* \). Here we have also reintroduced the earlier definition, namely the electromotive force or emf, by

\[ \mathcal{E} = [\xi_e^-(l) - \xi_e^-(r)]/F. \]  

(4.6.4)
Note the following: (i) The emf, \( \mathcal{E} \), is in a sense an 'open circuit voltage' that must be multiplied by a charge, \( F \) in this case, to be compatible with the Gibbs free energy, which is the proper thermodynamic function of state for use at constant \( T \) and \( P \). More precisely, \( \mathcal{E} \) is directly related to the difference in electrochemical potential at the left and right terminals. (ii) We have set up the circuit of Fig. 4.6.2 and the corresponding inequalities by assuming spontaneous, reversible electron flow from \( l \) to \( r \). Since \( \xi_l > \xi_r \), it follows that \( \mathcal{E} > 0 \) corresponds to such a spontaneous transfer. (iii) The fact that the preceding discussion is based on electron transfers means that \( F \) represents the magnitude of the charge transport. (iv) The emf (4.6.4) is governed solely by the spontaneous net chemical reaction abstracted from (4.6.1); we can therefore introduce our prior definition \( \Delta G_d = \mu_{Zn^{2+}} + \mu_{Cu^-} - [\mu_{Zn} + \mu_{Cu^{2+}}] \) that involves solely the chemical potentials of the various species involved in the battery operation. Thus,

\[
\mathcal{E} = - \frac{\Delta G_d}{2F} \tag{4.6.5}
\]

for the net chemical reaction \( \sum \nu_i A_i = 0 \) as written; moreover, \( \Delta G_d < 0 \), as expected. (v) In the final expressions there is no explicit reference to electron participation. It is not that these quantities have 'canceled out' from Eq. (4.6.1); rather, their effect is subsumed in the definition for \( \mathcal{E} \). Correspondingly, contrary to what is often stated, a potentiometer does not measure differences in electrostatic potential but differences in electrochemical potential of the electrodes. (vi) The use of the term electromotive force is clearly a most undesirable appellation. Unfortunately, this nomenclature is now so firmly rooted that it is unlikely to be displaced by a more appropriate terminology.

The preceding discussion presents an obviously very schematic representation of the actual processes that occur in the operation of the Daniell cell. Nevertheless, all the essentials for a thermodynamic analysis have been included. Although we have based our discussion on a specific example,
the preceding discussion is capable of immediate
generalization, to which we now devote the subsequent
presentation.

EXERCISES

4.6.1 Provide evidence to show that the emf for the
combination Zn|M|Cu is the same as for the Zu|Cu couple; here
M is any desired metal.

4.6.2 Provide a physical model which, on a microscopic
basis, accounts for the fact that an emf is set up at the phase
boundary between dissimilar substances, which permit electron
transfer to occur.

4.7 GALVANIC CELLS: GENERAL TREATMENT

(a) When a cell is functioning reversibly, work is being
performed on or by the system in transferring electric charge
through any cross section of the circuit. The reversible
operation of the cell according to the generalized chemical
equation \( \Sigma_{(i)} \nu_i A_i = 0 \) is carried out only to an infinitesimal
extent, so that it does not alter either the concentration of
chemical species or the emf (open circuit potential
difference). Then, a unit advancement \( \delta \lambda \) in the chemical
process (see Section 2.9) involves the transfer of \( nF \delta \lambda \)
electrons through the external circuit, where \( n \) is the number
of equivalents, determined by the nature of the process, and
where \( F \), the Faraday (i.e., the charge for Avogadro's number of
electrons), is 96,487 coulombs. The work done by the cell,
when the opposing emf is infinitesimally less that required for
maintaining static conditions, is \( nF \delta \lambda \). As argued in Section
1.16, for reversible processes, at constant \( T \) and \( P \), the work
other than mechanical is given by \( \delta W = - \delta G \). In the present
case the cell reaction must occur spontaneously, hence for an
infinitesimal virtual advancement \( \delta \lambda \), \( + nF \delta \lambda = - (\delta G/\delta \lambda)_{T,P} \delta \lambda \),
or

\[ nF \delta \lambda = - \Delta G_d, \quad (4.7.1) \]
where $\Delta G_d$ is the increase in free energy accompanying the chemical cell reaction $\Sigma_{1} \nu_{1} A_{1} = 0$ per unit of advancement. This is in agreement with the special case considered in deducing Eq. (4.6.5). We had shown in Section 4.6 why one can use the expression for the net chemical equilibrium in dealing with electrochemical processes.

(b) The subsequent formulation depends on the choice of standard states. We shall follow convention by adopting the hybrid system discussed in Section 3.7(c): (i) For pure solids or liquids that participate in the electrochemical process, the standard state is that at which the isolated component is subjected to a total pressure of one atmosphere at the temperature of interest. As shown in Eq. (3.6.3b) the relative activity for such species is given by $a_s(T,P,q_s) = \gamma_s(T,P,q_s^*)a_s^*(T,P)$, in which $q$ represents either $x$, $c$, or $m$ (note again that $q/q^* = 1$ for pure materials); the relative activity so defined is almost invariably close to unity. (ii) For substances forming homogeneous mixtures in the solid, liquid, or gaseous phases, the standard state is chosen to be that in which each substance in the mixture is present at unit activity and subjected to one atmosphere at the temperature of interest. As used in Eq. (3.5.21) the activity of these species is specified by $a_j(T,P,q_j) = \gamma_j(T,P,q_j)a_j^*(T,P)q_j$. The summation for $j$ runs over all ionic species, as well as over any dissolved but un-ionized species, which participate in the electrochemical reaction. It is customary to replace the $\gamma_j$, $a_j$, and $q_j$ for the individual ions by corresponding mean quantities $\gamma_\pm$, $a_\pm$, and $q_\pm$, as discussed in Section 4.1, and as illustrated in later sections. Also, we frequently adopt atmospheric pressure as the operating condition, in which case $a_l^*(T,1) = 1$ for all species ($l = s,j$), as may be ascertained by examination of Eqs. (3.4.10b), (3.4.12), (3.5.17), and (3.5.20) in conjunction with Eqs. (3.7.15), (3.7.16).

The equation for $\Delta G_d$ consistent with the above choice is Eq. (3.7.12); on introducing this relation in (4.7.1) we find
\[\varepsilon = \frac{RT}{nF} \ln K_q - \frac{RT}{nF} \left[ \sum_s \nu_s \ln a_s(T,P,q^*_s) + \sum_j \nu_j \ln a_j (T,P,q_j) \right], \tag{4.7.2a}\]

which under operating conditions of one atmosphere, reduces to

\[\varepsilon = \frac{RT}{nF} \ln K_q - \frac{RT}{nF} \sum_j \nu_j \ln (\gamma_j q_j) \quad (P = 1 \text{ atm}), \tag{4.7.2b}\]

where Eq. (3.5.21) has been used.

It is conventional to designate by \(\varepsilon^o\) the **standard emf** of the same cell, in which all species are at unit activity; from (4.7.2a) it is seen that

\[\varepsilon^o = \frac{RT}{nF} \ln K_q = - \frac{\Delta G^o_{eq}}{nF}, \tag{4.7.3}\]

so that Eq. (4.7.2a) becomes

\[\varepsilon = \varepsilon^o - \frac{RT}{nF} \left[ \sum_s \nu_s \ln a_s(T,P,q^*_s) + \sum_j \nu_j \ln a_j (T,P,q_j) \right], \tag{4.7.4}\]

which is known as the Nernst equation (1889). Clearly, \(\varepsilon^o\) depends on the choice of concentration units, but the sum (4.7.4), i.e. \(\varepsilon\), does not. One immediately sees the tremendous utility of \(\varepsilon^o\) measurements: For any cell which can be set up to simulate ionic, solid state, liquid or gaseous reactions of interest, such a determination directly yields the corresponding equilibrium constant \(K_q\).

(c) It is helpful at this state to introduce a systematic nomenclature and several conventions that permit a unified analysis of cell performance. The general procedure is explained in terms of a particular example: Let a Pt electrode, surrounded by hydrogen gas at pressure P, dip into an aqueous HCl solution of molality \(m_1\), in contact with a similar solution at molality \(m_2\), and saturated with respect to
GALVANIC CELLS

AgCl, into which is immersed a silver electrode. To save on such descriptive verbiage one represents such a cell by Pt, H₂(P)|HCl (m₁, sat by H₂)|HCl (m₂, sat by AgCl)|AgCl(s), Ag(s), where vertical bars separate different portions of the cell. Pt is used here as an inert electrode material which does not participate in any oxidation processes in aqueous solution but which provides an interface for H⁺, H₂, e⁻ interactions.

We now introduce Convention 1: For the cell as written the oxidative process always occurs on the left and the reductive process on the right. According to this scheme electrons are given off at the left and move through the external circuit to the right, where they are taken up by species in solution, as illustrated in Fig. 4.6.1; conventional current flows in the opposite direction. The overall process is best visualized in terms of the two half reactions at the anode and cathode respectively. In the present scheme these read as follows: anodic: ½H₂(P) = H⁺(m₁) + e⁻, on the left; cathodic: e⁻ + AgCl(s) = Ag(s) + Cl⁻(m₂), on the right; so that the overall process is representable as ½H₂(P) + AgCl(s) = Ag(s) + H⁺(m₂) + Cl⁻(m₂), accompanied, in accord with Convention (1), by the electron flow through the external circuit from the Pt to the Ag electrode and by H⁺ transfer from left to right.

By Convention 2 the emf developed by the cell as written, under open circuit conditions, is taken as

$$\mathcal{E} = \mathcal{E}_l - \mathcal{E}_r - (\xi_l - \xi_r)/F,$$  \hspace{1cm} (4.7.5)

where l and r refer to the left and right electrodes for the cell as written under Convention 1; \( \xi \) is the electrochemical potential introduced in Section 4.6. This step reflects the process of splitting the cell operation into an oxidative and a reductive half reaction. Convention 2 is consistent with our prior discussion, as was shown for the general cell depicted by Fig. 4.6.1.

A further check for self-consistency is the following: A cell for which an additional electron is brought up from infinity and placed on the negative terminal, is at higher
energy than the same cell for which the additional electron is placed on the positive terminal. Hence, the movement of an electron from the negative to the positive terminal lowers the energy and thus the free energy, of the cell. The spontaneous advancement of the cell reaction by $d\lambda$ requires the concomitant transfer of $nF\delta\lambda$ electrons through the external circuit from left ($-$) to right ($+$) past a difference of electrochemical potential under near-open circuit conditions. There is a concomitant change in electrochemical potential in the amount $\zeta_1 - \zeta_r$ per transferred electron, yielding an overall change of $nF\zeta\delta\lambda$ in the electrochemical potential. According to Eq. (4.5.3), this leads to a corresponding decrease $-dG = -(\partial G/\partial \lambda)_T, P d\lambda$ in Gibbs free energy at constant temperature and pressure. It now follows that $\Delta G_d = -nF\zeta$, as before.

(d) The determination of $\zeta$ and of $-\Delta G_d/nF$ according to (4.7.4) proceeds in an orderly fashion by first dealing with the quantity $\zeta^0$. Here, advantage is taken of the prior step in which the overall reaction is written as a sum of the half reactions. By Convention 3 one associates with each half-reaction a standard oxidation potential $\zeta^0$, which is to be computed as a special case of (4.7.5):

$$\zeta^0 = \zeta^0_l - \zeta^0_r,$$

(4.7.6)

where $\zeta^0_l$ and $\zeta^0_r$ are the standard oxidation potentials for the half reactions at the left and right electrodes for the cell as written. Extensive tabulations, from which Table 4.7.1 is excerpted, are available for specifying the $\zeta^0$ values; take note that these quantities themselves may be positive or negative. All half reactions in the table are written as oxidative processes, so that the complete cell reaction must be obtained by turning one of the half reactions around, thereby changing the sign of its emf value. That is, the operation required by Eq. (4.7.6) necessitates that one take for $\zeta^0_l$ and $\zeta^0_r$ the standard values for the half reactions cited in the table; the sign change is attended to by the formulation (4.7.6). One
notes that indeterminacies can arise from sign problems in (4.7.5) and (4.7.6) and from the fact that (4.7.6) could equally well be written as \( E^0 = (E^0_1 - c_1) - (E^0_2 - c_1) \), where \( c_1 \) is any arbitrary constant. The first matter is dealt with by **Convention 4**: The emf is regarded as positive for the operating cell when the electrons tend spontaneously to flow from the electrode written on the left to that written on the right. The second item is attended to by **Convention 5**: The standard electrode potential for the half reaction \( \frac{1}{2}H_2(P = 1 \text{ am.}) = H^+(a_+ = 1) + e^- \) is arbitrarily set at zero: \( E^0_{H_2,H^+} = 0 \).

It now should be very clear how Table 4.7.1 for the \( E^0 \) values can be constructed: One successively couples appropriate half cells to the half cell in which the reaction \( e^- + H^+ (aq^+ = 1) = \frac{1}{2}H_2 \ (P_{H_2} = 1 \text{ atm}) \) is carried out on the right; in the half cell to be tested all dissolved species must be at unit activity and all reacting gases, at atmospheric pressure. The resulting emf has a sign that is positive or negative according to whether the electrode on the left is at a lower or higher electrostatic potential than the electrode on the right; this emf represents the value of \( E^0 \) for the half cell under study, since \( E^0 \) for the standard hydrogen electrode is zero by convention. Once a set of such measurements has been completed, the corresponding half cells can be used as secondary reference standards for other half cells whose \( E^0 \) is to be determined. With appropriate cross checks a self consistent tabulation can thus be constructed.

One must be very cautious in the use of Eqs. (4.7.5) and (4.7.6). Their physical interpretation is that the emf arises as a competition between the two half reactions in the extent to which the chemical entities can give up electrons to their respective terminals. That half reaction which renders its electrode more negative 'wins,' in the sense that the opposing one is forced to undergo a reduction process. The spontaneous cell operation is thus driven by the electrode at which oxidation occurs. \( E^0_1 \) and \( E^0_2 \) are both standard oxidation emfs which are a measure of the tendency for the half reaction to generate electrons.
### Table 4.7.1  SHORT TABLE OF STANDARD EMF VALUES (IN VOLTS)

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrolyte</th>
<th>EMF (Volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>Ba^{2+}</td>
<td>Ba - Ba^{2+} + 2e^{-}</td>
</tr>
<tr>
<td>Mg</td>
<td>Mg^{2+}</td>
<td>Mg - Mg^{2+} + 2e^{-}</td>
</tr>
<tr>
<td>Al</td>
<td>Al^{3+}</td>
<td>Al - Al^{3+} + 3e^{-}</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn^{2+}</td>
<td>Zn - Zn^{2+} + 2e^{-}</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe^{2+}</td>
<td>Fe - Fe^{2+} + 2e^{-}</td>
</tr>
<tr>
<td>Cd</td>
<td>Cd^{2+}</td>
<td>Cd - Cd^{2+} + 2e^{-}</td>
</tr>
<tr>
<td>Pt</td>
<td>Ti^{2+}, Ti^{3+}</td>
<td>Ti^{2+} - Ti^{3+} + e^{-}</td>
</tr>
<tr>
<td>Pb</td>
<td>PbSO_{4}</td>
<td>Pb + SO_{4}^{2-} - PbSO_{4} + 2e^{-}</td>
</tr>
<tr>
<td>Cu</td>
<td>CuI</td>
<td>Cu + I^{-} - CuI + e^{-}</td>
</tr>
<tr>
<td>Pt</td>
<td>H_{2}</td>
<td>H_{2} - 2H^{+} + 2e^{-}</td>
</tr>
<tr>
<td>Ag</td>
<td>AgBr</td>
<td>Ag + Br^{-} - AgBr + e^{-}</td>
</tr>
<tr>
<td>Pt</td>
<td>Cu^{+}, Cu^{2+}</td>
<td>Cu^{+} - Cu^{2+} + e^{-}</td>
</tr>
<tr>
<td>Ag</td>
<td>AgCl</td>
<td>Ag + Cl^{-} - AgCl + e^{-}</td>
</tr>
<tr>
<td>Pt</td>
<td>Hg</td>
<td>2Cl^{-} + 2Hg = Hg_{2}Cl_{2} + 2e^{-}</td>
</tr>
<tr>
<td>Pt</td>
<td>I_{2}</td>
<td>3I^{-} = I_{3}^{-} + 2e^{-}</td>
</tr>
<tr>
<td>Pt</td>
<td>Fe^{2+}, Fe^{3+}</td>
<td>Fe^{2+} - Fe^{3+} + e^{-}</td>
</tr>
<tr>
<td>Ag</td>
<td>Ag^{+}</td>
<td>Ag - Ag^{+} + e^{-}</td>
</tr>
<tr>
<td>Pt</td>
<td>Tl^{+}, Tl^{3+}</td>
<td>Tl^{+} - Tl^{3+} + 2e^{-}</td>
</tr>
<tr>
<td>Pt</td>
<td>Cl_{2}</td>
<td>2Cl^{-} - Cl_{2} + 2e^{-}</td>
</tr>
<tr>
<td>Pt</td>
<td>Mn^{2+}, MnO_{4}^{-}</td>
<td>Mn^{2+} + 4H_{2}O - MnO_{4}^{-} + 8H^{+} + 5e^{-}</td>
</tr>
<tr>
<td>Pt</td>
<td>SO_{3}^{2-}, SO_{4}^{2-}</td>
<td>SO_{3}^{2-} + 2OH^{-} = SO_{4}^{2-} + H_{2}O + 2e^{-}</td>
</tr>
<tr>
<td>Pt</td>
<td>H_{2}</td>
<td>H_{2} + 2OH^{-} = 2H_{2}O + 2e^{-}</td>
</tr>
<tr>
<td>Pt</td>
<td>O_{2}</td>
<td>4OH^{-} - O_{2} + 2H_{2}O + 4e^{-}</td>
</tr>
<tr>
<td>Pt</td>
<td>MnO_{2}</td>
<td>MnO_{2} +4OH^{-} = MnO_{4}^{-} + 2H_{2}O +3e^{-}</td>
</tr>
</tbody>
</table>
There is obviously nothing compelling in the use of standard oxidation emfs. One could equally well deal with a tabulation in which all the half reactions are reversed. These data are compiled by coupling the appropriate half cell to the hydrogen cell operating according to the scheme $\frac{1}{2}H_2 (P_{H_2} = 1 \text{ atm}) - H^+ (a_{H^+} = 1) + e^-; all species must be present under standard conditions. It should be clear that the corresponding emf values are reversed in sign relative to those compiled in Table 4.7.1; these new values are a measure of the tendency of the half reactions to remove electrons from the electrode. Correspondingly, one would write $\varphi^o = \varphi^r - \varphi^i$ for the standard reduction emfs. Many writers prefer this particular formulation; when used self-consistently one naturally obtains the same numerical values for $\varphi^o$ as by the method involving standard oxidation emfs.

(e) We provide a very elementary example to illustrate the preceding remarks. Consider the cell

$$\text{Pt, Cl}_2(P = 1 \text{ atm})|\text{HCl (a}_x = 1)|\text{AgCl(s), Ag(s)},$$

whose operation, in accord with Convention 1, is given by (25°C)

$$2\text{Cl}^- (a_\text{Cl}^- = 1) = \text{Cl}_2 (P = 1 \text{ atm}) + 2e^- \quad \varphi^i = -1.3595 \text{ V}$$

$$2\text{AgCl(s)} + 2e^- = 2\text{Ag(s)} + 2\text{Cl}^- (a_\text{Cl}^- = 1) \quad -\varphi^r = +0.2225 \text{ V}$$

$$2\text{AgCl(s)} = \text{Cl}_2(g) + 2\text{Ag(s)} \quad \varphi^o = -1.1370 \text{ V}$$

(4.7.7)

One should carefully note how Convention 3 is applied: $\varphi^o = \varphi^i - \varphi^r$; $\varphi^i$ may be read off from Table 4.7.1. However, in writing the lower half reaction as a reduction equation, we need a sign reversal in converting $\varphi^o$ for an oxidative process to $\varphi^o$ for a reductive process. The contributions from Cl\(^-\) cancel in the algebraic addition process because the activity is the same on both sides.
One can now compute $\Delta G^\circ_2$ for the net reaction $2\text{AgCl}(s) = \text{Cl}_2(P = 1\text{ atm}) + 2\text{Ag}(s)$ according to $\Delta G^\circ_2 = -2F\varphi^\circ = -2(96,487)(-1.1370)\text{ J/mol} = 219,420\text{ J/mol}$. Since $\Delta G^\circ_2 > 0$ the reaction proceeds spontaneously in the reverse direction. The reader should be able to verify readily the following statements: (i) If the half reactions had been written as $\text{Cl}^- = \frac{1}{2}\text{Cl}_2 + e^-$ and $e^- + \text{AgCl} = \text{Ag} + \text{Cl}^-$, the $\varphi^\circ$ values for the half reactions and the total $\varphi^\circ$ would have remained unaltered; however, $n = 1$ in this case and $\Delta G^\circ_2 = 109,710\text{ J/mol}$. (ii) If the cell and cell reactions had been reversed according to the scheme $\text{Ag}(s),\text{AgCl}(s)|\text{HCl}(a_\text{H} = 1)|\text{Cl}_2(P = 1\text{ atm}),\text{Pt}$, with half reactions $2\text{Ag}(s) + 2\text{Cl}^-(a_\text{Cl} = 1) = 2\text{AgCl}(s) + 2e^-$, $2e^- + \text{Cl}_2(P = 1\text{ atm}) = 2\text{Cl}^-(a_\text{Cl} = 1)$, then one would have obtained $\varphi^\circ = +1.1370\text{ V}$ and $\Delta G^\circ_2 = -219,420\text{ J/mol}$. This illustrates the general principle that if Conventions 1 and 2 yield a reaction which runs spontaneously in the direction opposite to that written down, then one finds $\varphi^\circ < 0$ and $\Delta G^\circ_2 > 0$. (iii) Silver tends to react spontaneously with chlorine gas to form solid silver chloride, but under standard conditions this spontaneous reaction can be reversed by electrolysis when the applied potential exceeds $1.1370\text{ V}$. (iv) If the operation of the cell is altered to read $\text{Pt},\text{Cl}_2(P)|\text{HCl}(a_\text{H})|\text{AgCl}(s),\text{Ag}(s)$, one obtains a net reaction $2\text{AgCl}(s) = \text{Cl}_2(P) + 2\text{Ag}(s)$. The Nernst equation now reads

$$\varphi = -1.1370 - \frac{RT}{2F} \ln \left( \frac{a_{\text{Ag}}}{a_{\text{AgCl}}} \right) - \frac{RT}{2F} \ln a_{\text{Cl}_2}$$

$$= -1.1370 - \frac{RT}{2F} \ln \left( \frac{a_{\text{Ag}}}{a_{\text{AgCl}}} \right) - \frac{RT}{2F} \ln a_{\text{Cl}_2},$$

in which the ratio $a_{\text{Ag}}/a_{\text{AgCl}}$ differs only slightly from unity and $a_{\text{Cl}_2}$ may ordinarily be replaced with $P_{\text{Cl}_2}$. (v) The reader should convince himself that precisely the same result, Eq. (4.7.7), would be obtained if the net reaction had been written in the form $\text{AgCl}(s) = \frac{1}{2} \text{Cl}_2(P) + \text{Ag}(s)$. Thus, the emf is independent of how the net reaction is balanced, which is a physically
sensible result. On the other hand, $\Delta G_d^*$ does depend on $n$, which again is a physically sensible result.

The reader should carefully study the manner in which oxidation – reduction potentials are handled in every experimental investigation of electrochemical cells.

EXERCISES

4.7.1 Do the two cells $\text{Cu(s)}|\text{Cu}^{++}||\text{Cu}^+|\text{Cu(s)}$ and $\text{Pb}|\text{Cu}^+$, $\text{Cu}^{++}||\text{Cu}^+|\text{Cu(s)}$ correspond to the same reaction and do they have the same value $E^*$?

4.7.2 The emf of the cell $\text{Zn}|\text{ZnCl}_2(\text{m})|\text{AgCl}(\text{s})|\text{Ag}$, with various molalities $m$ of zinc chloride, was found to be as follows at $25^\circ\text{C}$:

<table>
<thead>
<tr>
<th>$m$</th>
<th>$E$ (volts)</th>
<th>$m$</th>
<th>$E$ (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002941</td>
<td>1.1983</td>
<td>0.04242</td>
<td>1.10897</td>
</tr>
<tr>
<td>0.007814</td>
<td>1.16502</td>
<td>0.09048</td>
<td>1.08435</td>
</tr>
<tr>
<td>0.01236</td>
<td>1.14951</td>
<td>0.2211</td>
<td>1.05559</td>
</tr>
<tr>
<td>0.02144</td>
<td>1.13101</td>
<td>0.4499</td>
<td>1.03279</td>
</tr>
</tbody>
</table>

Determine the standard potential of the $\text{Zn, Zn}^{++}$ electrode.

4.7.3 Why does the electron concentration in the wire not enter the Nernst equation?

4.7.4 Discuss the difference in operation and in emf between the two cells $\text{Pt, H}_2(\text{P})|\text{HCl}(\text{m}_1)|\text{HCl}(\text{m}_2)|\text{AgCl, Ag}$ and $\text{Pt, H}_2(\text{P})|\text{HCl}(\text{m})|\text{AgCl, Ag}$. Illustrate the difference in terms of the Nernst equation.

4.8 TYPES OF ELECTRODES

The following types of electrodes are in common use:

(a) 'Gas' Electrodes: In this scheme, gas at a fixed pressure $P$ is forced over an immersed, inert metal electrode and is bubbled through the solution. An example of this cell is given by $\text{Pt}|\text{H}_2(\text{P atm}), \text{H}^+(\text{c mol/liter})$, corresponding to the half reaction $\frac{1}{2}\text{H}_2(g) = \text{H}^+ + e^-$. 
(b) **Oxidation-Reduction Electrodes**: Here, an inert metal dips into a solution containing ions in two distinct oxidation states. An example is furnished by Pt|Fe^{2+}(c_1), Fe^{3+}(c_2), corresponding to the half reaction Fe^{2+} = Fe^{3+} + e^-.

(c) **The Quinhydrone Electrode**: This is a specialization of case (b): Here, an equimolar mixture of hydroquinone (H_2Q) and quinone (Q), as obtained from quinhydrone (H_2Q-Q), is in contact with an inert metallic electrode. Schematically this half cell may be represented here by Pt|H_2Q, Q, H^+(c_1), corresponding to the half reaction H_2Q = Q + 2H^+ + 2e^-.

(d) **Metal-Metal Ion Electrodes**: Here metal ions in solution are equilibrated with a metallic electrode of the same material. An example is furnished by a silver electrode dipping into a solution of silver nitrate: Ag|Ag^+(c_1), corresponding to Ag = Ag^+ + e^-. Very active metals such as Na which react with water obviously cannot be employed in this manner.

(e) **Amalgam Electrodes**: In this setup the metal to be equilibrated with its ion is dissolved in a pool of mercury into which is dipped a wire made of a noble metal. This setup is used for active metals which normally would react directly with water; mercury does not participate in the reactions. An example is given by Pt|Hg-Na(c_1)|Na^+(c_2), corresponding to the reaction Na(c_1) = Na^+(c_2) + e^-.

(f) **Metal-Insoluble Salt Electrodes**: Here, a metal is in contact with an insoluble salt of the metal, which in turn is equilibrated with a solution containing the anion. This scheme is illustrated by the half cell Ag|AgCl(s)|Cl^-(c), corresponding to the reactions Ag = Ag^+ + e^- and Ag^+ + Cl^- = AgCl, with a net half reaction Ag + Cl^- = AgCl + e^-.

(g) **The Calomel Electrode**: A special case of the above is the widely used calomel electrode, where a Pt wire dips into
mercury in contact with a Hg₂Cl₂ paste, which is in contact with a KCl solution saturated with Hg₂Cl₂. Here the reactions \( \text{Hg} = \text{Hg}^+ + e^- \) and \( \text{Hg}^+ + \text{Cl}^- = \frac{1}{2} \text{Hg}_2\text{Cl}_2 \) occur, yielding a net half reaction \( \text{Hg} + \text{Cl}^- = \frac{1}{2} \text{Hg}_2\text{Cl}_2 + e^- \). This electrode frequently serves as a reference standard because use of the hydrogen electrode for a calibration standard is usually quite inconvenient.

EXERCISES

4.8.1 (a) The "dry cell" or Leclanché cell operates by oxidation of Zn(s) to Zn²⁺(aq), and by reduction of MnO₂(s) to Mn₂O₃(s) in the presence of NH₄Cl(aq), forming NH₄OH(aq). Write out the half reactions and the complete reaction for this process. (b) Inclusive of a 50% safety factor, what are the minimum masses of Zn and MnO₂ required to guarantee generation of a 10 mA current for 100 hours?

4.8.2 Devise a cell in which the half reactions \( \text{Fe(CN)}_6^{4-} = \text{Fe(CN)}_6^{3-} \) and \( \text{Mn}^{2+} = \text{MnO}_4^- \) can be carried out.

4.8.3 Write down the half reactions and complete cell reactions corresponding to the following galvanic cell diagrams:
   (a) K(Hg) | KCl(aq) | AgCl(s) | Ag
   (b) Pt | FeCl₂(aq,m₂) | FeCl₂(aq,m₃) | Fe
   (c) Hg, HgO(s) | NaOH(aq) | Zn(OH)₂(s), Zn
   (d) Pt, Cl₂(g) | KCl(aq) | Br⁻(aq) | Br₂(ℓ), Pt
   (e) Hg | H₂SO₄(s), Na₂SO₄(aq,m₄) | Na₂SO₄(aq,m₅), Hg₂SO₄(s) | Hg.

4.8.4 Devise galvanic cells in which the following reactions can in principle be carried out:
   (a) \( \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) = \text{H}_2\text{O}(ℓ) \)
   (b) \( \text{Zn}(s) + 2\text{AgBr}(s) = \text{ZnBr}_2(aq) + 2\text{Ag}(s) \)
   (c) \( 2\text{Hg}(ℓ) + \text{Cl}_2(g) = \text{Hg}_2\text{Cl}_2(s) \)
   (d) \( \text{Ag}(s) + \frac{1}{2} \text{O}_2(g) = \text{AgO}(s) \)
   (e) \( \text{Ag}^+(c_1) + I^-(c_2) = \text{AgI}(s) \)
   (f) \( \text{Pb} + 2\text{AgCl}(s) = \text{PbCl}_2(s) + 2\text{Ag} \).

4.9 LIQUID JUNCTION POTENTIALS

So far we have bypassed the problems arising from the juxtaposition of two dissimilar solutions in the cathodic and anodic compartments of the electrochemical cell. As already
indicated in the discussion of Section 4.6, contact between such solutions produces a contribution to the overall cell emf which ought to be taken into account. Nevertheless, it is generally dismissed as being small.

On a microscopic level, the liquid junction emf arises because two dissimilar solutions are obviously not in equilibrium. Interdiffusion of the various ions takes place; if allowed to proceed indefinitely, this process ultimately renders both solutions identical. If the diffusion process can be maintained at a sufficiently slow pace that the constitution of the solution surrounding the electrodes is not appreciably altered during the operation of the cell the junction potential problem may be ignored. In these circumstances the solutions surrounding the electrodes will remain homogeneous; no appreciable concentration of foreign ions will be generated in either compartment, and thus the chemical reactions associated with the operation of the cell are strictly reversible. To approximate this ideal condition one allows the two homogeneous electrolytes to intermingle over a considerable distance at a location well removed from the electrodes. Within the boundary zone each differential layer of solution will differ only infinitesimally from the neighboring layers, and an infinitesimal advancement of the cell reaction can be carried out without appreciably violating the conditions for reversibility.

Different ions in a given solution are characterized by distinct diffusion coefficients that govern their net rates of diffusion in the direction opposite to the concentration gradient. Since any electrolyte solution contains at least two ions of opposite charge, a net charge separation will occur in a process, whereby the faster ions move ahead of their slower counterparts. The resulting internal electric field retards the faster ions and accelerates the slower ones. A steady state thus sets in, whereby both types of ions begin to move across the junction at comparable rates under the influence of a fairly steady electric field in the region of the junction.

Suppose the boundary region is large in extent, so that
the transfer of an infinitesimal quantity of charge across the boundary layers does not appreciably alter the composition of each differential layer. Charges are carried by different ions in proportion to their transport numbers. Suppose for a flow of one Faraday in an infinite copy of the system from left to right a fraction $t_i^+$ of the transferred charge is carried by the $i$th cation of valence $z_i^+$, and a fraction $t_j^-$ is carried by the $j$th anion of valence $z_j^- = -|z_j^-|$; the $t$'s are termed transference numbers. Necessarily, $\Sigma_{(i)} t_i^+ + \Sigma_{(j)} t_j^- = 1$. At each location in the bridging layer between solutions a flow of $t_i^+/z_i^+$ equivalents of cation $i$ occurs from right to left, and a flow of $-t_j^-/|z_j^-|$ equivalents of anions $j$ takes place from left to right. This produces a net increase in Gibbs free energy of

$$dG = \sum_i \left( \frac{t_i^+/z_i^+}{z_i^+} \right) d\mu_i^+ - \sum_j \left( \frac{t_j^-/|z_j^-|}{z_j^-} \right) d\mu_j^-$$

for each layer in the junction region. The overall change in $G$ and the concomitant emf for the entire junction solution is then

$$-F[\varphi_j^B] = \Delta G_j = RT \sum_i \int_A \frac{t_i^+}{z_i^+} d\ln a_i^+ - RT \sum_j \int_A \frac{t_j^-}{|z_j^-|} d\ln a_j^-.$$  

(4.9.2)

One notes that in general the $t$'s are themselves functions of the composition or activity of the solution. One defines mean transference numbers as

$$\bar{t}_i^+ = \frac{\int_A t_i^+ d\ln a_i^+}{\ln a_i^+(B) - \ln a_i^+(A)},$$

(4.9.3)

and similarly for $\bar{t}_j^-$; then

$$A\varphi_j^B = \frac{RT}{F} \left[ \sum_i \frac{\bar{t}_i^+}{|z_i^+|} \ln \left( \frac{a_i^+(B)}{a_i^-(A)} \right) - \sum_j \frac{\bar{t}_j^-}{|z_j^-|} \ln \left( \frac{a_j^+(B)}{a_j^-(A)} \right) \right].$$

(4.9.4)

By appropriate regrouping of terms for cations and anions that belong together one obtains ($\ell$ designates such a group)
\[ \Phi_j^* = \frac{RT}{F} \sum_i \left( \frac{\bar{t}_i^+}{|z_i^+|} - \frac{\bar{t}_i^-}{|z_i^-|} \right) \ln \left( \frac{c_i(B)}{c_i(A)} \right) \]

\[ + \frac{RT}{F} \left( \sum_i \frac{\bar{t}_i^-}{|z_i^-|} \ln \frac{\gamma_i^-(B)}{\gamma_i^-(A)} - \sum_j \frac{\bar{t}_j^+}{|z_j^+|} \ln \frac{\gamma_j^+(B)}{\gamma_j^+(A)} \right). \]

(4.9.5)

For very dilute solutions only the first term need be retained. It is clear that the junction potentials cannot be unambiguously determined because they involve the activities of individual ions which cannot be measured experimentally. On the other hand, if activities can be calculated successfully by the Debye-Hückel relation then \( \Phi_j \) may be evaluated. In the limit of dilute solution the activities are replaced by concentrations. It is seen that at room temperature each ionic species contributes of the order of \( \pm 0.0592 \left( \frac{t_i}{|z_i|} \right) \log \left[ \frac{a_i^+(B)}{a_i^+(A)} \right] \) volts to \( \Phi_j \), and that the portions arising from cations and anions tend to cancel. Thus, unless \( \frac{a_i^-(B)}{a_i^-(A)} \) is of order 10 or more and \( t_i^+/|z_i^+| \) is of order unity for a particular species, the value of \( \Phi \) at room temperature remains well below 0.06 V. Equation (4.9.4) shows further that \( \Phi_j \) can be minimized by taking several precautions: One should use salts of the same valence type having a common cation or anion such as KCl, KBr or Na₂SO₄, K₂SO₄; the concentration of electrolyte on both sides of the junction should be equal; and the transport numbers for the various ionic species should be comparable. In many practical cases of interest, \( \Phi_j \) can then be reduced to \( \pm 0.003 \) V, which is within the range of experimental error of many measurements.

As a practical matter, liquid junction potential effects are frequently minimized by use of salt bridges, involving a separate region connecting the two electrode compartments. The solution in the salt bridge consists of high concentrations of a salt in which the cations and anions have comparable mobilities. Interdiffusion of the various solutions is minimized by use of parchment, collodion, or agar-agar gels.
EXERCISES

4.9.1 For the cell with liquid junction
\[ \text{Hg}(l)|\text{Hg}_2\text{SO}_4(s)|\text{K}_2\text{SO}_4(aq, m_1) ||\text{K}_2\text{SO}_4(aq, m_2)|\text{Hg}_2\text{SO}_4(s)|\text{Hg}(l) \]
show that under reversible operating conditions
\[ E_j = - \left( \frac{3RT}{2F} \right) \int_{m_1}^{m_2} t_{K^+} \, d\ln (m_{T^+}), \]
where \( t_{K^+} \) is the transference number for the \( K^+ \) ion.

4.9.2 Derive an expression for the liquid junction potential of a concentration cell of the type
\[ A|A_{\mu+}B_{\mu-}(c_s)|A_{\mu+}B_{\mu-}(c_r)|A. \]

4.9.3 Determine the liquid junction emf for the cell
\[ \text{Pb}|\text{H}_2(P = 1 \text{ atm}) |\text{HCl}(m = 0.01)|\text{HCl}(m = 0.1)|\text{H}_2(P = 1 \text{ atm})|\text{Pt}, \]
given that \( t_+ = 5/6. \)

4.9.4 The emf of the cell \( \text{Ag}|\text{AgNO}_3(a_t = 10^{-3})|\text{AgNO}_3(a_r = 10^{-2})|\text{Ag} \)
is 63.1 mV at 25°C. The two solutions are separated by a porous plug. Determine the average transference number of \( Ag^+ \) in the solution.

4.10 CONCENTRATION AND ACTIVITY DEPENDENCE OF THE EMF

The dependence of \( E \) on the activity of all gaseous or dissolved species is manifested by Eq. (4.7.2). At 25°C, for which the standard electrode potentials are generally reported, one finds

\[ E = E^0 - \frac{0.05915}{n} \log \left[ \frac{j}{\prod a_j^{v_j} \prod a_s^{v_s}} \right] \text{(25°C, E in volts),} \]

(4.10.1)

where the numerical value cited includes not only \( RT/F \) but also the factor 2.303 for conversion from natural (\( \ln \)) to common (log) logarithms.

To calculate \( E \) it is thus necessary to know both \( E^0 \) and the various activities \( a_j \) and \( a_s \). One should recall that \( j \) enumerates the activities of all dissolved or gaseous species, whereas \( s \) refers to components present as pure condensed phases. The standard emfs were dealt with in Section 4.7; activities for solutes were discussed in Sections 4.1 and 4.2, and the fugacities for gases may be computed according to the procedures outlined in Section 3.1. When the Debye–Hückel
limiting law may be applied in the form shown in Section 4.2, one has an alternative method for computing activities on the right-hand side of Eq. (4.10.1). At room temperature (25°C) the limiting law reads

\[ \log \gamma_\pm = -0.5092 z_\pm |z_\pm| \sqrt{S}, \]  

(4.10.2)

where \( S = \frac{1}{2} \sum_{(j)} z_j^2 c_j \).

As an illustration of this procedure consider the cell \( \text{Pt}, \text{H}_2(\text{P})|\text{HCl}(\text{m})|\text{AgCl}(\text{s})|\text{Ag}(\text{s}) \), for which the half reactions are given by the pairs \( \frac{1}{2}\text{H}_2(\text{g}) = \text{H}^+ + e^- \) and \( e^- + \text{AgCl} = \text{Cl}^- + \text{Ag} \), for a net reaction \( \frac{1}{2}\text{H}_2(\text{g}) + \text{AgCl}(\text{s}) = \text{Ag}(\text{s}) + \text{H}^+ + \text{Cl}^- \). Correspondingly,

\[ E = E^\circ - \frac{RT}{F} \ln \frac{(a_{\text{H}^+})(a_{\text{Cl}^-})(a_{\text{Ag}})}{a_{\text{H}_2}^{1/2} a_{\text{AgCl}}} \]  

(4.10.3)

Considerable simplification is achieved at one atmosphere and 300 K. In that event \( a_{\text{AgCl}} = a_{\text{Ag}} = 1 \). Further, for \( \text{H}_2 \) gas it is then an excellent approximation to set \( a_{\text{H}_2} = P_{\text{H}_2} = 1 \). Finally, we write \( a_{\text{H}^+}^{(\text{m})} a_{\text{Cl}^-}^{(\text{m})} = (a_\pm^{(\text{m})})^2 \), whence

\[ E = E^\circ - (2RT/F) \ln (a_\pm^{(\text{m})}). \]  

(4.10.4)

One notes that a knowledge of the mean molal activity of HCl in a solution of molality \( m \) and the tabulation of standard emfs enables one to calculate the \( E \) value for the schematized cell. Normally, however, the procedure is used in reverse; i.e., from a measurement of emfs the mean activity coefficients for ions in solution may then be determined. The procedure is now illustrated, using the present example.

We first set \( a_\pm^{(\text{m})} = \gamma_\pm^{(\text{m})} m_\pm \) and rewrite Eq. (4.10.4) as

\[ E + (2RT/F) \ln m_\pm = E^\circ - (2RT/F) \ln (\gamma_\pm^{(\text{m})}) \]  

(4.10.5)

We next utilize the extended Debye–Hückel equation, Eq. (4.2.5), in the following form
EMF CONCENTRATION AND ACTIVITY DEPENDENCE

\[
\log \gamma_{\pm}^{(m)} = \frac{-0.5092z_+|z_-|\sqrt{S}}{1 + \sqrt{S}} + \frac{2\nu_+\nu_-}{\nu_+ + \nu_-} Cm_{\pm}.
\] (4.10.6)

On setting \( z_+ = |z_-| = \nu_+ - \nu_- = 1, \sqrt{S} = \sqrt{m_{\pm}} \) (see Exercise 4.2.2), converting Eq. (4.10.5) to common logarithms, introducing (4.10.6), and using appropriate numerical factors one finds (\( T = 25^\circ C \))

\[
L = \mathcal{E} + 0.11833 \left( \log m_{\pm} - \frac{0.5092\sqrt{m_{\pm}}}{1 + \sqrt{m_{\pm}}} \right) = \mathcal{E}^0 - 0.11833Cm_{\pm}.
\] (4.10.7)

Measurements of \( \mathcal{E} \) are then taken for a variety of \( m_{\pm} \) values in very dilute solutions, yielding a set of \( L \) values. As seen from the expression on the right, a plot of the left-hand side, \( L \), versus \( m_{\pm} \) should produce a straight line in that range of molalities where Eq. (4.10.6) is found to be valid. From the slope one may determine the value of \( C \) appropriate to the HCl solution under study. Extrapolation of the straight line back to \( m_{\pm} = 0 \) yields \( \mathcal{E}^0 \) as the intercept. This provides a convenient alternative method for determining the standard emf with respect to molality; in the present case \( \mathcal{E}^0 = 0.22234 \) V at 25°C.

Next, one returns to Eq. (4.10.5), which was derived, as should be noted, without recourse to the Debye-Hückel Law. This relation may be rewritten as

\[
\log \gamma_{\pm} = -\frac{\mathcal{E} - \mathcal{E}^0}{0.11833} - \log m_{\pm}.
\] (4.10.8)

With \( \mathcal{E}^0 \) known, one now measures \( \mathcal{E} \) at any desired value of \( m_{\pm} \) to obtain the corresponding value of \( \gamma_{\pm} \). Very accurate determinations of \( \gamma_{\pm} \) are obtained in this manner. It turns out that the extended Debye-Hückel Law, as given in (4.10.6), is very good approximation to the actual \( \gamma_{\pm}^{(m)} \) up to values of \( m_{\pm} = 0.1 \) molal, but for greater HCl concentrations it is necessary to determine \( \gamma_{\pm}^{(m)} \) experimentally using Eq. (4.10.8).
One must recall that whereas Eq. (4.10.6) is unrestricted, Eqs. (4.10.7) and (4.10.8) are specialized to the case of a uni-univalent electrolyte at room temperature and therefore must be suitably generalized to be applicable to other cases.

EXERCISES

4.10.1 (a) Devise a galvanic cell for which the reaction \( \frac{1}{2}H_2(P=1 \text{ atm}) + \text{AgBr}(s) = \text{HBr}(m) + \text{Ag}(s) \) may be carried out. (b) Measurements show that at 298 K \( E^\circ = 0.07103 \text{ V} \) and \( E = 0.27855 \text{ V} \) for \( m = 0.02 \text{ molal} \). Determine \( \gamma_\pm \) and compare this with the value calculated on the basis of the Debye-Hückel Theory.

4.10.2 In the operation of the cell \( \text{Ag(s)} | \text{AgBr}(x_2) \) in molten \( \text{LiBr} | \text{Br}_2(1 \text{ atm}) \) the emf at 500°C was found to be 0.7865 V when AgBr is the electrolyte, and to be 0.8085 V at a mole fraction \( x_2 = 0.5937 \). Determine the mean activity coefficient for AgBr.

4.10.3 At 500°C and 1 atmosphere the emf for the cell \( \text{Ag(s)} | \text{AgCl}(x_1) \) in molten \( \text{LiCl} | \text{Cl}_2(1 \text{ atm}) \) was reported as follows:

<table>
<thead>
<tr>
<th>( x_1 )</th>
<th>0.000</th>
<th>0.690</th>
<th>0.469</th>
<th>0.136</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \psi (V) )</td>
<td>0.9001</td>
<td>0.9156</td>
<td>0.9249</td>
<td>0.9629</td>
</tr>
</tbody>
</table>

(a) Determine the activity coefficient of AgCl at these mole fractions. (b) Calculate the Gibbs free energy of transfer of one mole of AgCl from its pure state to a solution at 500°C in which its mole fraction is 0.469.

4.10.4 In the operation of the cell \( \text{Pt, } H_2(P=1 \text{ atm}) | \text{HCl}(c) | \text{AgCl}(s), \text{Ag(s), Pt. at 300 K} \) the following emf measurements have been reported:

<table>
<thead>
<tr>
<th>( c (M) )</th>
<th>( 10^{-1} )</th>
<th>( 5 \times 10^{-2} )</th>
<th>( 10^{-2} )</th>
<th>( 10^{-3} )</th>
<th>( 10^{-4} )</th>
<th>( 10^{-5} )</th>
<th>( 10^{-6} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \psi (V) )</td>
<td>0.3598</td>
<td>0.3892</td>
<td>0.4650</td>
<td>0.5791</td>
<td>0.6961</td>
<td>0.8140</td>
<td>0.93</td>
</tr>
</tbody>
</table>

(a) Write out the half reaction and net reaction. (b) Determine \( \gamma_\pm \) corresponding to \( c = 10^{-2}, 5 \times 10^{-2}, 10^{-1} \text{ M} \); compare the values so determined with those calculated from the Debye-Hückel Law.

4.10.5 Consider the cell schematized as \( \text{Ag(s)} | \text{Ag}, m_1(s) | \text{NaCl}(\text{aq,} m_1) | \text{Na(Hg)} | \text{NaCl}(\text{aq,} m_2) | \text{Na}_3\text{PO}_4(\text{aq,} m_3) | \text{AgCl}(s) \). Taking account of nonideality, derive an expression for the cell emf in terms of \( m_1, m_2, \) and \( m_3 \). What is the function of the \( \text{Na}_3\text{PO}_4 \) in the operation of the cell?

4.10.6 Consider the cell schematically indicated as: \( \text{H}_2(P_1), \text{Pt} | \text{C}_2\text{H}_5\text{OH}, \text{CH}_3\text{NH}_3\text{Cl}(c_1), \text{CH}_3\text{NH}_2(c_2) | \text{AgCl}(s) | \text{Ag(s)} \), where \( \text{C}_2\text{H}_5\text{OH} \) is the solvent for \( \text{CH}_3\text{NH}_3\text{Cl} \) which is in a saturated solution formed with solid \( \text{CH}_3\text{NH}_3\text{Cl} \). \( \text{C}_2\text{H}_5\text{OH} \) is also the solvent for \( \text{CH}_3\text{NH}_2 \), which is in equilibrium with gaseous \( \text{CH}_3\text{NH}_2 \) that is
maintained at pressure $P_2$. At 25°C the emf of a cell, operating under conditions where $P_1 = 0.983 \, \text{atm}$ and $P_2 = 4.15 \times 10^{-3} \, \text{atm}$, is 0.697 V. (a) What is the emf of the cell when $P_1 = P_2 = 1 \, \text{atm}$? (b) What is the overall reaction for the operation of this cell? (c) Determine the equilibrium constant for the cell reaction.

4.10.7 For the 'CaCl2 cell' operating at 25°C, Ca(Hg)|CaCl2(m)|AgCl|Ag, one finds the following data:

<table>
<thead>
<tr>
<th>$m$ (molal)</th>
<th>0.0500</th>
<th>0.0563</th>
<th>0.0690</th>
<th>0.1159</th>
<th>0.1194</th>
<th>0.1305</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$ (V)</td>
<td>2.0453</td>
<td>2.0418</td>
<td>2.0348</td>
<td>2.0205</td>
<td>2.0175</td>
<td>2.0147</td>
</tr>
<tr>
<td>$E$ (V)</td>
<td>2.0094</td>
<td>1.9953</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Determine $E^\circ$ for the cell reaction and evaluate $\gamma_i^{(m)}$ for CaCl2 in water when $m = 0.02, 0.2 \, \text{M}$.

4.10.8 The results reported below pertain to the operation of the cell at 25°C: Pt|H2(latm)|HBr(aq,m)|AgBr(s)|Ag.

<table>
<thead>
<tr>
<th>$m$ (x10^{-4} molal)</th>
<th>1.262</th>
<th>1.775</th>
<th>4.172</th>
<th>10.994</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$ (V)</td>
<td>18.50</td>
<td>37.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E$ (V)</td>
<td>0.53300</td>
<td>0.51618</td>
<td>0.47211</td>
<td>0.42280</td>
</tr>
<tr>
<td>$E$ (V)</td>
<td>0.39667</td>
<td>0.36172</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Determine the activity coefficient for HBr when $m = 2 \times 10^{-4}$, $10^{-3}$, $10^{-2}$, 0.05, 0.10, 0.50.

4.10.9 For a cell in which the half reaction Fe(CN)$^{5-} \rightarrow$ Fe(CN)$^{3-}$ + e$^-$ and Mn$^{2+}$ + 4H$_2$O $\rightarrow$ MnO$_4^-$ + 8H$^+$ + 5e$^-$ are to be carried out, indicate the dependence of $E$ on the mean activities of all species participating in the cell reaction.

4.10.10 The following data are reported for operation of the cell at 25°C: Zn|ZnCl2(aq,m)|AgCl(s)|Ag(s):

<table>
<thead>
<tr>
<th>$m$ (molal)</th>
<th>2.0941x10^{-3}</th>
<th>7.814x10^{-3}</th>
<th>1.236x10^{-2}</th>
<th>2.144x10^{-2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$ (V)</td>
<td>1.1983</td>
<td>1.16502</td>
<td>1.14951</td>
<td>1.13101</td>
</tr>
<tr>
<td>$E$ (V)</td>
<td>4.242x10^{-2}</td>
<td>9.048x10^{-2}</td>
<td>0.2211</td>
<td>0.4499</td>
</tr>
<tr>
<td>$E$ (V)</td>
<td>1.10987</td>
<td>1.08435</td>
<td>1.05559</td>
<td>1.03279</td>
</tr>
</tbody>
</table>

Determine $\gamma_i^{(m)}$ for ZnCl2 at $m = 10^{-3}$, $10^{-2}$, $10^{-1}$ molal.

4.11 TYPES OF OPERATING CELLS

The following types of operating cells are in common use:

(a) **Chemical Cells**: An example of this type of cell was provided in Section 4.7. We list a second example:
Zn|ZnCl₂(m), AgCl(s)|Ag(s), which corresponds to a net chemical reaction represented by Zn(s) + 2AgCl(s) = 2Ag(s) + Zn²⁺(m) + 2Cl⁻(2m). By the standard methodology described earlier, we obtain

\[
\mathcal{E} - \mathcal{E}^\circ = \frac{RT}{2F} \ln \frac{a_{Ag}^2 a_{ZnCl_2}}{a_{AgCl}^2 a_{Zn}} - \mathcal{E} - \frac{RT}{2F} \ln a_{ZnCl_2} - \mathcal{E}^\circ - \frac{RT}{2F} \ln (a_{Zn}^+ a_{Cl}^-)
\]

\[- \mathcal{E} - \frac{3RT}{2F} \ln a_x = \mathcal{E}^\circ - \frac{3RT}{2F} \ln \left[ \gamma_x^{(m)} \right].
\]

(4.11.1)

Here it is assumed that the operation is carried out close to a total pressure of one atm, so that \(a_x = 1\). Once again we see that a determination of \(\mathcal{E}\), corresponding to a given value of \(m\), permits the computation of \(\gamma_x^{(m)}\). The contributions of Ag⁺ and Cl⁻ ions arising from the slight solubility of AgCl(s) have been neglected in the preceding analysis.

(b) **Electrode Concentration Cells:** In this case a cell is made up of two electrodes that differ solely in the concentration of electrode materials or in the pressure of reactive gases over the electrodes.

The first case is illustrated by the example Zn, Hg(c₁)|ZnSO₄(c)|Zn, Hg(c₂), which involve amalgams of Zn in mercury at concentrations \(c_1\) and \(c_2\) on the left and right hand electrodes. The net reactions for the cell as written are:

\[
Zn_x(c_1) = xZn^{2+}(c) + 2xe^- \text{ and } xZn^{2+}(c) + 2xe^- = Zn_x(c_2),
\]

leading to the combined reaction \(Zn_x(c_1) = Zn_x(c_2)\). Evidently, for this case equilibrium is established when \(a_1 = a_2\), in which case \(K_q = a_1/a_2 = 1\), and \(\mathcal{E}^\circ = 0\). For this cell

\[
\mathcal{E} = \frac{RT}{nF} \ln \frac{a_1}{a_2},
\]

(4.11.2)

where \(n = 2x\) if \(Zn_x\) is the molecular aggregation of Zn in the amalgam.
The second case is illustrated by the cell Pt, H₂(P₁)|HCl(c)|H₂(P₂), Pt, for which the processes read: H₂(P₁) → 2H⁺(c) + 2e⁻, 2H⁺(c) + 2e⁻ → H₂(P₂) to yield a net reaction H₂(P₁) → H₂(P₂). Once again the equilibrium constant is unity, E° = 0, and therefore

\[ E = \frac{RT}{2F} \ln \frac{P₁}{P₂}. \]  

(4.11.3)

As expected, \( E > 0 \), \( \Delta G_d < 0 \) or \( E < 0 \), \( \Delta G_d > 0 \) according to whether \( P₁ > P₂ \) or \( P₁ < P₂ \) for the reaction as written. We see then that concentration cells afford a means of reversibly transferring material from one electrode chamber to the other.

(c) Ordinary Concentration Cells With Liquid Junctions:
A cell in this category is typified by the example Ag|AgNO₃(c₁)|AgNO₃(c₂)|Ag. We examine the processes which occur inside an infinite copy of the cell when one equivalent of silver enters the solution on the left and one equivalent of silver deposits on the electrode on the right, resulting in the transfer of one Faraday of electrons through the external circuit. This is best done by reference to Table 4.11.1.

In the table, the various processes are broken down into several steps, although it should be obvious that all of the steps outlined in the table occur simultaneously. When 1 F of electrons is transferred through the external circuit, the mole number of Ag⁺ is increased from \( nₙ \) to \( nₙ + 1 \) on the left and decreased from \( nᵣ \) to \( nᵣ - 1 \) on the right. This is accompanied by a transfer of \( t_+ \) moles of Ag⁺ from the left to the right compartment, and of \( t_- \) moles of NO₃⁻ in the reverse direction, where \( t_+ \) and \( t_- \) are the transference numbers of the positive and negative ions, respectively. The mole number of Ag⁺ on the left is thus changed to \( nₙ + 1 - t_+ \) and on the right, to \( nᵣ - 1 + t_+ \), whereas the corresponding mole numbers for NO₃⁻ become \( nₙ + t_- \) and \( nᵣ - t_- \), respectively. It then emerges that the net transfer reduces to \( t.Ag^+(a_+) + t.NO₃^-(a_-) = t.Ag^+(a_+) + t.NO₃^-(a_-) \). Here again, \( E° = 0 \), so that
$\mathcal{E} = -\frac{RT}{2F} \ln \left[ \frac{(a_+)^t (a_-)^t}{(a_+)^r (a_-)^r} \right] - t_+ \frac{2t \cdot RT}{F} \ln \frac{(a_+)^r}{(a_+)^t}$. \hfill (4.11.4)

Note how the transference number for the anion makes its appearance in this expression.

### Table 4.11.1

**Schematic Representation of Processes Taking Place in the Electrode Compartments of a $\text{AgNO}_3$ Concentration Cell**

<table>
<thead>
<tr>
<th>Initial mole numbers</th>
<th>Left-Hand Side Species</th>
<th>Right-Hand Side</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_1$</td>
<td>$\text{Ag}^+$</td>
<td>$n_2$</td>
</tr>
<tr>
<td>$n_1$</td>
<td>$\text{NO}_3^-$</td>
<td>$n_2$</td>
</tr>
</tbody>
</table>

After passage of $1F$ of charge through the external circuit, one finds as a result of reactions involving the oxidation of $\text{Ag}$ and reduction of $\text{Ag}^+$

Mole numbers in each electrode

| $n_1 + 1$ | $\text{Ag}^+$ | $n_2 - 1$ |

To preserve electroneutrality, there now occur the following two compensating transfers across the liquid junctions

<table>
<thead>
<tr>
<th>Net mole numbers in each electrode</th>
<th>$n_1 + 1 - t_+$</th>
<th>$t_+ \text{Ag}^+ \rightarrow \text{Ag}^+$</th>
<th>$n_2 - 1 + t_+$</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Net mole numbers in each electrode</th>
<th>$n_1 + t_-$</th>
<th>$t_- \text{NO}_3^- \rightarrow \text{NO}_3^-$</th>
<th>$n_2 - t_-$</th>
</tr>
</thead>
</table>

**Net Result**

<table>
<thead>
<tr>
<th>Final mole numbers in each compartment</th>
<th>$n_1 + t_-$</th>
<th>$\text{Ag}^+$</th>
<th>$n_2 - t_-$</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Final mole numbers in each compartment</th>
<th>$n_1 + t_-$</th>
<th>$\text{NO}_3^-$</th>
<th>$n_2 - t_-$</th>
</tr>
</thead>
</table>

**(d) Double Concentration Cells:** These are two ordinary concentration cells connected back-to-back in combinations such
as Zn\(\mid\)ZnSO\(_4(c_t)\), Hg\(_2\)SO\(_4(s)\)\(\mid\)Hg\(\mid\)Hg\(_2\)SO\(_4(s)\), ZnSO\(_4(c_r)\)\(\mid\)Zn. Here the sparingly soluble salt Hg\(_2\)SO\(_4\) furnishes some Hg\(^+\) ions for transfer into or out of the central Hg electrode, while the concentration of SO\(_{4}^-\) in the left- and right-hand compartments remains nearly constant. Under normal conditions where \(c_t, c_r \gg [\text{Hg}^+]\) one can set \([\text{Zn}^{2+}] = [\text{SO}_4^-]\).

The processes on the left may be described by the sequence

\[
\begin{align*}
\text{Zn}(s) &= \text{Zn}^{2+}(c_t) + 2e^- \\
2\text{Hg}^+(c_t) + 2e^- &= 2\text{Hg}(l) \\
\text{Hg}_2\text{SO}_4(s) &= 2\text{Hg}^+(c_t) + \text{SO}_4^-\text{(c}_t\text{)}
\end{align*}
\]

\[
\begin{equation}
\text{Zn}(s) + \text{Hg}_2\text{SO}_4(s) = \text{Zn}^{2+}(c_t) + \text{SO}_4^-\text{(c}_t\text{)} + 2\text{Hg}(l)
\end{equation}
\]

Similarly, on the right, \(\text{Zn}^{2+}(c_r) + \text{SO}_4^-\text{(c}_r\text{)} + 2\text{Hg}(l) = \text{Zn}(s) + \text{Hg}_2\text{SO}_4(s)\), so that as an overall net reaction one obtains

\[
\text{Zn}^{2+}(c_r) + \text{SO}_4^-\text{(c}_r\text{)} = \text{Zn}^{2+}(c_t) + \text{SO}_4^-\text{(c}_t\text{)},
\]

which shows that one is dealing with a concentration cell. Accordingly, the emf is given by

\[
E = -\frac{RT}{2F} \ln \frac{(a_+)_t(a_-)_t}{(a_+)_r(a_-)_r} = -\frac{RT}{2F} \ln \frac{(a_+)_r}{(a_+)_t}.
\] (4.11.5)

(e) Electrolyte Concentration Cell with Transference: As an example of this case consider the scheme \(\text{H}_2,\text{Pt}\mid\text{HCl(c}_1\text{)}\mid\text{HCl(c}_2\text{)}\mid\text{Pt}, \text{H}_2\) in which the \(\text{H}_2\) gas pressure at both electrodes is maintained at 1 atm. The electrode reactions are

\[
\begin{align*}
\text{H}_2 &= \text{H}^+(c_1) + e^- \quad \text{at the left electrode} \\
\text{H}^+(c_2) + e^- &= \text{H}_2 \quad \text{at the right electrode} \\
\text{H}^+(c_2) &= \text{H}^+(c_1) \quad \text{net reaction at the electrodes.}
\end{align*}
\]
What actually happens at the interface between the two HCl solution in this process in an infinite copy of the cell may be understood by noting that in the transfer of 1 F of electronic charge through the external circuit from left to right, one mole of compensating ionic charge must move through the solutions and hence, across their interface. This particular process is quite analogous to that discussed in subsection (c); we provide only a brief summary. The fraction of ionic current carried by H⁺ ions moving from left to right is \( t_+ \); the fraction of ionic current carried by Cl⁻ ions from right to left is \( t_- \). The junction reactions are therefore \( t_+H^+(c_1) - t_+H^+(c_2) \) and \( t_-Cl^-(c_2) - t_-Cl^-(c_1) \). The first of these transfer reactions may be rewritten as \((1 - t_-)H^+(c_1) = (1 - t_-)H^+(c_2)\). When the last two equations are combined with the net reaction occurring at the electrodes one obtains for the overall cell reaction the expression \( t_+[H^+(c_2) + Cl^-(c_2)] = t_-[H^+(c_1) + Cl^-(c_1)] \). Corresponding to this net reaction, the emf of such a cell is given by (\( \Psi^o = 0 \))

\[
\Psi = -0.05915 \log \left( \frac{a_+(c_1)}{a_+(c_2)} \right)^{2t_-} - 0.11830 \ t_- \log \left[ a_+(c_1)/a_+(c_2) \right].
\]

(4.11.6)

Thus, emf measurements of cells with transference yield transference numbers.

EXERCISES

4.11.1 (a) Prove that the concentration cell shown below may be used to obtain thermodynamic information on the process

\[
\text{NaCl}(m_1) = \text{NaCl}(m_2) : \text{Hg}(\ell)|\text{Hg}_2\text{Cl}_2(s)|\text{NaCl}(aq,m_1)|\text{Na(Hg)}|\text{NaCl}(aq,m_2)|\text{Hg}_2\text{Cl}_2(s)|\text{Hg}(\ell).
\]

(b) Describe what measurements are needed to ascertain \( \Delta H_d \) for the above process.

4.11.2 Show that the following cells may be used to study the thermodynamics of phase transitions and identify these transitions:

(a) \( \text{Hg}(\ell)|\text{HgO}(s,\text{red})|\text{NaOH}(aq,m_1)|\text{Na(Hg)}|\text{NaOH}(aq,m_2)|\text{HgO}(s,\text{yellow})|\text{Hg}(\ell) \).

(b) \( \text{Pb(Hg)}|\text{PbCO}_3(s),\text{CaCO}_3\text{calcite})|\text{CaCl}_2(aq,m_1)|\text{Hg}_2\text{Cl}_2(s)|\text{Hg}(\ell) \)

\( 2 \text{ phases} \)

(2 phases)

\( -\text{Hg}(\ell)|\text{Hg}_2\text{Cl}_2(s)|\text{CaCl}_2(aq,m_1)|\text{CaCO}_3\text{aragonite}),\text{PbCO}_3|\text{Pb(Hg)} \).

\( 2 \text{ phases} \)
4.11.3 Consider the quadruple cell
\[ ^7\text{Li}(s)|^7\text{LiBr}(\text{pc})|^7\text{LiCl}(\text{aq})|\text{Hg}_2\text{Cl}_2(s)|\text{Hg}(l)-\text{Hg}(l) | \]
\[ \text{Hg}_2\text{Cl}_2(s)|^6\text{LiCl}(\text{aq})|^6\text{Li}(s)|^6\text{LiBr}(\text{pc})|^6\text{Li}(s), \]
in which pc represents propylene carbonate. (a) What is the net reaction? (b) From the viewpoint of thermodynamics, is the portion of the cell dealing with LiBr in pc essential? If not can you think of a practical reason why this portion is included? (c) Given that for this cell \( \mathcal{E}^\circ = 1.16 \) mV at 297 K, what is the equilibrium constant for the overall reaction? Is the value reasonable?

4.11.4 Consider the cell
\[ \text{Pb}|\text{D}_2(\text{pc})|\text{DCl}(\text{aq})|\text{TlCl}(\text{aq})|\text{HCl}(\text{aq})|\text{H}_2(\text{pc})|\text{Pb}. \]
(a) What net process is involved in the operation of the cell? (b) At 297 K, \( \mathcal{E}^\circ = 764 \) mV; what is the equilibrium constant for the net reaction?

4.11.5 Explain why \( \mathcal{E}^\circ = 0 \) in Eq. (4.11.4).

4.12 THERMODYNAMIC QUANTITIES FROM EMF MEASUREMENTS

Corresponding to the general equation \( \Sigma_i \nu_i A_i = 0 \) which may involve pure components, gases, and ionic species, one obtains an equilibrium constant \( K_q = \prod_{(s)}(a_s)^{\nu_s} \prod_{(j)}(a_j)^{\nu_j} \). When galvanic cell operations can be carried out that exactly reproduce the particular chemical reaction of interest one has

\[ \mathcal{E} = - \frac{\Delta G_d}{nF}, \quad (4.12.1) \]

and if one chooses as standard states the pure substance for condensed phases forming no solutions, and the state at unit activity for dissolved substances, then

\[ \mathcal{E}^\circ = - \frac{\Delta F_0}{nF} = + \left( \frac{RT}{nF} \right) \ln K_q. \quad (4.12.2) \]

Equation (4.12.1) shows how the value of \( \Delta G_d \) appropriate to the chemical equation under study can be computed from emf measurements: Eq. (4.12.2) accomplishes the same for the equilibrium constant.

On account of the relation \( \Delta G_d = - (\partial \Delta S_d/\partial T)_{P,n_i} \) one further finds
\[ \Delta S_d = nF(\partial \mathcal{E} / \partial T)_{p,n_l}; \quad \Delta S^0_d = nF(\partial \mathcal{E}^0 / \partial T)_{p,n_l}; \quad (4.12.3) \]

and from either the Gibbs-Helmholtz equation or from the interrelation between \( G, S, \) and \( H \) one obtains

\[ \Delta H_d = - nF[\mathcal{E} - T(\partial \mathcal{E} / \partial T)_{p,n_l}] \quad (4.12.4a) \]

\[ \Delta H^0_d = - nF[\mathcal{E}^0 - T(\partial \mathcal{E}^0 / \partial T)_{p,n_l}]. \quad (4.12.4b) \]

Eqs. (4.12.3) and (4.12.4) relate to the determination of differential entropy and enthalpy changes for the reaction of interest.

**EXERCISES**

4.12.1 For the reaction \( \text{Ag}(s) + (1/2)\text{Cl}_2(g) = \text{AgCl}(l) \) at \( T = 1000 \text{ K} \) the standard emf has been reported as 0.8401 V. (a) Find the equilibrium constant for this reaction. (b) The measured emf under these conditions is 0.8283 V; what is the activity of \( \text{Cl}_2 \) gas (assuming that the activity of the pure condensed phases is unity).

4.12.2 For the cell \( \text{Pb}|\text{PbSO}_4(s), \text{H}_2\text{SO}_4 \text{ (0.01 molal)}|\text{PbO}_2(s)|\text{Pt} \) the standard emf as a function of temperature (in °C) is given as \( \mathcal{E} = 1.80207 - 265 \times 10^{-6}t + 129 \times 10^{-8}t^2 \) V, and \( \mathcal{E}^0 = 2.0402 \) V at 25°C. (a) Write out the corresponding reaction for this cell and determine \( \Delta G^0_d, \Delta S^0_d, \Delta H^0_d \) at 298 K. (b) Obtain the equilibrium constant for the reaction. (c) Determine \( \mathcal{E} \) at 25°C when the electrolyte is 1 molal in \( \text{H}_2\text{SO}_4 \) and has a mean molal activity coefficient of \( \gamma^{(m)} = 0.131 \). Assume \( a_{\text{H}_2\text{O}} = 1 \).

4.12.3 A cell that is made to operate reversibly to carry out the reaction \( \text{H}_2(p = 1 \text{ atm}) + 2\text{AgCl}(s) = 2\text{HCl}(0.1238 \text{ molal}) + 2\text{Ag}(s) \) exhibits an emf of +0.3420 V and an \( \mathcal{E}_o \) value of +0.222 V at 298.3 K. Find \( \Delta G^0_d \) and the equilibrium constant for this reaction at 298.3 K.

4.12.4 The emf for a neutral, saturated Weston standard cell is given by the relation \( \mathcal{E} = 1.018410 - 4.93 \times 10^{-5}(t-25) - 8.0 \times 10^{-7}(t-25)^2 + 1 \times 10^{-8}(t-25)^3 \) in the range 5 < \( t \) < 50°C. (a) Determine \( \Delta G^0_d, \Delta S^0_d, \Delta H^0_d, \Delta C^0_p \) for the operation of the cell. (b) What is the emf of two Weston cells connected as shown below with \( t_1 = 10^\circ C, \ t_2 = 40^\circ C \)?

\[ \text{Pt}|\text{Cd},\text{Hg}|\text{CdSO}_4|\text{Hg}|\text{Pt}|\text{Hg}|\text{HgSO}_4,\text{CdSO}_4|\text{Cd},\text{Hg}|\text{Pt} \]

4.12.5 For the cell schematically shown below, the standard cell emf at 25°C is 0.2681 V: \( \text{Pb}|\text{H}_2(g)|\text{HCl(aq)}|\text{Hg}_2\text{Cl}_2(s)|\text{Hg}(l) \).
Determine the equilibrium constant for the dissociation of \( \text{Hg}_2\text{Cl}_2 \) into ionic constituents. Determine both the mean molal activity coefficient and molality of the ions in equilibrium with the undissolved salt at 25°C.

4.12.6 (a) Devise one cell by which the reaction \( 5\text{Pb}^{2+} + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \rightarrow 5\text{PbO}_2(s) + 2\text{Mn}^{2+} + 4\text{H}^+ \) may be advanced infinitesimally. (b) What is \( \mathcal{E}^\circ \) for this cell? Given that \( d\mathcal{E}^\circ/dT = 0.42 \) mV/deg determine \( \Delta G_d^\circ, \Delta S_d^\circ, \Delta H_d^\circ \) for this reaction.

4.12.7 Consider the cell \( \text{Na}(s)\mid \text{NaI in C}_2\text{H}_5\text{NH}_2\mid \text{Na}(\text{Hg}) \mid \text{NaCl}(aq, m=1.022) \mid \text{Hg}_2\text{Cl}_2(s) \mid \text{Hg}(l) \). At 25°C and 1 atm, one finds \( \mathcal{E} = 3.0035 \) V and \( d\mathcal{E}^\circ/dT = 0.455 \) mV/deg. At the indicated molality \( \gamma_x^{(m)} = 0.650 \) for \( \text{NaCl} \) in water. (a) How does \( \mathcal{E} \) depend on the NaI concentration in \( \text{C}_2\text{H}_5\text{NH}_2 \)? (b) Determine \( \mathcal{E}_o \) for this cell. (c) Determine \( \Delta H_d^\circ \) for the cell reaction.

4.12.8 The equilibrium constant for the reaction \( \text{CuCl}(s) + \text{AgCl}(s) + \text{aq} = \text{Cu}^{2+}(m) + 2\text{Cl}^-(2m) + \text{Ag}(s) \) was found to be \( 1.85 \times 10^{-8} \) at 25°C. Using the known standard potentials of the \( \text{Ag}\mid \text{AgCl}(s)\mid \text{Cl}^- \) and \( \text{Cu}\mid \text{Cu}^{2+} \) electrodes, calculate that of the \( \text{CuCl}(s)\mid \text{Cl}^- \) electrode.

4.12.9 The standard potential of the silver azide electrode, i.e., \( \text{Ag}\mid \text{AgN}_3(s)\mid \text{N}_3^- \), is \( -0.2919 \) V at 25°C. If the solubility of silver chloride is \( 1.314 \times 10^{-5} \) molal, calculate that of silver azide at 25°C. (Complete dissociation may be assumed for the dissolved material in the saturated solution in each case.)

4.12.10 (a) Set up schematically a cell for which the reaction \( (1/2)\text{H}_2(1 \text{ atm}) + \text{AgBr}(s) \rightarrow \text{HBr}(aq, m) + \text{Ag}(s) \) can be reversibly carried out. (b) Write out expressions by which the equilibrium constant may be determined for the reaction. (c) Write out an expression that permits determination of \( \gamma_x^{(m)} \) for \( \text{HBr} \) in solution. (d) Given that \( \mathcal{E}^\circ = 0.07103 \) V and that \( \mathcal{E} = 0.27855 \) V for the molality \( m = 0.02 \) molal, determine \( \gamma_x^{(m)} \) of \( \text{HBr} \) at 25°C.

4.12.11 The emf of the cell \( \text{Pt, H}_2(1 \text{ atm})\mid \text{HCl}(aq, a_e=1) \mid \text{AgCl}(s), \text{Ag} \) is reported to be \( 0.22551, 0.22239, 0.21912 \) V at \( 20.0, 25.0, 30.0^\circ \text{C} \), respectively. Determine \( \Delta G_d^\circ, \Delta S_d^\circ, \Delta H_d^\circ \) at \( 23^\circ \text{C}, 27^\circ \text{C} \).

4.12.12 Given the following data:
\[
\begin{align*}
\text{Pb}^{2+} + 2\text{H}_2\text{O}(l) & \rightarrow \text{PbO}_2(s) + 4\text{H}^+ + 2\text{e}^- & \mathcal{E}^\circ & = -1.455 \text{ V}, \\
\delta\mathcal{E}/\delta T & = -0.42 \text{ mV/deg} \\
\text{Mn}^{2+} + 4\text{H}_2\text{O}(l) & \rightarrow \text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- & \mathcal{E}^\circ & = -1.512 \text{ V}, \\
\delta\mathcal{E}/\delta T & = +0.66 \text{ mV/deg}
\end{align*}
\]

obtain \( \Delta G_d^\circ, \Delta S_d^\circ, \Delta H_d^\circ \) for the reaction (at 25°C) \( 5\text{Pb}^{2+} + 2\text{MnO}_4^- + 2\text{H}_2\text{O}(l) = 5\text{PbO}_2(s) + 2\text{Mn}^{2+} + 4\text{H}^+ \).

4.12.13 For the cell corresponding to the reaction \( (1/2)\text{H}_2(g) + \text{AgCl}(s) = \text{Ag}(s) + \text{H}^+(0.1m) + \text{Cl}^-(0.1m) \) one finds that the emf is related to the temperature \( t \) in °C by the
4. THERMODYNAMIC PROPERTIES OF ELECTROLYTES

empirical relation \( \mathcal{E} = 0.35510 - 0.3422 \times 10^{-4}t - 3.2347 \times 10^{-6}t^2 + 6.314 \times 10^{-9}t^3 \) V. Determine the differential quantities \( \Delta H_d^\circ, \Delta S_d^\circ, \Delta C_{pl}^d \) for the cell reaction.

4.12.14 Derive formulas showing how \( \Delta C_{pl}^d \) and \( \Delta V_d \) may be determined from emf measurements of galvanic cells.

4.12.15 Devise a fuel cell arrangement in which the reaction \( 2H_2 + O_2 = 2H_2O \) may be carried out to a finite extent, such that the measured Gibbs free energy change is identical with \( \Delta G_d \).

4.12.16 Compare the advantages and disadvantages of experimentally determining chemical potentials by gas pressure, solution concentration, and emf measurements.

4.13 APPLICATIONS OF EMF MEASUREMENTS

We briefly review below several applications of emf measurements:

(a) Determination of Activity Coefficients: This method was reviewed in Section 4.10.

(b) Determination of Thermodynamic Quantities: Repeated reference has been made to the relations involving \( \mathcal{E}, \mathcal{E}^\circ \), and its temperature derivatives on the one hand and \( \Delta G_d, \Delta H_d, \Delta S_d, \Delta G_d^\circ, \Delta H_d^\circ, \Delta S_d^\circ \), and \( K_q \) on the other hand. These matters will not be reviewed further.

(c) Determination of Dissociation Constants for Weak Acids: This is illustrated by the following example, where \( Ac^- \) stands for the acetate anion. Consider the equilibrium \( HAc = H^+ + Ac^- \) in conjunction with the cell:

\[ \text{Pt,} \; H_2(p) | HAc(m_1), \text{NaAc}(m_2), \text{NaCl}(m_3) | \text{AgCl}(s), \text{Ag(s)}, \]

for which the cell reaction reads

\[ \begin{align*}
\frac{1}{2}H_2(g) &- H^+ + e^- \\
e^- + \text{AgCl}(s) &- \text{Ag(s)} + \text{Cl}^- \\
\frac{1}{2}H_2(g) + \text{AgCl}(s) &- \text{Ag(s)} + \text{Cl}^- + H^+.
\end{align*} \]
Accordingly,

\[ \varphi = \varphi^\circ - \frac{RT}{F} \ln \frac{a_{H_2}^{1/2} a_{AS}}{a_{H_2}^{1/2} a_{AS}} \quad (4.13.1) \]

Now \( \varphi^\circ \) is the standard emf for the cell \( \text{Pt, } H_2(g) | \text{HCl} | \text{AgCl} (s), \text{Ag} (s) \), which corresponds to the net reaction shown above. Now set \( \varphi_1 = \varphi^\circ + \frac{RT}{2F} \ln a_{H_2} - \frac{RT}{F} \ln \left( \frac{a_{AS}}{a_{AS}} \right) \). Also, set \( K_a = a_{H^+} a_{\text{Ac}^-} / a_{\text{HAc}} \); then Eq. (4.13.1) reads

\[ \varphi = \varphi_1^\circ - \frac{RT}{F} \ln K_a - \frac{RT}{F} \ln \frac{a_{\text{Ac}^-} - a_{\text{HAc}}}{a_{\text{Ac}^-}}. \quad (4.13.2) \]

It is clear from the cell setup that at equilibrium, and in terms of molality, \( [\text{HAc}] = m_1 - m, [\text{Ac}^-] = m_2 + m, \) and \( [\text{Cl}^-] = m_3 \), whence

\[ \varphi = \varphi_1^\circ - \frac{RT}{F} \ln K_a - \frac{RT}{F} \ln \frac{\gamma_{\text{Ac}^-} - \gamma_{\text{HAc}}}{\gamma_{\text{Ac}^-}} - \frac{RT}{F} \ln \frac{m_3(m_1 - m)}{(m_2 + m)} \quad (4.13.3) \]

in which the activity coefficients have been referred to molalities. Next, multiply the numerator and denominator of the argument in the third term on the right by \( \gamma_{\text{Na}^+} \). This yields

\[ L = \frac{F(\varphi_1^\circ - \varphi^\circ)}{2.303RT} + \log \frac{m_3(m_1 - m)}{(m_2 + m)} = - \log \frac{\gamma_{\text{HAc}}(\gamma_{\text{NaCl}})^{1/2}}{\gamma(\text{NaAc})^{1/2}} - \log K_a. \quad (4.13.4) \]

Now let emf measurements be carried out for a variety of solutions made up for different values of \( m_1, m_2, \) and \( m_3 \). A rough value of \( K_a \) suffices to estimate \( m = K_a m_1/m_2 \), so long as \( m \ll m_1, m_2 \). \( \varphi^\circ \) may be easily estimated, since it does not greatly differ from \( \varphi^\circ \); if the experiment is carried out at a total \( H_2 \) pressure of one atmosphere, \( \varphi_1^\circ = \varphi^\circ \). The left-hand side \( L \) is now known for a series of values of \( m_1, m_2, m_3 \) and may be plotted against \( m_1 \), keeping \( m_2, m_3 \) constant, where \( i \neq j \neq k = 1, 2, 3 \). Alternatively, \( L \) may be plotted against \( m_1 + m_2 + m_3 \), which sum does not involve \( m \). As the solutions become
increasingly dilute the logarithmic terms involving the $\gamma$'s becomes very small; the left hand side should then become very nearly constant which, by extrapolation to infinite dilution ($m_1 + m_2 + m_3 \to 0$), leads to the constant value $- \log K_a$. If necessary, a method of successive approximations can be devised whereby $K_a$ is initially estimated by setting $m = 0$; this value is then used to obtain a first approximation to $m$. Insertion of the latter in (4.13.4) then yields an improved value of $K_a$.

(d) **Determination of the Dissociation Constant for Water:**
The procedure here is exactly the same as in the preceding subsection; now $A^-$ represents $\text{OH}^-$, and $\text{HAc}$ represents $\text{H}_2\text{O}(l)$. The value of $K_a$ now is appropriate to the equilibrium $\text{H}_2\text{O}(l) = \text{H}^+(a_+) + \text{OH}^-(a_-)$.

(e) **Determination of pH:** Certain cells readily lend themselves to pH measurements. For example, consider the cell $\text{Pt, H}_2(g) | \text{H}^+(aq) | \text{KCl}(c) | \text{Hg}_2\text{Cl}_2(s), \text{Hg}(l)$ which involves a liquid junction potential that we shall represent by $\varphi_J$. The cell reactions are $\text{H}_2(P) = \text{H}^+(aq) + e^-$ and $\text{Hg}_2\text{Cl}_2(s) + e^- = \text{Hg}(l) + \text{Cl}^-(c)$ for an overall reaction $\text{H}_2(P) + \text{Hg}_2\text{Cl}_2(s) = \text{H}^+(aq) + \text{Cl}^-(c) + \text{Hg}$. At a pressure of 1 atm,$$
\frac{RT}{F} \ln a_{\text{H}^+}(aq) = \frac{RT}{F} \ln a_{\text{Cl}^-}(c),
$$
where $a_{\text{H}^+}$ and $a_{\text{Cl}^-}$ refer to different solutions. Suppose that $[\text{Cl}^-]$ is maintained constant by operating in a saturated solution, in which case one can reasonably expect $\varphi_J$ also to remain constant. Collecting $\varphi^o$, $\varphi_J$, and $-(RT/F) \ln a_{\text{Cl}^-}(\text{sat})$ into a single term, $\varphi_1$, we obtain

$$\varphi = \varphi_1 - \frac{RT}{F} \ln a_{\text{H}^+}(aq).$$

One may now calibrate the cell to obtain $\varphi_1$ with a known dilute acid solution, though considerable care has to be exercised to obtain a proper calibration. The cell is then
ready for pH measurements.

Clearly such a cell tends to be awkward in use, inasmuch as a gas electrode is involved. One therefore generally uses an alternative arrangement involving a glass electrode and a calomel electrode in the combination Ag,AgCl(s)|HCl(c-l)|glass|Hg₂Cl₂(sat)|Hg₂Cl₂(s),Hg. This operation of the cell depends on the fact that glasses can be made that allow passage of only H⁺ ions. By proceeding as for the H₂-calomel cell one obtains a relation of the form

\[ \mathcal{E} = \mathcal{E}_2 - (RT/F) \ln a_{H^+}, \]

(4.13.7)
from which pH = - log a_{H⁺} can be directly evaluated.

EXERCISES

4.13.1 In examining the thermodynamic properties of NbO at t > 600°C it has been proposed to employ a solid state electrolytic cell Pt,O₂(Pt)|Pb-NbO,|ThO₂|Fe-FeO|O₂(P₂),Pt in which oxygen is equilibrated at pressure P₁ over a two-phase Nb-NbO mixture on the left and at pressure P₂ over the two-phase iron-'wüstite' mixture on the right. The thermodynamic properties of wüstite and of iron are presumed to be known. The ThO₂-CaO mixture in the central compartment permits the diffusion of O₂⁻ in either direction at rates sufficient to allow rapid equilibration above 600°C. (a) Write out the half reactions occurring on the left and on the right. Examine carefully the role of NbO and wüstite in the electrochemical processes, under the assumption that the anode and cathode compartments are sealed off from the atmosphere. (b) Write out the full reaction for operation of the cell and show that it acts as a concentration cell. Write down the expression for the overall emf in terms of appropriate pressures and/or activities. (c) Show by an appropriate formula how a measurement of \( \mathcal{E} \) and of \( \mathcal{E} \) versus T provides a measure of the equilibrium involving niobium and its monoxide. State for what process free energy, entropy and enthalpy changes may be computed from these measurements. (d) Design a cell that would measure the same quantities for NbO₂.

4.13.2 (a) Show that the variation of emf with pressure is given by the expression \( (\partial \mathcal{E} / \partial P)_T = -\Delta V_d / nF \). (b) Apply this result to the cell H₂(p)|HCl(aq,m)|Hg₂Cl₂(s),Hg(ℓ) by specifying \( \Delta V_d \). (c) Prove that to a good degree of approximation \( \mathcal{E}_2 - \mathcal{E}_1 \)
4. THERMODYNAMIC PROPERTIES OF ELECTROLYTES

- \((2RT/nF) \ln (f_2/f_1)\), where \(f_1, f_2\) are the fugacities of \(H_2\) gas at two different pressures.
- When the hydrogen pressure (fugacity) is 1 atm over a 0.1 m HCl solution at 25°C, \(\mathcal{E} = 0.3990\) V; when the gas pressure is raised to 568.8 atm, the emf reads \(\mathcal{E} = 0.4850\) V. Determine the fugacity of \(H_2\) gas at that pressure.

4.13.3 Consider the operation of the cell at 25°C at 1 atm: \(Cd(s) \mid CdSO_4(m_1), K_2SO_4(m_2) \mid Hg_2SO_4(s) \mid Hg(\ell)\), for which one finds \(\mathcal{E} = 1.1647\) V, corresponding to \(m_1 = 1.25 \times 10^{-3}\), \(m_2 = 2.50 \times 10^{-2}\) molal. Determine the equilibrium constant for the cell reaction.

4.13.4 Consider the cell \(Ag(s) \mid AgCl(s) \mid NaI(c, H_2O) \mid NaI(c, D_2O) \mid AgCl(s) \mid Ag(s)\). (a) To what net process does operation of this cell correspond? (b) Is \(\mathcal{E}^\circ = 0\) here? Justify your answer.

4.13.5 Consider the cell \(^7Li(s) \mid ^7LiBr(pc) \mid LiBr(s) \mid Tl(\ell) \mid TlBr(s) \mid ^6LiBr(pc) \mid ^6Li(s)\) in which pc stands for propylene carbonate. (a) Write down the net reaction corresponding to the operation of the cell. (b) Given that \(\mathcal{E} = 0.76\) mV at 297°C, determine the equilibrium constant for the process. (c) Is the answer reasonable? Explain.

4.13.6 (a) Show that the cell \(Pb(s) \mid H_2(g) \mid NaOH(aq) \mid O_2(g) \mid Pb\) operates as a fuel cell in which \(H_2\) is "burned." (b) Assuming ideal behavior, look up \(\mathcal{E}^\circ\) and determine \(\mathcal{E}\); then determine the maximum useful electrical work that is available from such a fuel cell operating under partial pressures of 1 atm in which the NaOH concentration is 2 molal. (c) Determine \(\Delta H^\circ_d\) for this cell, given that \(d\mathcal{E}/dT = 0.846\) mV/deg. (d) Compare (b) with the maximum useful work available for a Carnot engine operating between 600 and 300 K on the basis of this reaction.

4.13.7 The \(Ag_2S-AgI\) cell uses a solid electrolyte, since the ions can diffuse rapidly through the matrix at temperatures from 150 to 500 degrees above room temperature. The cell may be represented as \(Ag(s) \mid AgI(s) \mid Ag_2S(s) \mid S(\ell) \mid C\), in which graphite is an inert electrode. Write out the half reaction and the net reaction corresponding to the operation of this cell. Show that \(\mathcal{E} - \mathcal{E}^\circ = - \Delta G_d/2F\).

4.13.8 The reported activities \(\gamma_s\) corresponding to various molalities \(m\) for aqueous solutions of HCl at 25°C and at \(P = 1\) atm are shown below:

<table>
<thead>
<tr>
<th>(m) (molal)</th>
<th>(10^{-3})</th>
<th>(10^{-2})</th>
<th>(10^{-1})</th>
<th>1</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma_s)</td>
<td>0.965</td>
<td>0.904</td>
<td>0.796</td>
<td>0.796</td>
<td>10.44</td>
</tr>
</tbody>
</table>

Determine the differential free energy change for the process \(HCl(1.00) = HCl(m)\) \(m = 10^{-2}, 10^{-3}\) molal.

4.13.9 At 25°C the standard half reaction potential for the process \(2H_2O + 2e^- = H_2 + 2OH^-\) is \(-0.8277\) V; determine the dissociation constant for water at that temperature.

4.13.10 At 25°C the equilibrium constant for the reaction
CuCl(s) + AgCl(s) – CuCl₂(aq) + Ag(s) reads \( K = 1.86 \times 10^{-6} \).

Using appropriate standard oxidation potentials, calculate the standard oxidation potentials for the Cu, CuCl(s)|Cl⁻ half cell.

4.13.11 Consider the cell
\[
Pb(Hg)|Pb₂Fe(CN)₆·3H₂O(s)|K₄Fe(CN)₆(aq,m₁)|
\[
K(Hg)|KCl(aq,m₂)|Hg₂Cl₂(s)|Hg(ℓ)
\]
(a) Write down the various partial reactions pertaining to the operation of this cell. (b) Write down an expression for the emf in terms of \( m₁, m₂ \) and involving mean molal activity coefficients.

4.13.12 For the cell Cd(Hg)(c₁)|CdI₂|Cd(Hg)(c₂) operating at 16.3°C, \( \xi = 0.0433 \) V when \( c₁ = 1.7705 \times 10^{-3}, c₂ = 5.304 \times 10^{-5} \) molar. Determine the molar activity coefficient for Cd in Hg at concentrations close to \( 10^{-3} \) molar.

4.13.13 The dissociation pressure of Ag₂O at 25°C is \( 5.0 \times 10^{-4} \) atm. Calculate the emf of the cell Ag|Ag₂O(s) in H₂O|O₂ (1 atm), Pt.

4.13.14 Determine the pH in the solution constituting the following cells at 25°C:
(a) \( H₂(1 \text{ atm})|\text{acidic solution}|\text{normal calomel electrode} \)
\( \xi = 0.784 \) V
(b) Pt|quinhydrone, acid solution||normal calomel electrode
\( \xi = -0.231 \) V
(c) \( H₂(1 \text{ atm})|\text{KOH(0.01 M)}|\text{normal calomel electrode} \)
\( \xi = 0.9894 \) V

4.13.15 For the galvanic cell Pb|PbSO₄(s)|H₂SO₄(m)|H₂(1 atm)|Pt operating at 25°C the following emf values are cited:
\[
\begin{array}{cccccc}
m (\text{molal}) & 10^{-3} & 2 \times 10^{-3} & 5 \times 10^{-3} & 10^{-2} & 2 \times 10^{-2} \\
\xi (V) & 0.1017 & 0.1248 & 0.1533 & 0.1732 & 0.1922 \\
\end{array}
\]
Determine the solubility product constant of PbSO₄ in water.

4.13.16 At 25°C the galvanic cell Pt,H₂(P)|HCl(m=0.1)|AgCl(s)|Ag(s) was subjected to the conditions shown below
\[
Pb₂ (\text{atm}) & 10.0 & 37.9 & 51.6 & 110.2 & 286.6 & 731.8 & 1035.2 \\
\xi (mV) & 399.0 & 445.6 & 449.6 & 459.6 & 473.4 & 489.3 & 497.5 \\
\]
Determine the fugacity coefficients for \( H₂ \) at 100, 300, 500, 700, and 900 atm.