

10

Ionized Systems

Eminent British Politician: “What good is electricity?”

Michael Faraday: “I don’t know yet, but some day you’ll tax it.”¹

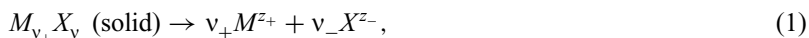
In solutions of electrolytes, dissociation into ions and long-range interactions of these ions must be considered. Because solutions containing a single ion cannot be prepared, mean ionic concentrations and activity coefficients are considered. In very dilute ionic solutions, the mean ionic activity coefficient can be estimated by the Debye–Huckel theory or extensions of this theory. Higher ionic concentrations, polyvalent ions, and solvents of low dielectric constants may require the consideration of ion pairs. In electrochemical systems, the electrostatic potential of ions due to charging of phases is added to the chemical potential to give the electrochemical potential. Different types of electrode can be combined to form electrochemical cells. Cells with more than one liquid phase are not reversible. Standard cell potentials can be conveniently obtained from a table of standard electrode potentials. The Nernst equation gives the concentration dependence of the potential of galvanic cells and may be used to extrapolate measured potentials to provide standard free-energy changes of chemical reactions involving ions.

Activity coefficients of ions and the pH's of solutions can also be obtained from electrochemical measurements.

10.1 Ionic Solutions

Solutions of electrolytes, substances that are ionized to some degree in solution, differ greatly from those of nonelectrolytes. The most obvious difference is the greater electrical conductivity of electrolyte solutions. The conductivity of electrolyte solutions span a wide range, depending in part on whether the electrolyte is completely ionized (a strong electrolyte, e.g., NaCl) or only partially ionized (a weak electrolyte, e.g., acetic acid). Although conductivity measurements provide a number of parameters used in treating the thermodynamics of electrolyte solutions, such measurements will not be discussed in this volume.

The ionization of electrolytes is clearly manifest in the thermodynamic properties of their solutions. For example, in the ideally dilute solution limit, a solution of a strong electrolyte behaves as ions, rather than molecules, interacting with solvent molecules. A NaCl solution of molality m behaves, in the limit of infinite dilution, as an ideally dilute solution of concentration $2m$, as 2 mol of ions are produced from each mole of NaCl dissolved in solution. A general strong electrolyte, dissociating by the equation



behaves as a solution of molality $(v_+ + v_-)m$, where m is the nominal molality of the solution (calculated from the mass of the solid dissolved per kilogram of solvent).

Another difference between solutions of electrolytes and nonelectrolytes is that the ideally dilute solution model holds for strong electrolyte solutions only up to extremely low concentrations. This maximum concentration is considerably lower when the electrolyte dissociates to polyvalent ions (z_+ or $|z_-|$ greater than 1). Because, in the ideally dilute limit, solute particles interact only with solvent molecules, deviations from ideally dilute behavior must result from interactions between solute particles. These deviations are much larger in solutions of strong electrolytes, because the solute particles are ions, which interact by Coulomb's law. The energy of the electrostatic interaction is inversely proportional to the separation of the ions, as compared with the interaction between neutral particles, in which energy generally falls off as the sixth power of the separation between the particles. The electrostatic interaction is also proportional to the product of the charges on the ions, explaining the larger deviations observed in solutions of polyvalent ions. When considering thermodynamic properties of ionic solutions, it is almost always necessary to deal with activities, rather than concentration.

10.2 Mean Ionic Activity Coefficients

In a solution of a strong electrolyte of molality m , we can write the contribution of the solute to the Gibbs free energy per 1.0 kg of solvent as

$$G_i = m_i \mu_i = m_i v_+ \mu_+ + m_i v_- \mu_- \quad (2)$$

where the last equation expresses the free energy as the contribution of the ions produced by the electrolyte. (For a strong electrolyte, no un-ionized molecules exist in solution.) The chemical potential of the electrolyte can therefore be written as

$$\mu_i = v_+ \mu_+ + v_- \mu_- \quad (3)$$

The chemical potential of an individual ion in solutions can never be measured because it depends on the other ions in the solution with which it interacts. We can, however, discuss $\mu_{\pm} \equiv \mu_i/v$, the *mean ionic chemical potential*, or the average chemical potential of an ion produced from the electrolyte. Writing μ_+ , μ_- , μ_{\pm} , and μ_i each in the form $\mu = \mu^0 + RT \ln a$ gives

$$\begin{aligned} \mu_i &= \mu_i^0 + RT \ln a_i = v(\mu_{\pm}^0 + RT \ln a_{\pm}) \\ &= v_+(\mu_+^0 + RT \ln a_+) + v_-(\mu_-^0 + RT \ln a_-) \end{aligned} \quad (4)$$

With

$$\mu_i^0 = v\mu_{\pm}^0 = v_+\mu_+^0 + v_-\mu_-^0 \quad (5)$$

we get

$$a_i = a_{\pm}^v = a_+^{v_+} a_-^{v_-} \quad (6)$$

a_{\pm} is the *mean ionic activity*. Writing each activity in the form $a = \gamma m$,

$$\gamma_i m_i = \gamma_{\pm}^v m_{\pm}^v = \gamma_+^{v_+} m_+^{v_+} \gamma_-^{v_-} m_-^{v_-} \quad (7)$$

As a result, m_{\pm} , the *mean ionic molality*, is given by

$$m_{\pm} = (m_+^{v_+} m_-^{v_-})^{1/v} = [(v_+ m_i)^{v_+} (v_- m_i)^{v_-}]^{1/v} = v_{\pm} m_i \quad (8)$$

where $v_{\pm} = (v_+^{v_+} v_-^{v_-})^{1/v}$

Note that for a 1 : 1 electrolyte (e.g., NaCl, CaSO₄, $v_{\pm} = 1$.

γ_{\pm} , the *mean ionic activity coefficient*, is from Eq. (7):

$$\gamma_{\pm} = (\gamma_+^{v_+} \gamma_-^{v_-})^{1/v} \quad (9)$$

The overall expression for μ_i is

$$\mu_i = \mu_i^0 + vRT \ln \gamma_{\pm} m_{\pm} = \mu_i^0 + vRT \ln \gamma_{\pm} v_{\pm} m_i \quad (10)$$

Note that a_{\pm} , m_{\pm} , v_{\pm} , and γ_{\pm} are geometric means, whereas μ_{\pm} is an arithmetic mean. Because, at infinite dilution, the solution follows the ideally dilute model,

$\gamma_+ = \gamma_- = \gamma_{\pm} \rightarrow 1$ as $m_{\pm} \rightarrow 0$. The standard state of the electrolyte is thus the hypothetical state of unit mean ionic molality, assuming that the solution remains ideally dilute to this concentration.

Example 1. For 0.02 *m* ZnCl₂, find the following:

- (a) m_{\pm}
- (b) γ_{\pm} in terms of γ_+ and γ_-

Solution:

- (a) $m_{\pm} = v_{\pm} m_i = (v_+^v v_-^v)^{1/v} m_i = (1 \times 2^2)^{1/3} (0.02) = 0.0318 \text{ mol/kg}$
- (b) $\gamma_{\pm} = (\gamma_+ \gamma_-^2)^{1/3}$

10.3 Mean Ionic Activity Coefficients from Experimental Data

Just as we discussed in [Chapter 9](#), we can use measured activities of solvents (determined from vapor pressure, freezing-point depression, boiling-point elevation, or osmotic pressure) to determine activity coefficients of electrolytes in solution. For an ionic substance, the Gibbs–Duhem equation is

$$n_A d\mu_A + n_i d\mu_i = n_A RT d \ln a_A + n_i v RT d \ln \gamma_{\pm} m_{\pm} = 0, \quad (11)$$

which can be rearranged to

$$d \ln \gamma_{\pm} = -d \ln m_{\pm} - \frac{n_A}{v n_i} d \ln a_A = -d \ln m_{\pm} - \frac{1}{v m_i M_A} d \ln a_A. \quad (12)$$

To circumvent the last term blowing up when integrating this equation from infinite dilution, we define the *osmotic coefficient for an electrolyte* as

$$\phi \equiv -\frac{n_A}{v n_i} \ln a_A = -\frac{1}{v m_i M_A} \ln a_A \quad (13)$$

Using this to substitute for $d \ln a_A$ gives

$$d \ln a_A = -v M_A (m_i d\phi - \phi dm_i) \quad (14)$$

Equation 12 then becomes²

$$d \ln \gamma_{\pm} = d\phi + \frac{(\phi - 1)}{m_i} dm_i \quad (15)$$

which can be integrated without difficulty to

$$\ln \gamma_{\pm} = (\phi - 1) + \int_0^{m_i} \frac{(\phi - 1)}{m'} dm' \quad (16)$$

because ϕ approaches unity in the infinitely dilute limit. (See Problem 3.)

10.4 Calculation of Mean Ionic Activity Coefficient

As we have noted, electrolyte solutions deviate from ideally dilute behavior even at a very low concentration because of the long-range Coulombic interaction between charged particles. However, because these solutions are overall electrically neutral, the escaping tendency of ions from these solutions must result from the arrangement of the ions in the solution. Ions can be distributed in such a way as to lower their energies and escaping tendencies from a system. The most obvious example of such a distribution is the regular arrangement of ions in crystals, in which the nearest neighbors of positive ions are negative ions and vice versa. Of course, in solution, the positions of ions are not fixed, and thermal motion opposes their tendency to attain the most energetically favorable distribution. In addition, solvent molecules lie between charged particles in solution, and the orientation of solvent dipoles reduces the forces between the charged particles. This latter effect is measured by the dielectric constant of the solvent and is quite large in aqueous solution. (The dielectric constant of water is 78.4 at 25°C.) Nevertheless, at short distances around a positive ion in solution, a small excess of negative charge exists, and around a negative ion, the opposite occurs. The effect of the nonuniform distribution of ions in solution on their energy (and thus on their activity coefficients) was first treated by Debye³ and Huckel in 1923. The result of the theory will be stated and discussed, but not derived. The theory is illustrated in Fig. 1.

In the *Debye-Huckel theory*, an ion in solution is treated as a conducting sphere. The distance of closest approach of two ions is a .⁴ The solution beyond a

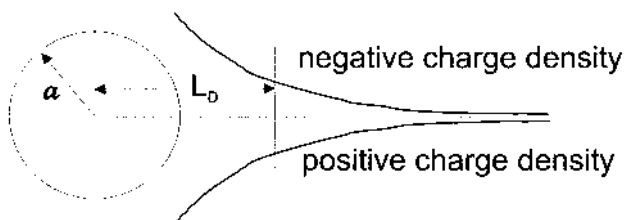


Figure 1 Distribution of charge around a positive ion.

is treated as a medium with relative dielectric constant $\epsilon_{r,A}$, containing continuous distributions of positive and negative ions. The charge density in the solution around an ion is determined by a Boltzmann distribution in the energy of the electrostatic interaction with both the charge of the ion and the other charged particle in the solution. The distributions (charge densities) of positive and negative charge are shown in Fig. 1. Around a positive charge, there is excess negative charge in the solution and depletion of positive charge in the solution. The ionic character of the solution is characterized by its *concentration-scale ionic strength*, I_c , defined by

$$I_c \equiv \frac{1}{2} \sum_j z_j^2 c_j \quad (17)$$

with the sum extending over all the ions in the solution. The charge imbalance caused by an ion dies out beyond a distance L_D , the *Debye length* of the solution, which is defined by

$$L_D \equiv \sqrt{\frac{\epsilon_0 \epsilon_{r,A} RT}{2 \mathcal{F}^2 I_c}} \quad (18)$$

ϵ_0 and $\epsilon_{r,A}$ are the permittivity of free space and the dielectric constant (relative permittivity) of the solvent, respectively, and \mathcal{F} is the Faraday constant (the charge on 1 mol of hydrogen ions, 94,485 C). Charge imbalances die out in a shorter distance if there is more charge in the solution, the temperature is lower, and dielectric constant is smaller.

For the activity coefficient of an ion, the theory gives

$$\ln \gamma = -\frac{z^2 A \sqrt{I_c}}{1 + B a \sqrt{I_c}} \quad (19)$$

where z is the charge on the ion. The constants A and B are independent of concentrations in the solution and are given by

$$A = \frac{(2N_A)^{1/2}}{8\pi} \left(\frac{e^2}{\epsilon_0 \epsilon_{r,A} kT} \right)^{3/2} \quad \text{and} \quad B = e \left(\frac{2N_A}{\epsilon_0 \epsilon_{r,A} kT} \right)^{1/2} \quad (20)$$

N_A , e , and k are universal constants (Avogadro's number, electronic charge, and Boltzmann's constant, respectively).

Solutions with a single ion cannot be prepared, and because ions influence each other, only the mean ionic activity coefficient can be measured. For a binary

electrolyte (one producing only two types of ions in solution, i.e., M_{v+} , X_{v-}), Eq. (18) leads to

$$\ln \gamma_{\pm} = -\frac{z_+|z_-|A\sqrt{I_c}}{1 + Ba\sqrt{I_c}} \quad (21)$$

In the lowest level of the theory, the B term in the denominator of Eq. (18) is dropped, to give the *Debye–Huckel limiting law* (DHLL),

$$\ln \gamma_{\pm} = -z_+|z_-|A\sqrt{I_c} \quad (22)$$

a relation with no adjustable parameters. At this level of the theory, the mean ionic activity coefficient depends only on the charge state of the ion and not on the chemical nature of the ion. Thus, at the same concentration, all 1:1 electrolytes would have the same mean ionic activity coefficient. For aqueous solutions at 25°C ($\epsilon_{r,A} = 78.4$). A has the value 1.17 (L/mol)^{1/2}. It is more usual to use a logarithm to the base 10, which gives with I_c in units of moles/liter:

$$\log_{10} \gamma_{\pm} \stackrel{\text{aq}, 25^\circ\text{C}}{=} -0.51z_+|z_-|\sqrt{I_c} \quad (23)$$

It is noteworthy that in the Debye–Huckel theory, $\ln \gamma_{\pm}$ is always negative, corresponding to γ_{\pm} less than 1. This is expected because the ions are distributed in a manner that lowers their energy and escaping tendency in solution and produces negative deviation from ideal behavior. The effect is larger for electrolytes that produce multiply-charged ions, and it is the ionic strength of *all* of the ions in solution that is a measure of the attraction for an ion of an electrolyte. Ionic strength enters in a square-root dependence (i.e., less than linear) because the larger I_c , the smaller the region around any ion that is disturbed from electrical neutrality (as indicated by L_D). Inspection of the constant A shows that increased temperature acts to reduce the ordering of ions in solution, as does increased dielectric constant. Large dielectric constants occur in polar solvents, the molecules of which align, so that their dipoles cancel some of the ion-generated electric field.⁵

The Debye–Huckel theory is accurate in solutions in which the interactions between ions are not too great (i.e., at low ionic strengths in solutions of monovalent ions in solvents with large dielectric constants). In Fig. 2, the predictions of Eq. (21) are compared with experimental data for some strong electrolytes with different ionic charges.

It can be seen that Eq. (21) shows the proper limiting behavior as concentrations approach zero. However, its quantitative predictions are reliable only up to $I_c \approx 0.01 M$. Better agreement is obtained between experiment and the full theoretical result, Eq. (21). However, there does not seem to be a good way to choose a , the ionic size, other than fitting experimental data to Eq. (21). Typical

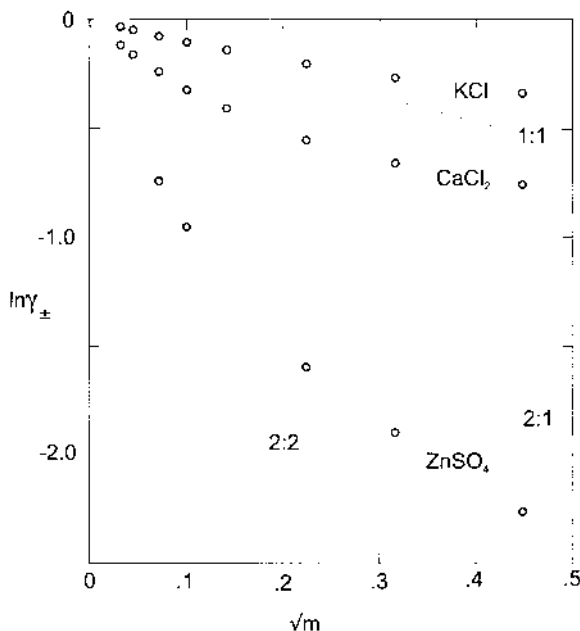


Figure 2 Comparison of measured mean ionic activity coefficients with those predicted by the Debye–Hückel limiting law. (Data from Handbook of Chemistry and Physics, 77th ed. A James, M Lord. VNR Index of Chemical Physical Data. New York: Van Nostrand Reinhold, 1992.

values of a found for small inorganic ions by this procedure range from 0.3 to 0.9 nm, which are physically reasonable values.

Some workers, noting that in aqueous solutions at 25°C, $B = 3.3 \times 10^9$ (L/mol)^{1/2} m⁻¹, take $a = 0.3$ nm = 0.3×10^{-9} m, giving $Ba = 1$, and for Eq. (21),

$$\log_{10} \gamma_{\pm}^{\text{aq}, 25^\circ\text{C}} = -0.51z_+|z_-| \frac{\sqrt{I_c}}{1 + \sqrt{I_c}} \quad (24)$$

The addition of a term linear in I_c to Eq. (24) has been found to improve its accuracy, and an empirical equation proposed by Davies,

$$\log_{10} \gamma_{\pm}^{\text{aq}, 25^\circ\text{C}} = -0.51z_+|z_-| \left(\frac{\sqrt{I_c}}{1 + \sqrt{I_c}} - 0.3I_c \right) \quad (25)$$

with no parameters, has been shown to give good agreement with experiment up to $I_c = 0.1$ M, for singly-charged ions. In Fig. 3, mean ionic activity coefficients are shown for a number of compounds to high concentrations.

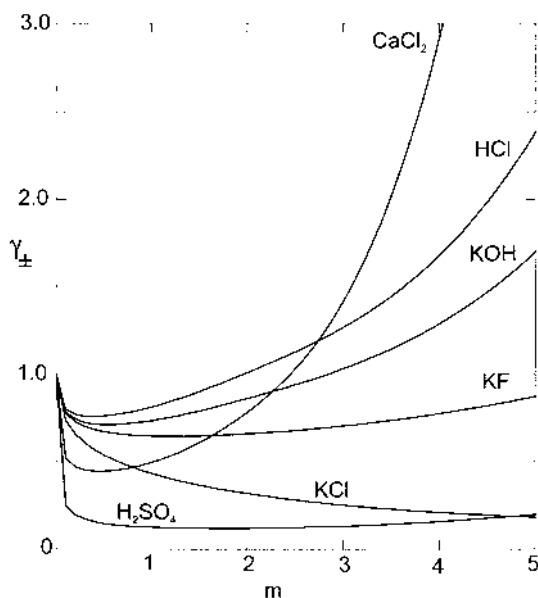


Figure 3 Mean ionic activity coefficients to high concentrations. (Data from Handbook of Chemistry and Physics. 77th ed.)

It can be seen that γ_{\pm} usually increases at high concentrations and, in some cases, becomes larger than 1, in disagreement with the Debye–Huckel theory. Some of the reasons proposed for the failure of the Debye–Huckel theory are ion pairing (loose association of oppositely charged ions in solution) and hydration of ions, with accompanying reduction of the amount of free solvent.

Example 2. Calculate the activity of a 0.05 *m* HCl solution using the following:

- The Debye–Huckel limiting law [Eq. (22)]
- The Debye–Huckel theory in the form of Eq. (24)
- The Davies equation [Eq. (25)]

Solution:

$$a_i = a_{\pm}^{\nu_{\pm}} = m_{\pm}^{\nu_{\pm}} \gamma_{\pm}^{\nu_{\pm}} = m_{+}^{\nu_{+}} m_{-}^{\nu_{-}} \gamma_{\pm}^{\nu_{\pm}}$$

In this case, $\nu_{+} = \nu_{-} = 1$, $m_{+} = m_{-} = m_{\pm} = 0.05$, and $I_c = 0.05$. We obtain the following

- $\log_{10} \gamma_{\pm} = -0.51(1)(1)\sqrt{0.05} = -0.114$, $\gamma_{\pm} = 0.769$, and $a_i = [(0.05)(0.769)]^2 = 1.47 \times 10^{-3}$

- (b) $\log_{10}\gamma_{\pm} = -0.114/1.223 = -0.0932$, $\gamma_{\pm} = 0.807$, and $a_i = [(0.05)(0.807)]^2 = 1.63 \times 10^{-3}$
- (c) $\log_{10}\gamma_{\pm} = -0.51(1)(1)[\sqrt{0.05}/(1 + \sqrt{0.05}) - 0.3(0.05)] = -0.0856$, $\gamma_{\pm} = 0.821$, and $a_i = [(0.05)(0.821)]^2 = 1.68 \times 10^{-3}$.

Note that because HCl produces two ions, in each case the activity varies as the square of the HCl molality, modified by the activity coefficient.

The very important chemical quantity pH^6 is defined as⁷

$$\text{pH} \equiv -\log a_{\text{H}^+} \quad (26)$$

a_{H^+} includes all of the hydrated forms of the hydrogen ion. Because of its logarithmic nature, nonideality has a smaller effect on pH than it does on a_{H^+} ; thus, the particular method of correcting for nonideal behavior is less important.

Example 3. Calculate the pH of a 0.5 *m* HCl solution, assuming it is ideally dilute and also using each of the approximations for γ_{\pm} employed in Example 2.

Solution: $\text{pH} = -\log a_{\text{H}^+} = -\log(\gamma_{+}m_{\text{H}^+}) = -\log(\gamma_{\pm}m_{\text{H}^+})$, where, in the last step, we take the result of the Debye–Huckel theory for a 1 : 1 electrolyte.

Assuming ideally dilute, $\text{pH} = -\log(0.05) = 1.301$.

With DHLL, $\text{pH} = -\log[(0.769)(0.05)] = -\log(0.0384) = 1.415$.

With Eq. (24), $\text{pH} = -\log[(0.807)(0.05)] = -\log(0.0403) = 1.394$.

With the Davies equation, $\text{pH} = -\log[(0.821)(0.05)] = -\log(0.04105) = 1.387$.

10.5 Ionic Equilibrium

In calculations of ionic equilibria, the required activity coefficients depend on ionic strength and, thus, on the equilibrium. As a result, such calculations are usually carried out by the method of successive approximations. Fortunately, convergence to a unique solution is usually achieved very rapidly in these problems.

Example 4. Calculate m_{H^+} and the pH of an aqueous 1.0 *m* acetic acid solution at 25°C. For acetic acid, $K_a = 1.75 \times 10^{-5}$. Use the DHLL approximation for activity coefficients.

Solution: The equilibrium constant is

$$K_a = K_m K_{\gamma} = \frac{m_{\text{H}^+} m_{\text{Ac}^-}}{m_{\text{HAc}}} \frac{\gamma_{\pm}^2}{\gamma_{\text{HAc}}}$$

For this solution, γ_{HAc} can be taken as unity. For the first approximation, we also take $\gamma_{\pm} = 1$. Choosing as a basis 1.0 kg of solvent, we have for the reaction $\text{HAc} \leftrightarrow \text{H}^+ + \text{Ac}^-$,

$$m_{\text{H}^+} = m_{\text{Ac}^-} = \xi_e, \quad m_{\text{HAc}} = 1.0 - \xi_e, \quad \frac{\xi_e^2}{1.0 - \xi_e} = 1.75 \times 10^{-5}$$

The solution of this quadratic equation is $\xi_e = m_{\text{H}^+} = m_{\text{Ac}^-} = 0.00417 m$, which is also the ionic strength. $\log \gamma_{\pm} = -0.51(1)(1)\sqrt{0.00417} = -0.0329$, $\gamma_{\pm} = 0.927$, and $K_{\gamma} = 0.859$. This gives

$$\frac{\xi_e^2}{1 - \xi_e} = \frac{1.75 \times 10^{-5}}{0.859} = 2.04 \times 10^{-5}$$

resulting in $\xi_e = m_{\text{H}^+} = 0.00451$.

Recalculating γ_{\pm} , $\log \gamma_{\pm} = -0.51(1)(1)\sqrt{0.00451} = -0.0342$ for $\gamma_{\pm} = 0.924$, which is a negligible change. Following Example 2,

$$\text{pH} = -\log[(0.00451)(0.924)] = -\log(0.00417) = 2.38.$$

Note that if we neglected the nonideality of the solution, we would also have $\text{pH} = -\log(0.00417) = 2.38$. This is because pH depends on the *activity* of the hydrogen ions, which, in the limit of small percent dissociation, is almost independent of the activity coefficient.

Example 5. Calculate m_{H^+} and the pH of an aqueous solution at 25°C that is 0.05 *m* in acetic acid and 0.3 *m* in NaCl.

Solution: Because NaCl is a strong electrolyte, the Na^+ and Cl^- ionic concentrations will determine the ionic strength.

$I_c = 0.3$: For HAc, $\log \gamma_{\pm} = -0.51(1)(1)\sqrt{0.3} = -0.279$, $\gamma_{\pm} = 0.526$, and $K_{\gamma} = 0.277$.

Following Example 4,

$$K_m = \frac{\xi_e^2}{1 - \xi_e} = \frac{1.75 \times 10^{-5}}{0.277} = 6.3 \times 10^{-5},$$

$$\xi_e = m_{\text{H}^+} = 0.0079$$

The considerable increase in the hydrogen ion concentration produced by the addition of NaCl is called *salting in*.

Following Example 2,

$$\text{pH} = -\log[(0.0079)(0.526)] = 2.38$$

Once again, the pH is almost independent of the activity coefficient.

10.6 Ion Pairs and Ion Solvation

The Debye–Huckel theory deals with long-range interaction between ions. In more detailed consideration of ionic activity coefficients, short-range interactions between ions, or *ion pairs*, must also be considered. An ion pair is a transient association of opposite-charged ions held together by Coulombic force, rather than by specific chemical or coordination bonding. Ion pairing is strongest when the forces between ions are the largest (i.e., between polyvalent ions at high concentrations in solvents of low dielectric constants). The oppositely charged ions do not have to be in contact at the distance of closest approach, but their energy of attraction has to be greater than or comparable to their thermal energy, so that they remain associated for an appreciable time. The Bjerrum theory of ion pairs requires that the energy of the attractive interaction be at least $2kT$.⁸ Simple monovalent ions, such as K^+ and Cl^- , are too large to approach to distances where their interaction reaches this value in aqueous solution. Therefore, these ions are considered to not form ion pairs.

The magnitude of ion-pair formation in other cases is described by means of a dissociation constant, K_{dis} , in much the same manner as for the treatment of weak electrolytes. These constants may be obtained from Bjerrum's theory or from measurements of solution conductivity. A selection of pK_{dis} values is given in Table 1. The larger pK_{dis} , the smaller the dissociation constant and the larger the tendency for ion-pair formation. Interestingly, K^+ and NO_3^- are found to form ion pairs. Because the size of NO_3^- is larger than Cl^- , treatment of polyatomic ions as spheres cannot be correct. Most probably, K^+ interacts with charge localized on one of the oxygen atoms of NO_3^- . Ion-pair formation lowers the escaping tendency of ions from solution.

Example 6. Find the fraction of ion pairs in 0.1 *m* aqueous KNO_3 at 25°C.

TABLE 1 Dissociation constants (pK_{dis}) for ion pairs at 25°C in aqueous solution

Substance	pK_{dis}
KNO_3	−0.2
NaOH	−0.7
$Ca(OH)_2$	1.30
$CaSO_4$	2.3

Note: More extensive data in CW Davies. In WJ Hamer, ed. The Structure of Electrolytic Solutions. New York: Wiley, 1959.

Solution: From Table 1,

$$K_{\text{dis}} = 10^{0.2} = 1.58 = K_m K_\gamma = \frac{m_{\text{K}^+} m_{\text{NO}_3^-}}{m_{\text{K}^+ \text{NO}_3^-}} \gamma_\pm^2$$

where we have used the assumption that the activity coefficient of the ion pair is unity, because it is uncharged.

First iteration: Take $\gamma_\pm = 1$, for the reaction $\text{K}^+ \text{NO}_3^- \leftrightarrow \text{K}^+ + \text{NO}_3^-$,

$$1.58 = \frac{\xi_e^2}{0.1 - \xi_e}, \quad \xi_e = 0.0943, \quad I_c = 0.0943$$

Because this is fairly high, we use Eq. (24) to calculate γ_\pm :

$$\log \gamma_\pm = -0.51 \frac{0.307}{1 + 0.307} = -0.12, \quad \gamma_\pm = 0.76$$

Second iteration:

$$\frac{1.58}{(0.76)^2} = 2.73 = \frac{\xi_e^2}{0.1 - \xi_e}, \quad \xi_e = 0.0966$$

which is close enough to our first iteration that further calculation is not necessary. Note that the fraction of the ions that form ion pairs is only $(0.1 - 0.0966)/0.1 = 0.034$.

The fraction of ions that are associated to ion pairs is much greater than calculated in Example 6, when concentrations are higher, with polyvalent ions and in solvents of low dielectric constants.

For a 1 : 1 strong electrolyte with ion pairing, the concentration of both ions is αm_i , where α is the fraction of ion pairs that are dissociated. ($\alpha m_i = \xi_e$, the extent of the dissociation reaction). The chemical potential and activity of such electrolytes are easily calculated, because, at equilibrium,

$$\mu_{\text{IP}} \stackrel{1:1}{=} \mu_+ + \mu_- \quad (27)$$

$$\mu_i = \alpha \mu_+ + \alpha \mu_- + (1 - \alpha) \mu_{\text{IP}} = \mu_+ + \mu_- \quad (28)$$

Note that Eq. (28) is identical to Eq. (3) for a strong electrolyte with no ion-pair formation. However, for ion pairing, we have

$$\begin{aligned} \mu_i &\stackrel{1:1}{=} \mu_i^0 + RT \ln a_i \\ &= \mu_+ + \mu_- \\ &= (\mu_+^0 + RT \ln \gamma_+ \alpha m_i) + (\mu_-^0 + RT \ln \gamma_- \alpha m_i) \\ &= (\mu_+^0 + \mu_-^0) + RT \ln (\gamma_\pm \alpha)^2 m_i^2 \end{aligned} \quad (29)$$

In the limit of infinite dilution, $\gamma_{\pm} \rightarrow 1$, $\alpha \rightarrow 1$, and $a_i \rightarrow m_i^2$. Therefore, at noninfinite dilution,

$$\gamma_i = \gamma_{\pm}^2 \alpha^2 \quad (30)$$

Ions also interact at short distances with solvent molecules. (The hydration of the proton to H_3O^+ and higher-hydrated species in aqueous solutions is well known.) Hydration of ions reduces the concentration of free water and can result in an increase in the escaping tendency of ions from solution, because their “effective concentration” is greater than their actual concentration.

10.7 Electrochemical Systems

In using the chemical potential of ions as a measure of their escaping potential from a phase, we are implicitly assuming that the phase is electrically neutral. In fact, due to electrostatic forces, the escaping tendency of a charged particle from a phase can be dramatically affected by the charge state of the phase.⁹ This is illustrated by the phenomenon of field emission, where sufficient numbers of electrons are forced onto a sharply pointed metallic surface, so that some of them are ejected into the surrounding vacuum by their mutual electrostatic repulsion. Electrostatic attraction and repulsion are very strong and long range, so it takes only a tiny net charge transfer to a phase to have an appreciable effect.

Charge will spontaneously develop at the interface between two phases when there is a difference in the ease with which particles with charge of opposite sign can be transferred across the phase boundary. One example of this is at the interface between a metal and a solution, where metallic ions, but not electrons, can dissolve in the solution.¹⁰ Another example is at the interface between two metals, where electrons, but not ions, undergo rapid transfer. In the latter case, the electron transfer depends on temperature and forms the basis for measuring temperature differences by means of thermocouples.

The variable used to describe the differences in escaping tendency of charged particles from charged phases is the *electrostatic potential*, ϕ . The electrostatic potential at a point, a , is defined as the work per unit charge required to bring a positive test charge reversibly from infinity to the point,

$$\phi(a) \equiv \frac{\delta w_{\infty \rightarrow a}}{dQ} \quad (31)$$

Note that potentials are defined with respect to a positive test charge, whereas electrochemical systems produce or consume negative charge (electrons). The test charge is of infinitesimal magnitude, so that it does not change the charge distribution in the system. The selection of infinity as the zero of electrostatic

energy is arbitrary. Only differences in electrostatic potential between the various phases of the system are important.

The electrostatic potential at a distance r from a charge dQ is

$$\phi(r) = \frac{1}{4\pi\epsilon_0} \frac{dQ}{r} \quad (32)$$

where ϵ_0 is the permittivity of vacuum ($8.854 \times 10^{-12} \text{ C}^2/\text{N m}$). Equation (32) has to be integrated over the existing charge distribution.

When a (real) charge is moved reversibly in an electrostatic potential, the work done increases U and G of the charged particle (with respect to its value at infinity) by $\phi(a) dQ$. The change in electrostatic energy for transferring dn moles of ions from infinity to a phase at a is $\phi(a)z\mathcal{F} dn$, where z is the charge on the ion (a small positive or negative integer) and \mathcal{F} is the *Faraday constant*, the charge on 1 mol of hydrogen ions, 96,485 C/mol. This change in the Gibbs free energy due to the position-dependent electrostatic potential must be added to the change in G due to the chemical potential of the ions:

$$dG_i = \mu_i dn_i + z_i\mathcal{F} \phi(a) dn_i \quad (33)$$

The *electrochemical potential*, $\tilde{\mu}_i(a)$, of an ion at an electrostatic potential $\phi(a)$ is defined as

$$\tilde{\mu}_i(a) \equiv \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} = \mu_i + z_i\mathcal{F} \phi(a) \quad (34)$$

and is the true measure of the escaping tendency of the ion from the phase a .

To find thermodynamic relationships for charged systems, we just replace chemical potentials in equations for uncharged systems by electrochemical potentials. For example, for equilibrium of a charged particle at a phase boundary, we have, in analogy to Eq. (24) of [Chapter 6](#),

$$\tilde{\mu}_i(a) = \mu_i(a) + z\mathcal{F} \phi(a) = \tilde{\mu}_i(b) = \mu_i(b) + z\mathcal{F} \phi(b) \quad (35)$$

Thus, when two phases are in contact, an ion that can exist in both phases will be transferred until

$$\phi(b) - \phi(a) = \frac{\mu_i(a) - \mu_i(b)}{z_i\mathcal{F}} \quad (36)$$

For example, if a Pt rod containing some Zn is placed in contact with an aqueous ZnCl_2 solution, Zn^{+2} ions are transferred between the solution and the metal, until Eq. (36) holds. It takes only a minuscule transfer of Zn^{+2} to build up a very appreciable electrostatic potential, because electrons from the rod cannot transfer into the solution. Chemical potentials, which depend on concentrations, can therefore be calculated neglecting the ionic transfer. If the electrons could also

transfer, much more of the rod would dissolve and equilibrium would have to be established by changing chemical potentials by changing concentrations.

For chemical reactions involving charged species in multiple (but contact-ing) phases, the condition for equilibrium is, in analogy to Eq. (30) of [Chapter 7](#),

$$\sum_i v_i \tilde{\mu}_i = 0 \quad (37)$$

A *battery* (or *galvanic* or *voltaic cell*) is a device that uses oxidation and reduction reactions to produce an electric current. In an *electrolytic cell*, an external source of electric current is used to drive a chemical reaction. This process is called *electrolysis*. When the electric potential applied to an electrochemical cell is just sufficient to balance the potential produced by reactions in the cell, we have an electrochemical cell at equilibrium. This state also occurs if there is no connections between the terminals of the cell (open-circuit condition). Our discussion in this chapter will be limited to electrochemical cells at equilibrium.

The voltage produced by galvanic cells is due to the transfer of charged particles at a number of phase interfaces. In order for the battery to be able to produce an electric current, each phase must be able to conduct electricity, usually either by electron flow in solid or liquid metals or by ionic mobility in solutions. The voltage of the battery is measured at its *terminals*, which are metallic and permit electron flow. Each terminal is part of an *electrode*, at which an oxidation or reduction half-reaction occurs. The electrode at which oxidation occurs (in both galvanic and electrolytic cells) is called the *anode*, whereas that at which reduction occurs is called the *cathode*. The basic principle of the galvanic cell is the separation of these two reactions, so that electrons produced by oxidation must flow through an external circuit before causing reduction. For quantitative measurements, the terminals of the cell should be constructed from the same metallic material, so that the driving force for electrons at the terminals is due exclusively to an electrostatic potential difference within the cell, not to additional potential differences at the connecting wires.

10.8 Types of Electrodes

Most electrodes employed can be classified as being of the following types:

1. Gas electrode: Here, a gas is in equilibrium with its ions in solution. The most important example is the *hydrogen electrode* (or H^+/H_2 electrode), for which the electrode reaction is



Hydrogen gas is bubbled over a platinum surface that is coated with “platinum black,” an electrolytically deposited coating of colloidal platinum, which is an excellent catalyst for the above equilibrium. The hydrogen electrode has been selected as the standard against which the potentials of other electrodes are measured. Equations of the type of reaction (I) are called half-cell reactions, because they include electrons. Reaction I is a reduction half-cell reaction.

2. Metal–metal ion electrode: Here, a metal is in equilibrium with its ion in solution. Metals such as Cu or Zn have an appreciable tendency to dissolve and form ions in water, but little tendency to react with water.
3. Amalgam electrode: Metals such as Ca or Na react with water and cannot be used directly as electrodes. They can be used, however, by dissolving them in liquid mercury, forming an *amalgam*. In the amalgam solution, the activity of the metal is reduced below what it is when pure; thus, its reaction with water is suppressed. Mercury does not dissolve in the aqueous solution.
4. Metal-insoluble salt electrode: Metal-insoluble salt electrodes are convenient for batteries. For example, the AgCl/Ag electrode consists of metallic silver, coated with the insoluble salt AgCl, and suspended in a solution or paste saturated with the salt. The electrode reaction is



Note that the metal does not dissolve in the solution. An electrode of this type, which is often used because of its stability, is the *calomel electrode* shown in Fig. 4. This consists of a platinum wire inserted into liquid mercury, which is coated with mercurous chloride. The electrode reaction is



5. Oxidation-reduction electrodes: These electrodes consist of an inert metal in a solution containing ions that can undergo oxidation–reduction reactions. An example is a platinum wire immersed in a solution containing Fe^{2+} and Fe^{3+} ions. Transfer of electrons into the solution is accompanied by reduction of some Fe^{3+} to Fe^{2+} .
6. Membrane electrode: The membrane electrode is a thin phase through which charge can be transported (by ion migration) so that electrochemical equilibrium can be maintained for at least one type of ion across the electrode. For example, pH is often measured in a solution (X) by means of a glass electrode between an HCl solution of known

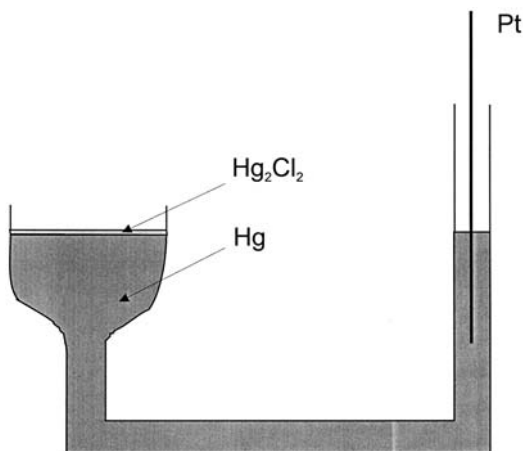


Figure 4 Calomel electrode.

$a(\text{H}^+)$ and the unknown solution. Assuming that the HCl solution is on the left-hand side of the glass membrane, the equilibrium condition is

$$\begin{aligned}\tilde{\mu}_{\text{H}^+}(\text{HCl}) &= \tilde{\mu}_{\text{H}^+ \text{ glass}}(\text{L}) \\ \tilde{\mu}_{\text{H}^+}(X) &= \tilde{\mu}_{\text{H}^+ \text{ glass}}(\text{R})\end{aligned}\quad (38)$$

where L and R are within the membrane on its left-hand and right-hand sides, respectively. Writing these expressions in terms of chemical and electrical potentials gives

$$\begin{aligned}\mu_{\text{H}^+}(\text{HCl}) + \mathcal{F}\phi(\text{HCl}) &= \mu_{\text{H}^+}(\text{glass, L}) + \mathcal{F}\phi(\text{glass, L}) \\ \mu_{\text{H}^+}(X) + \mathcal{F}\phi(X) &= \mu_{\text{H}^+}(\text{glass, R}) + \mathcal{F}\phi(\text{glass, R})\end{aligned}\quad (39)$$

We subtract the second equation from the first. In doing this, the terms on their right-hand sides cancel for the following reasons: The chemical environment on the two sides of the glass is similar enough that $\mu_{\text{H}^+}(\text{glass, L}) = \mu_{\text{H}^+}(\text{glass, R})$, and, because the glass is weakly conducting, at equilibrium, $\phi(\text{glass, L}) = \phi(\text{glass, R})$. It is not the hydrogen atoms that are transported through the glass to establish this equilibrium. The transport is by sodium and potassium ions that have some freedom to move through the pores of the silicon dioxide matrix of the glass. The potential difference introduced by the membrane is thus

$$\phi(\text{HCl}) - \phi(X) = \frac{\mu_{\text{H}^+}(X) - \mu_{\text{H}^+}(\text{HCl})}{\mathcal{F}}\quad (40)$$

and is proportional to the difference in chemical potential of hydrogen ions in the two solutions. Because chemical potentials are proportional to logarithms of hydrogen ion activity, the potential difference across the electrode is proportional to the difference of pH's of the two solutions. In Sec. 10.12, we show how this type of membrane is incorporated into a pH-measuring electrode.

10.9 Electrochemical Cells

When drawing a galvanic cell, by convention, the anode is drawn on the left and the cathode on the right. In Fig. 5, an electrochemical cell using a hydrogen electrode as the anode and an AgCl/Ag electrode as the cathode is shown. The electrolyte is aqueous HCl and both terminals are Pt.

The balanced *electrochemical reaction* (so termed because it includes the electrons) occurring in the cell is obtained by subtracting reaction (I) from twice reaction (II) (to balance the number of electrons):

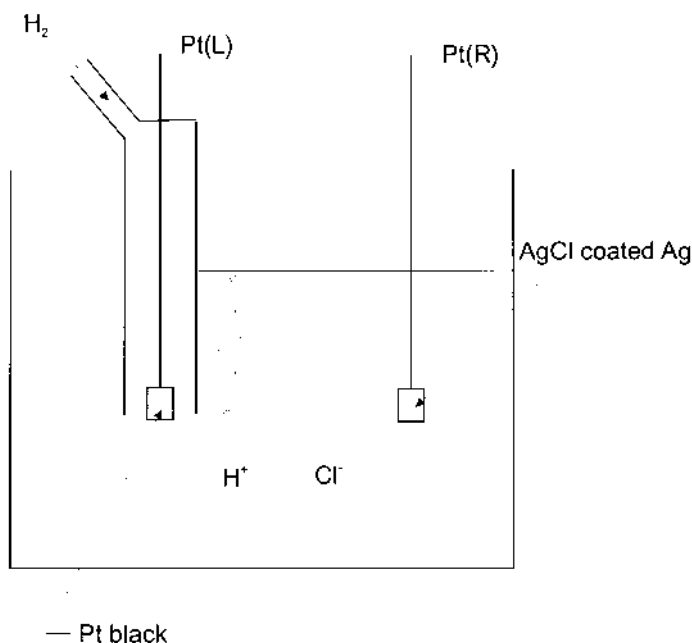
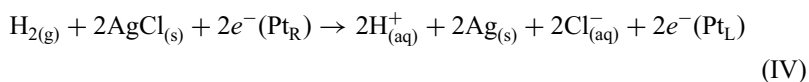
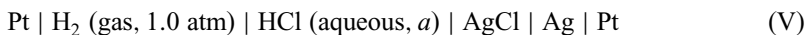


Figure 5 H₂/H⁺ - Ag/AgCl electrochemical cell.

Here, it is explicitly indicated that electrons are supplied to AgCl/Ag at the right electrode and removed from H^+/H_2 at the left electrode. In the external circuit, electrons move from the anode at the left to the cathode at the right.

Rather than using a diagram such as that in Fig. 5, to describe an electrochemical cell, a *standard simplified diagram* is used. Vertical lines separate the various phases in the cell. For the separation between two liquid phases (by a porous barrier), a dotted or dashed vertical line is used. The terminals of the cells are placed on the ends of the diagram, with the anode on the left. Any metals attached to the terminals are written next to them. Gas or insoluble materials in contact with the metals are written next, and the electrolytic solution of the cell is described in the center of the diagram. To completely define the cell, the concentrations or activities of solutions and the pressures of gases are included. The simplified diagram for the cell illustrated in Fig. 5 is therefore



where a is the activity of the HCl solution.

These diagrams may be a little misleading, because not every vertical line corresponds to a unique interface. In the above example, Pt, H_2 gas, and the HCl solution are all present at the same interface, as are Ag, AgCl, and the HCl solution. Thus, there are only two phase boundaries in the cell. By convention, we define the voltage of a galvanic cell as $\phi_{\text{R}} - \phi_{\text{L}}$. In the open-circuited condition, no current flows through the cell and $\phi_{\text{R}} - \phi_{\text{L}}$ is called the *potential*, \mathcal{E} , of the cell. With $a = 1.0$ at 298K, the cell above has an open-circuit voltage of 0.22 V. When the terminals are connected through a resistance, electrons flow from the anode to the cathode in the external circuit. In the solution, H^+ ions migrate from the anode to the cathode and Cl^- ions migrate in the opposite direction. The concentration of Ag^+ ions is negligible in the solution (because it reacts with Cl^- ions to form AgCl), so that migration of Ag^+ ions to the hydrogen electrode, followed by their direct chemical reduction can be ignored. The charge transferred by the cell for an extent of reaction ξ is 2ξ , by Eq. (5) of Chapter 7, because 2 mol of electrons are produced by the reaction as written in reaction (IV).

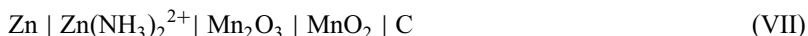
Another simple cell is the *Daniell cell*, diagramed as



This cell has two electrolytic solutions, aqueous CuSO_4 and aqueous ZnSO_4 , which are separated by a porous barrier. The barrier stops convective mixing of the two solutions. With the circuit open, there can be no net ionic flow through this barrier. However, ions of different size (e.g., Cu^{2+} and Zn^{2+}) have different rates of diffusion through the pores of the barrier. A *junction potential* must therefore develop at the barrier to counter the tendency for diffusion to produce a net current. Liquid junctions are indicated by broken vertical lines in the cell

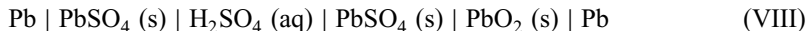
diagram. Junction potentials are of magnitude 5–20 mV. They can be reduced to just a few millivolts, by using a *salt bridge*, a tube filled with a gel containing a concentrated solution of KCl, between the two electrolyte solutions. A salt bridge is represented by a double broken line between the two electrolyte solutions, because there are two liquid junction interfaces between the solution in the salt bridge and the electrolytes of the cell. At reasonable concentrations of electrolyte solutions, the junction potential at each interface is mainly determined by the high concentration of K^+ and Cl^- ions. (Since these are the dominant ions diffusing at the interfaces.) K^+ and Cl^- ions have approximately equal diffusion rates, making the junction potentials very small. In addition, the potentials at the two interfaces are in the opposite direction, so that they almost cancel.

The design criteria for each electrochemical cell depend on the use that will be made of the cell. For example, for an inexpensive disposable dry-cell flashlight battery, a carbon electrode surrounded by a moist paste of MnO_2 and graphite in $ZnCl_2-NH_4Cl$ is used. The outer electrode is Zn foil. This cell is diagramed as



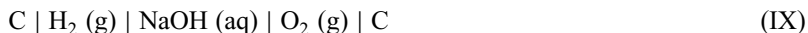
During operation of this cell, Zn and MnO_2 are consumed. The cell cannot be recharged.

For a rechargeable automobile battery, the lead–sulfuric acid cell is employed:



The cell is reversible because PbO_2 and $PbSO_4$ remain attached to the electrodes. Because this cell produces a voltage of ~ 2 V, six cells are connected in series for the standard 12-V automobile battery.

A fuel cell is an electrochemical cell in which the reagents of the cell reaction are continuously supplied and the products are continuously removed. The most commonly used fuel cell is the hydrogen–oxygen cell with a NaOH electrolyte and graphite electrodes:



The electrodes are often impregnated with a Pt catalyst to accelerate the electrode reactions and make more current available from the cell.

10.10 Thermodynamics of Electrochemical Cells

For comparison with theoretical analysis, the voltage of the cell is measured with an instrument that draws negligible current from the cell, by opposing the voltage generated by the cell with an external voltage. The voltage under these conditions is called \mathcal{E} , the potential of the cell. Under these conditions, the ionic and electronic transfers at each electrode reach equilibrium and the cell is reversible.

By raising or lowering the externally applied voltage an infinitesimal amount, the cell reactions can be made to go in either direction. An additional requirement for reversibility is that the cell has no liquid junctions. Diffusion at such junctions will proceed in the open-circuit condition and cannot be reversed by changing the externally applied voltage. Thus, the $\text{H}^+/\text{H}_2\text{--AgCl/Ag}$ cell in reaction (V) is reversible, whereas the Daniell cell in reaction (VI) is not reversible. This will generally limit our considerations to cells with a single liquid phase. Cells consisting of nonadjacent liquid phases can be treated as the sum of cells with single liquid phases.

The cell voltage is, by convention, written as a reduction potential, and because oxidation occurs at the left-hand electrode,

$$\mathcal{E} \equiv \phi_{\text{R}} - \phi_{\text{L}} \quad (41)$$

The condition for equilibrium of the cell is by Eq. (37),

$$\sum_j v_j \tilde{\mu}_j = 0 \quad (42)$$

This sum is over all species in the electrochemical reaction [e.g., reaction (IV)], including the electrons, which exist at different potentials at the two electrodes. Writing the reaction in terms of chemical and electrical potentials,

$$\sum_i v_i (\mu_i + z_i \mathcal{F} \phi_i) + \sum_{\text{elec}} n (\mu_{\text{elec}} + \mathcal{F} \phi_{\text{elec}}) = 0 \quad (43)$$

In the first summation, only the ions in the reaction are charged, and all of these exist in a single liquid phase, with a single electrical potential, in a reversible system. In the second summation, assuming that the same metal is used for the two terminals, the chemical potentials of the electrons are the same at these terminals. Equation (43) then becomes

$$\sum_i v_i \mu_i + \mathcal{F} \phi \sum_{\text{ions}} v_i z_i = n \mathcal{F} (\phi_{\text{L}} - \phi_{\text{R}}) \quad (44)$$

The first summation on the left-hand side of this equation is over all the species in the chemical reaction of the cell. The second term is zero, due to electroneutrality of chemical reactions. Using Eq. (41), Eq. (44) becomes

$$\mathcal{E} = - \frac{\sum_i v_i \mu_i}{n \mathcal{F}} = - \frac{\Delta_{\text{rxn}} G}{n \mathcal{F}} = \frac{A}{n \mathcal{F}} \quad (45)$$

where A is the affinity of the chemical reaction of the cell.

From Eq. (45), we see that the cell potential is the negative of the Gibbs free-energy change per mole of electrons transferred in the cell reaction. A spontaneous cell reaction with a large negative free-energy change (a large

affinity) gives a large positive cell potential. Defining the *standard potential of the cell*, \mathcal{E}^0 , as the open-cell voltage with all reactants in their standard states,

$$\mathcal{E}^0 = -\frac{\Delta_{rxn}G^\circ}{n\mathcal{F}} \quad (46)$$

we have

$$\mathcal{E} = \mathcal{E}^0 - \frac{RT}{n\mathcal{F}} \ln \prod_i a_i^{\nu_i} = \mathcal{E}^0 - \frac{RT}{n\mathcal{F}} \ln Q_a \quad (47)$$

where Q_a is the proper reaction quotient, introduced in [Chapter 7](#). Equation (47) is the *Nernst equation*, which gives the activity dependence (and thus the concentration dependence) of the voltage of an electrochemical cell. Although, strictly speaking, the above development does not hold for cells with liquid junctions, if appropriate liquid junction potentials are included, the Nernst equation holds to a high degree of accuracy for such cells in the open-circuit condition. It is inappropriate, however, to use the equation for cells through which current is passing and in which many nonequilibrium factors contribute to the potential.

Equations (45)–(47) show how the Gibbs free-energy change of many reactions involving ionic species can be measured by studying them in electrochemical cells. The enthalpy change of these reactions can be obtained from the temperature dependence of the potential. Combining the Gibbs–Helmholtz equation with Eq. (46),

$$\Delta_{rxn}H^\circ = \left(\frac{\partial(T^{-1}\Delta_{rxn}G^\circ)}{\partial(T^{-1})} \right)_P = -n\mathcal{F} \left(\frac{\partial(T^{-1}\mathcal{E}^0)}{\partial(T^{-1})} \right)_P \quad (48)$$

Knowing $\Delta_{rxn}G^\circ$ and $\Delta_{rxn}H^\circ$, the entropy of the cell reaction can be calculated from

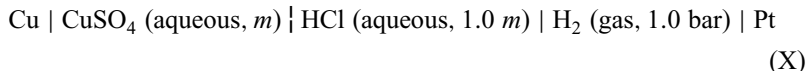
$$\Delta_{rxn}S^\circ = \frac{\Delta_{rxn}H^\circ - \Delta_{rxn}G^\circ}{T} \quad (49)$$

Alternatively, $\Delta_{rxn}S^\circ$ can be obtained from

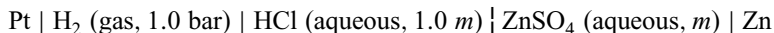
$$\Delta_{rxn}S^\circ = -\left(\frac{\partial\Delta_{rxn}G}{\partial T} \right)_P = n\mathcal{F} \left(\frac{\partial\mathcal{E}^0}{\partial T} \right)_P \quad (50)$$

10.11 Standard Electrode Potentials

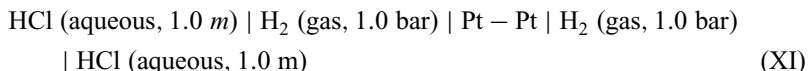
Although potentials of half-cell electrode reactions cannot be measured, their consideration is extremely useful. For example, consider the two cells in series, as indicated in reaction (X),



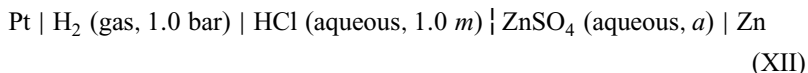
connected to



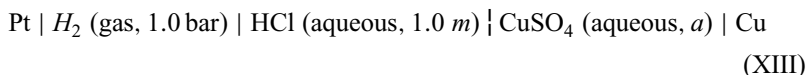
The first cell consists of a Cu/Cu^{2+} electrode combined with a H^+/H_2 electrode. It is connected in series with a second cell consisting of a H_2/H^+ electrode combined with a Zn^{2+}/Zn electrode. The combination



consists of hydrogen electrodes connected together with opposite polarities. The voltages of these electrodes cancel, and this part of the cell diagram in reaction (X) can be omitted. The voltage of reaction (X) must, therefore, just be that of the Daniell cell given in reaction (VI). Generalizing this reasoning leads to a particularly concise way of tabulating electrochemical data. For example, calling \mathcal{E}_R the potential of the cell XII



and \mathcal{E}_L the potential of cell XIII



we have for the potential of cell X (or of cell VI),

$$\mathcal{E} = \mathcal{E}_R - \mathcal{E}_L \quad (51)$$

In particular, at unit activity of the CuSO_4 and ZnSO_4 solutions,

$$\mathcal{E}^0 = \mathcal{E}_R^0 - \mathcal{E}_L^0 \quad (52)$$

We call \mathcal{E}_R and \mathcal{E}_L *electrode potentials* and \mathcal{E}_R^0 and \mathcal{E}_L^0 *standard electrode potentials* or *standard reduction potentials*. Notwithstanding these names, these quantities really are not the potentials of single electrodes, but rather the measured potentials of cells XII and XIII. These measured potentials contain

three contributions: the potential of the electrode reaction of interest, written as a reduction; the potential of the standard hydrogen electrode; and a metal–metal potential resulting from dissimilar metals at the two electrodes. By arbitrarily setting the potential of the H^+/H_2 electrode to zero,¹¹ the measured potentials of cells XI and XII become just those of the reduction reactions, $Zn^{2+} + 2e \rightarrow Zn$ and $Cu^{2+} + 2e \rightarrow Cu$, each combined with the metal–metal potential of its terminals, respectively. For example, the potential of cell XII becomes

$$\mathcal{E}^0 = \mathcal{E}_{Zn^{2+}/Zn}^0 + \mathcal{E}_{Pt/Zn}^0 \quad (53)$$

For cell X, we have

$$\begin{aligned} \mathcal{E}^0 &= \mathcal{E}_R^0 - \mathcal{E}_L^0 \\ &= \mathcal{E}_{Zn^{2+}/Zn}^0 + \mathcal{E}_{Pt/Zn}^0 - \left(\mathcal{E}_{Cu^{2+}/Cu}^0 + \mathcal{E}_{Pt/Cu}^0 \right) \\ &= \mathcal{E}_{Cu/Cu^{2+}}^0 + \mathcal{E}_{Zn^{2+}/Zn}^0 + \left(\mathcal{E}_{Cu/Pt}^0 + \mathcal{E}_{Pt/Zn}^0 \right) \\ &= \mathcal{E}_{Cu/Cu^{2+}}^0 + \mathcal{E}_{Zn^{2+}/Zn}^0 + \mathcal{E}_{Cu/Zn}^0 \end{aligned} \quad (54)$$

which, except for the junction potential, is that of the Daniell cell (VI).

Because any two oxidation–reduction reactions can be combined to make a cell, the tabulation of standard electrode potentials becomes a very efficient way of calculating cell potentials under standard conditions. As indicated by Eq. (54), if the electrode reactions involve the metals of the cell terminals, the metal–metal potential due to the cell terminals is automatically included in the result. A short table of standard electrode potentials is given in [Table 2](#).

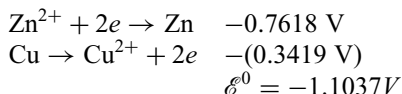
After calculating \mathcal{E}^0 , the Nernst equation can be used to adjust the potential to nonstandard conditions.

Example 7. Calculate the open-circuit voltage of the Daniell cell (VI) at 298 K for the following: (Neglect the liquid-junction potential.)

- Under standard conditions
- With $a(ZnSO_4) = 1.0$ and $a(CuSO_4) = 0.05$

Solution:

- The electrode reactions and their potentials are as follows



Equation (46) shows that under standard conditions, this cell, with a positive $\Delta_{rxn}G$, is not spontaneous. Copper does not spontaneously replace zinc ions in solution. With the zinc electrode as anode (i.e., with zinc replacing copper ions in solution), the cell

TABLE 2 Electrode (Reduction) Potentials at 298 K

Half-Reaction	Volts
$K^+ + e \rightarrow K$	-2.931
$Na^+ + e \rightarrow Na$	-2.71
$Mg^{2+} + 2e \rightarrow Mg$	-2.372
$2H_2O + 2e \rightarrow H_{2(g)} + 2OH^-$	-0.828
$Zn^{2+} + 2e \rightarrow Zn$	-0.7618
$Fe^{2+} + 2e \rightarrow Fe$	-0.447
$PbSO_4 + 2e \rightarrow Pb + SO_4^{2-}$	-0.359
$2H^+ + 2e \rightarrow H_{2(g)}$	0
$AgCl + e \rightarrow Ag + Cl^-$	+0.2223
$Hg_2Cl_2 + 2e \rightarrow 2Hg + 2Cl^-$	+0.2691
$Cu^{2+} + 2e \rightarrow Cu$	+0.3419
$O_2 + 2H_2O + 4e \rightarrow 4OH^-$	+0.401
$Cu^+ + e \rightarrow Cu$	+0.518
$Fe^{3+} + e \rightarrow Fe^{2+}$	+0.771
$Ag^+ + e \rightarrow Ag$	+0.7996
$Cl_{2(g)} + 2e \rightarrow 2Cl^-$	+1.3583
$PbO_2 + SO_4^{2-} + 4H^+ + 2e \rightarrow PbSO_4 + 2H_2O$	+1.6913

has $\mathcal{E}^0 = +1.1037$ V, and is spontaneous. If a load is placed across the terminals of the cell, electrons will flow from the Zn electrode to the Cu electrode in the external circuit.

- (b) The overall cell chemical reaction is $Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn$. Because the activities of the metals are unity,

$$\begin{aligned}\mathcal{E} &= \mathcal{E}^0 - \frac{RT}{2\mathcal{F}} \ln\left(\frac{a_{Cu^{2+}}}{a_{Zn^{2+}}}\right) \\ &= -1.1037 \text{ V} - \frac{8.314 \text{ J} \mid 298 \text{ K} \mid \text{mol}}{\text{mol K} \mid 2 \mid 96,485 \text{ C}} \ln(0.05) = -1.0652 \text{ V}\end{aligned}$$

Example 7a is the idea behind the *electrochemical series*, a list of elements whose ions will displace the ions of another element from solution, as shown in Table 3. At comparable concentrations, ions of elements with larger negative reduction potentials (more easily oxidized) will displace those of elements with smaller negative reduction potentials from solution. In the short electrochemical series shown in Table 3, an element will displace the ions of any element lower in the list from aqueous solution. In some cases, however, the displacement reactions may be slow due to kinetic factors.

The addition of voltages in part (a) of Example 7 is really a form of addition of Gibbs free energy (Hess' law). Because in the overall cell chemical reaction, the electrons cancel, both electrode reactions must involve the same

TABLE 3 Electrochemical Series

Potassium	Lead
Sodium	Hydrogen
Magnesium	Copper
Zinc	Mercury
Iron	Silver

number of electrons, and electrode potentials can be added directly. This is shown in Example 8, where the Gibbs free energies of the electrode reactions are calculated.

Example 8. Calculate \mathcal{E}^0 and ΔG° of the cell $\text{Cu} \mid \text{CuCl}_2 (\text{aq}) \mid \text{AgCl} (\text{s}) \mid \text{Ag}$.

Solution: The electrode reactions, standard electrode potentials, and Gibbs free energies are as follows:

Reaction	$\mathcal{E}^0 (\text{V})$	$\Delta G^\circ = -n\mathcal{F}\mathcal{E}^0$
$\text{Cu} \rightarrow \text{Cu}^{2+} + 2e$	-0.3419	$2(0.3419)\mathcal{F}$
$2(\text{AgCl} + e \rightarrow \text{Ag} + \text{Cl}^-)$	0.2223	$-2(0.2223)\mathcal{F}$
$2\text{AgCl} + \text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{Ag} + 2\text{Cl}^-$		$2(0.1196)\mathcal{F}$

Because two electrons are transferred in the reaction, $\mathcal{E}^0 = -\Delta G^0/n\mathcal{F} = -0.1196 \text{ V}$, as could be calculated directly, without calculating free energies.

In calculating the potential of a half-cell from those of other half-cells, electrons do not necessarily cancel and the calculation must be performed using free energies, as illustrated in Example 9.

Example 9. Calculate \mathcal{E}^0 of the Fe^{3+}/Fe electrode.

Solution:

Reaction	$\mathcal{E}^0 (\text{V})$	$\Delta G^\circ = -n\mathcal{F}\mathcal{E}^0$
$\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$	0.771	$-(0.771)\mathcal{F}$
$\text{Fe}^{2+} + 2e \rightarrow \text{Fe}$	-0.447	$2(0.447)\mathcal{F}$
$\text{Fe}^{3+} + 3e \rightarrow \text{Fe}$		$0.123\mathcal{F}$

Therefore, $\mathcal{E}^0 = -\Delta G^\circ/3\mathcal{F} = -0.041\text{V}$.

Example 10. Calculate \mathcal{E}^0 of the cell $\text{Pt} \mid \text{H}_2 \text{ (gas)} \mid \text{HCl (aqueous)} \mid \text{Cl}_2 \text{ (gas)} \mid \text{Pt}$. Use your calculated value to obtain ΔG_f° of aqueous Cl^- ions.

Solution:

Reaction	$\mathcal{E}^0 \text{ (V)}$	$\Delta G^\circ = -n\mathcal{F}\mathcal{E}^0 \text{ (kJ/mol)}$
$\text{H}_2 \text{ (gas)} \rightarrow 2\text{H}^+ + 2e$	0	0
$\text{Cl}_2 \text{ (gas)} + 2e \rightarrow 2\text{Cl}^-$	1.3583	-262.11
$\text{H}_2 \text{ (gas)} + \text{Cl}_2 \text{ (gas)} \rightarrow 2\text{H}^+ + 2\text{Cl}^-$		-262.11

Because ΔG_f° of $\text{H}_2 \text{ (gas)}$, $\text{Cl}_2 \text{ (gas)}$, and H^+ are all zero,¹¹
 $\Delta G^\circ = 2\Delta G_f^\circ(\text{Cl}^-)$, $\Delta G_f^\circ(\text{Cl}^-) = -131 \text{ kJ/mol}$.

Example 10 illustrates how thermochemical data for aqueous ions may be obtained from measurements in electrochemical cells. The problem of measuring cell potentials in the standard state, which is a hypothetical state, will be discussed in section 10.12. The temperature variation of the voltage of such cells would provide ΔH_f° of aqueous ions, through the use of Eq. (48).

10.12 Applications of Electrochemical Cells

10.12.1 Measurements of Thermodynamic Quantities

Equations (47)–(50) indicate how thermodynamic quantities can be obtained from cell potentials measured under standard conditions. However, standard states are *hypothetical* states (e.g., infinitely dilute behavior at 1.0 *m* concentration), which cannot be prepared in the cell. As a result, an extrapolation procedure is used to find \mathcal{E}^0 from measured cell voltages as a function of concentration. From Eq. (47), we write the dependence of \mathcal{E} on the concentration of the electrolyte in the form

$$\mathcal{E}(m_i) + \frac{RT}{n\mathcal{F}} \ln\left(\prod_i m_i^{v_i}\right) = \mathcal{E}^0 - \frac{RT}{n\mathcal{F}} \ln\left(\prod_i \gamma_i^{v_i}\right) \quad (55)$$

The left-hand side of this equation can be calculated from measurements of cell voltage as a function of concentration. The second term on the right-hand side becomes zero at infinite dilution. However, because no meaningful measurements can be made at zero concentration of reactants, we must extrapolate the equation to infinite dilution using the known concentration behavior of activity coefficients. In approaching infinite dilution, it is sufficient to use the Debye–Huckel

limiting law. Substituting the infinitely dilute limit of Eq. (19) into the last term of Eq. (55), we find the concentration dependence of the right side of Eq. (55) to be

$$\begin{aligned}\mathcal{E}^0 - \frac{RT}{n\mathcal{F}} \sum_i \nu_i \ln \gamma_i &= \mathcal{E}^0 + \frac{RT}{n\mathcal{F}} \sum_i \nu_i z^2 A I^{1/2} \\ &= \mathcal{E}^0 + I^{1/2} \left(\frac{RT}{n\mathcal{F}} \sum_i \nu_i z^2 A \right)\end{aligned}\quad (56)$$

The only concentration dependent term is $I^{1/2}$. Thus, plotting the left-hand side of Eq. (56) versus $I^{1/2}$ (versus $m_i^{1/2}$, if the electrolyte i is the only contributor to the ionic strength) gives, in the limit of low concentrations, a straight line with intercept \mathcal{E}^0 . From Eq. (46), ΔG° of the cell reaction is obtained. By repeating the procedure at different temperatures, ΔH° and ΔS° can be determined from Eqs. (48)–(50).

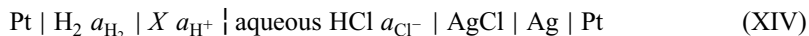
10.12.2 Measurements of Activity Coefficients

Once \mathcal{E}^0 is determined by the extrapolation procedure of Sec. 10.11 or from a table of electrode potentials (which implies that someone else has done the extrapolation), measurement of \mathcal{E} as a function of concentration allows determination of Q_a as a function of concentration of the cell electrolyte from Eq. (47). Often, the electrolyte consists of a single solute, whose activity can then be determined from Q_a . For example, for the cell in Fig. 5, assuming the activities of the H_2 gas and condensed phases are unity,

$$Q_a = a_{H^+}^2 a_{Cl^-}^2 = a_{HCl}^2 = a_{\pm}^4$$

10.12.3 Determination of pH

The pH may be measured by means of a hydrogen gas electrode in the solution of interest (X), connected by a salt bridge to a reversible electrode, such as the AgCl/Ag electrode or the calomel electrode:



The potential of this cell is

$$\mathcal{E}_X = \mathcal{E}^0 + \mathcal{E}_{JX} - \frac{RT}{\mathcal{F}} (\ln a_{H^+}(X) + \ln a_{Cl^-} - \frac{1}{2} \ln a_{H_2}) \quad (57)$$

where \mathcal{E}^0 is the standard potential of the AgCl/Ag electrode and \mathcal{E}_{JX} is the junction potentials in this cell. In order to account for the junction potential and variations in the activity of H_2 and Cl^- , measurements are made by comparison

with the potential generated by the same electrodes and salt bridge using a standard solution, for which the measured potential is

$$\mathcal{E}_S = \mathcal{E}^0 + \mathcal{E}_{JS} - \frac{RT}{\mathcal{F}} (\ln a_{H^+}(S) + \ln a_{Cl^-} - \frac{1}{2} \ln a_{H_2}) \quad (58)$$

The junction potential, being dominated by the concentrated solution in the salt bridge, can be taken as the same in these two measurements, giving

$$\mathcal{E}_X - \mathcal{E}_S = -\frac{RT}{\mathcal{F}} (\ln a_{H^+}(X) - \ln a_{H^+}(S)) = \frac{2.303RT}{\mathcal{F}} (\text{pH}_X - \text{pH}_S) \quad (59)$$

or

$$\text{pH}_X = \text{pH}_S + \frac{\mathcal{F}}{2.303RT} (\mathcal{E}_X - \mathcal{E}_S) \quad (60)$$

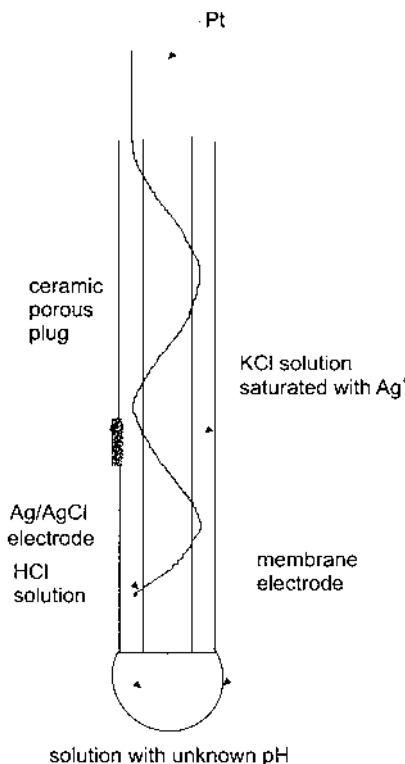


Figure 6 Membrane-type pH electrode.

The standard solution (which can be purchased from a chemical supply company) is chosen to have a pH close to that of the unknown solution. pH_S is calculated (by the company), using extended Debye–Huckel theory, to good accuracy.

Usually, rather than using a hydrogen gas electrode, a glass membrane electrode is used for the measurement. As discussed in Sec. 8, the potential across such a membrane can be proportional to the difference in pH's of the solutions on each side of the membrane. One design for a membrane-type pH electrode, which incorporates a Ag/AgCl reference electrode in a tube concentric to the membrane electrode, is shown in Fig. 6. The electrode is immersed in the solution whose pH is to be measured, with the solution level above the porous plug.

Questions

1. Show in two dimensions a typical arrangement of four positive ions and four negative ions in solution. How does your arrangement differ from that in a crystal?
2. Give a physical reason for the Debye length:
 - (a) increasing with the relative dielectric constant of the solvent
 - (b) increasing with the temperature of the solution
 - (c) decreasing with the ionic strength of the solution
3. Show that for the Debye–Huckel theory [Eq. (21)] γ_{\pm} is always less than 1.0 and that in concentrated solutions, γ_{\pm} is independent of ionic strength.
4. Which of the following properties of $\text{Ca}(\text{NO}_3)_2$ do not change when a 0.03 *m* solution of $\text{Ca}(\text{NO}_3)_2$ is made 1.0 *m* in NaCl: m_i , m_{\pm} , and γ_{\pm} .
5. Show that for the Davies equation [Equation (25)], γ_{\pm} may be greater than 1. Sketch the dependence of γ_{\pm} on ionic strength for the Davies equation.
6. Show that when $v_+ = v_- = 1$, $m_{\pm} = m_i$, and when $v_+ = v_- = p$, $m_{\pm} = pm_i$.
7. In terms of the molality of the solution, what is the activity of a NaCl solution for the following conditions:
 - (a) In the limit of infinite dilution
 - (b) At finite concentration
8. Which of the following increase γ_{\pm} above the DHLL value:
 - (a) Inclusion of the $\sqrt{I_c}$ term in the denominator [Eq. (24)]
 - (b) Inclusion of a linear term [Eq. (25)]
 - (c) Ion pairing
 - (d) Hydration of ions
9. Which of the following represents an ion pair in aqueous solution?
 - (a) HF
 - (b) $[\text{Fe}(\text{CN})]^{2+}$
 - (c) $[\text{CaCl}]^+$

10. Do you expect the formation of ion pairs to increase or decrease γ_i ? Why?
11. For which of the following systems do you expect ion pairing to be the most important? Why?
 - (a) 0.1 *m* (CH₃)₃NHCl in benzene
 - (b) 0.1 *m* CaCl₂ in water
 - (c) 0.3 *m* NaCl in water
12. What will happen if a piece of Zn metal is dropped into an essentially infinite volume of distilled water? Will all of the Zn dissolve? If not, why? Explain from a macro and a micro perspective.
13. For the Daniell cell, given by reaction (VI), what are the electrode reactions? Sketch the cell. How is current transported within the cell? Assuming that the smaller Zn²⁺ ions tend to diffuse faster, what is the direction of the junction potential?
14. What are the chemical reactions occurring in a lead–sulfuric acid car battery?
 - (a) During starting the car
 - (b) During charging the battery, while the car is driving

Which is the positive terminal of the battery?

15. The cells of automobile batteries used to include a capped opening for adding water that evaporated. The amount of charge stored on such cells could be determined with a *hydrometer*, a simple device that measured the density of the electrolyte in the cell. Explain why the density of the electrolyte is related to the charge state of the cell.
16. What is wrong with the following argument? If the terminals of an electrochemical cell are constructed from the same metal, the chemical potential of electrons [species *i* in Eq. (36)] at the terminals, which depends only on *T*, *P* and concentrations, are the same. From Eq. (36), the electromotive force of the cell is therefore zero!
17. Write down the standard simplified diagram for the electrochemical cell obtained when the pH electrode shown in Fig. 6 is placed in a solution with hydrogen ion activity, $a_{\text{H}^+}(X)$.

Problems

1. What is m_{\pm} for each of the following solutions:
 - (a) 0.03 *m* NaCl
 - (b) 0.02 *m* CaCl₂
 - (c) 0.01 *m* MgSO₄
 - (d) 0.03 *m* Ca₃(PO₄)₂
2. Write γ_{\pm} in terms of γ_+ and γ_- for each of the solutions in Problem 1.
3. Show that the definition in Eq. (13) gives $\phi \rightarrow 1$ in the limit of the infinitely dilute solution of a strong electrolyte. See Problem 2 of Chapter 9.

4. Derive Eq. (21) from Eq. (19) for an electrolyte that produces v_+ positive ions of charge z_+ and v_- negative ions of charge z_- .
5. Show that for a volatile electrolyte, such as HCl, the partial pressure above an aqueous solution, in the limit of infinite dilution, is proportional to m^2 , and not to m , as given by Henry's law.
6. Use both the Debye–Huckel limiting law [Eq. (23)] and Eq. (24) to calculate the mean ionic activity coefficient of CaCl_2 in a solution prepared by adding 0.01 mol of CaCl_2 to the following:
 - (a) 1.0 L of water
 - (b) 1.0 L of 0.5 m NaNO_3 solution
 - (c) Repeat part (b) using the Davies formula [Eq. (25)].
7. Calculate the activity of a 0.03 m ZnCl_2 solution using the following:
 - (a) The Debye–Huckel limiting law [Eq. (23)]
 - (b) The Debye–Huckel theory [Eq. (24)]
 - (c) The Davies equation [Eq. (25)]
8. Using the result of Example 10, calculate the partial pressure of HCl in equilibrium with a 1.0 m aqueous HCl solution at 25°C.
9. Use the DHLL to calculate m_{H^+} and the pH for an aqueous solution at 25°C that is
 - (a) 0.001 m in acetic acid
 - (b) 0.001 m in acetic acid and 0.3 m in NaCl

Why is there more of a difference in the pH for these two cases than was found for Examples 4 and 5?

10. Use the DHLL to calculate m_{H^+} and the pH for a 0.1 m aqueous solution of chloroacetic acid at 25°C. $K_a = 1.40 \times 10^{-3}$ for chloroacetic acid. Compare your results with those calculated assuming an ideally dilute solution.
11. K_a for the reaction $\text{CO}_2 (\text{gas}) + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^-$ is 4.45×10^{-7} . What is m_{H^+} and the pH of water that is in equilibrium with 320 ppm of CO_2 in the atmosphere at 1.0 bar total pressure? You can neglect the dissociation of HCO_3^- into CO_3^{2-} .
12. Find the fraction of ion pairs in 0.15 m aqueous CaSO_4 at 25°C.
13. Show that for the case that all reactants and products are in the same phase, Eq. (37), for the equilibrium condition for a reaction involving charged species, reduces to Eq. (30) of [Chapter 7](#).
14. For calculating the electrostatic potential of a charged metallic sphere, the charge on the sphere can be considered to reside at its center. What is the charge (in both Coulombs and moles of electrons) on a 1.0-cm-radius sphere so that the electrostatic potential at the surface of the sphere is 1.0 V?
15. Show that the potential difference across a membrane [Eq. (40)] between two solutions of different hydrogen ion activities is a linear function of the pH difference between the two solutions.

16. Write down the half-reactions for cell VII.
17. What is the voltage of the cell in reaction (V) when $P_{\text{H}_2} = 680$ torr and the molality of HCl is 0.05? See Example 2c for γ_{\pm} of HCl.
18. Use Table 2 to calculate ΔG° for the reaction $2\text{Fe}^{3+} + 2\text{Cl}^- \rightarrow 2\text{Fe}^{2+} + \text{Cl}_2$.
19. The voltage for the cell in reaction (VIII) at 1.0 *m* H_2SO_4 has been measured to be \mathcal{E} (volts) = $1.91737 + 5.61 \times 10^{-5}T + 1.08 \times 10^{-6}T^2$, with T (in $^\circ\text{C}$) from 0–60 $^\circ\text{C}$. (HS Harned, WJ Hammer. J Am Chem Soc 57:33, 1935.
 - (a) Write down the cell reaction.
 - (b) Calculate ΔG , ΔH , and ΔS for the cell reaction at 25 $^\circ\text{C}$.
 - (c) Calculate γ_{\pm} for 1.0 *m* H_2SO_4 at 25 $^\circ\text{C}$.
20. In a *hydrogen economy*, hydrogen for transportation fuels is produced by the electrolysis of water.
 - (a) Write down the electrode reactions for producing H_2 and O_2 in an alkaline water hydrolysis cell.
 - (b) Show the polarity of the external current source and indicate which electrode is the cathode.
 - (c) What is the minimum voltage required for the external current source in order to electrolyze water?
21. For the cell $\text{Pt} | \text{H}_2 (\text{gas}, 1.0 \text{ atm}) | \text{HCl} (\text{aqueous}, m) | \text{Hg}_2\text{Cl}_2 (\text{solid}) | \text{Hg} (1) | \text{Pt}$:
 - (a) Write the half-cell reactions and the overall chemical reaction.
 - (b) Express the open-circuit potential in terms of \mathcal{E}^0 and the activities of the components of the cell.
22. From the data in Table 2, find \mathcal{E}^0 for a $\text{Cu}^{2+}/\text{Cu}^+$ electrode.

Notes

1. From CP Jargodski, F Potter. Mad about Physics. New York: Wiley, 2001.
2. Because v_{\pm} is independent of concentration, $dm_{\pm} = d(v_{\pm}m_i) = v_{\pm} dm_i$.
3. Nobel laureate in 1936.
4. Conceptually, a is the sum of the radii of the positive and negative ions (because such ions are more likely to be at closest approach); practically, a is usually taken as a parameter, which is optimized by fitting to experimental data.
5. The dielectric constant of water, 78.4, is very large. Deviations from ideally dilute behavior are much greater in less polar solvents than they are in water.
6. The symbol p is used as a shorthand notation for $-\log_{10}$.
7. This is not the official definition, which is a practical definition based on the measured potentials of some exactly defined electrochemical cells in which the hydrogen ion activity is calculated by an extended Debye–Huckel theory.
8. The results of the theory are not overly sensitive to small changes in this criterion.

9. In addition to the charge on a phase, polarization, which is the orientation and distribution of molecules and ions in and adjacent to the phase, can influence the escaping tendency of charged particles from the phase.
10. Under some conditions, low concentrations of solvated electrons can exist in solution.
11. This is equivalent to setting the Gibbs free energy of formation of 1.0 *m* ideally dilute aqueous H^+ equal to zero and the chemical potential of Pt metal equal to zero.