Review chap. 10/11 ⑬ Quiz 2

⑭ - 1

$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow H^+(g) + Cl^+(g)$

is endothermic

$H^+(g) + Cl^-(g) \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$

hydration makes the overall reaction exothermic.

$\Delta H_R^\circ = \Delta_f H^\circ(H^+, aq) + \Delta_f H^\circ(Cl^-, aq)$

$\Delta_f H^\circ(H_2) = \Delta_f H^\circ(Cl_2) = 0$

<u>Conventions</u> $\Delta_f G^\circ(H^+, aq) = 0$ for all T

$S_f^\circ(H^+, aq) = -\frac{\partial \Delta_f G_f^\circ(H^+, aq)}{\partial T} = 0$

$\Delta_f H^\circ(H^+, aq) = \Delta_f G^\circ(H^+, aq) + T S_m^\circ(H^+, aq) = 0$

$\Delta S_R^\circ = S_m^\circ(Cl, aq) - \frac{1}{2} S_m^\circ(H_2, g) - \frac{1}{2} S_m^\circ(Cl_2, g)$

$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$

$\Delta H_R^\circ = \Delta_f H^\circ(Cl^-, aq) + \Delta_f H^\circ(Na^+, aq) - \Delta_f H^\circ(NaCl, s)$

conventional quantities tabulated:

relative to ~~H^+~~ $H^+(aq)$

$Mg^{2+}, Zn^{2+}, PO_4^{3-}$: $\frac{\text{charge}}{\text{size}}$ larger than for H^+

→ solvation shell more tightly bound than for H^+ = more ordered

→ negative value of conventional ΔS°

Na^+, Cs^+, NO_3^-: $\frac{\text{charge}}{\text{size}}$ smaller than H^+

→ solvation shell less tightly bound than for H^+ = less ordered

positive value of conv. ΔS°

Review chap. 10/11 ⑬ Quiz 2

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$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$

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conventional quantities tabulated:

relative to ~~H^+~~ $H^+(aq)$

Mg^{2+}, Zn^{2+}, PO_4^{3-}: $\frac{\text{charge}}{\text{size}}$ larger than for H^+

$\rightarrow$ solvation shell more tightly bound than for H^+ $\equiv$ more ordered

$\rightarrow$ negative value of conventional ΔS°

Na^+, Cs^+, NO_3^-: $\frac{\text{charge}}{\text{size}}$ smaller than H^+

$\rightarrow$ solvation shell less tightly bound than for H^+ = less ordered

Understanding the Thermodynamics of Ion Formation and Solvation

As discussed in the preceding section, ΔH_f°, ΔG_f°, and S_m° can be determined for a formula unit but not for an individual ion in a calorimetric experiment. However, as seen next, values for thermodynamic functions associated with individual ions can be calculated with a reasonable level of confidence using a thermodynamic model. This result allows the conventional values of ΔH_f°, ΔG_f°, and S_m° to be converted to absolute values for individual ions. In the following discussion, the focus is on ΔG_f°.

We first discuss the individual contributions to ΔG_f°, and do so by analyzing the following sequence of steps that describe the formation of $H^+(aq)$ and $Cl^-(aq)$:

$$\begin{aligned}
&1/2\, H_2(g) \rightarrow H(g) && \Delta G^\circ = 203.3 \text{ kJ mol}^{-1} \\
&1/2\, Cl_2(g) \rightarrow Cl(g) && \Delta G^\circ = 105.7 \text{ kJ mol}^{-1} \\
&H(g) \rightarrow H^+(g) + e^- && \Delta G^\circ = 1312 \text{ kJ mol}^{-1} \\
&Cl(g) + e^- \rightarrow Cl^-(g) && \Delta G^\circ = -349 \text{ kJ mol}^{-1} \\
&Cl^-(g) \rightarrow Cl^-(aq) && \Delta G^\circ = \Delta G^\circ_{solvation}(Cl^-, aq) \\
&H^+(g) \rightarrow H^+(aq) && \Delta G^\circ = \Delta G^\circ_{solvation}(H^+, aq) \\
\hline
&1/2\, H_2(g) + 1/2\, Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq) && \Delta G_R^\circ = -131.2 \text{ kJ mol}^{-1}
\end{aligned}$$

This pathway is shown pictorially in Figure 10.1. Because G is a state function, both the black and red paths must have the same ΔG value. The first two reactions in this sequence are the dissociation of the molecules in the gas phase, and the second two reactions are the formation of gas phase ions from the neutral gas phase atoms. ΔG° can be determined experimentally for these four reactions. Substituting the known values for ΔG° for these four reactions in ΔG° for the overall process,

$$\Delta G_R^\circ = \Delta G^\circ_{solvation}(Cl^-, aq) + \Delta G^\circ_{solvation}(H^+, aq) + 1272 \text{ kJ mol}^{-1} \qquad \textbf{(10.7)}$$

Equation 10.7 allows us to relate the $\Delta G^\circ_{solvation}$ of the H^+ and Cl^- ions with ΔG_R° for the overall reaction.

As Equation (10.7) shows, $\Delta G^\circ_{solvation}$ plays a critical role in the determination of the Gibbs energies of ion formation. Although $\Delta G^\circ_{solvation}$ of an individual cation or anion cannot be determined experimentally, it can be estimated using a model developed by Max Born. In this model, the solvent is treated as a uniform fluid with the appropriate dielectric constant, and the ion is treated as a charged sphere. How can $\Delta G^\circ_{solvation}$ be calculated with these assumptions? At constant T and P, the nonexpansion work for a reversible process equals ΔG for the process. Therefore, if the reversible work associated with solvation can be calculated, ΔG for the process is known. Imagine a process in which a neutral atom A gains the charge Q, first in a vacuum and secondly in a uniform dielectric medium. The value of $\Delta G^\circ_{solvation}$ of an ion with a charge q is the reversible work for the process $(A(g) \rightarrow A^Q(aq))_{solvation}$ minus that for the reversible process $(A(g) \rightarrow A^Q(g))_{vacuum}$.

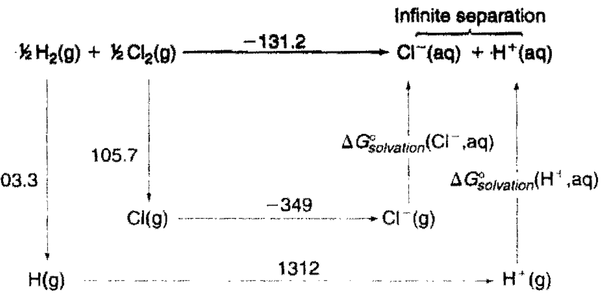

FIGURE 10.1
ΔG° is shown pictorially for two different paths starting with $1/2\, H_2(g)$ and $1/2\, Cl_2(g)$ and ending with $H^+(aq) + Cl^-(aq)$. The units for the numbers are kJ mol^{-1}. Because ΔG is the same for both paths, $\Delta G^\circ_{solvation}(H^+, aq)$ can be expressed in terms of gas-phase dissociation and ionization energies.

The electrical p
$\phi = Q'/4\pi\varepsilon r$. Fro
amount dQ is $\phi\, dQ$
charge Q is

where ε_0 is the p
$Q^2/8\pi\varepsilon_0\varepsilon_r r$, wh
Consequently, Δ

Because $\varepsilon_r >$
Values for ε_r
Data Tables).
To test the
of different ra
comparison
determined v
that ΔG°_{solvat}
lated. Becau

The value
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We use the tabulated value of $\Delta H_f^\circ(\mathrm{NaCl}, s) = -411.2$ kJ mol^{-1} and the value for $\Delta H_f^\circ(\mathrm{Cl}^-, aq)$ just determined to obtain a value for $\Delta H_f^\circ(\mathrm{Na}^+, aq) = -240.1$ kJ mol^{-1}. Proceeding to other reactions that involve either $\mathrm{Na}^+(aq)$ or $\mathrm{Cl}^-(aq)$, the enthalpies of formation of the counter ions can be determined. This procedure can be extended to include other ions. Values for ΔG_f° and S_m° can be determined in a similar fashion. Values for ΔH_f°, ΔG_f°, and S_m° for aqueous ionic species are tabulated in Table 10.1. These thermodynamic quantities are called **conventional formation enthalpies, conventional Gibbs energies of formation,** and **conventional formation entropies** because of the convention described earlier.

Note that ΔH_f°, ΔG_f°, and S_m° for ions are defined relative to $\mathrm{H}^+(aq)$. Negative values for ΔH_f° indicate that the formation of the solvated ion is more exothermic than the formation of $\mathrm{H}^+(aq)$. A similar statement can be made for ΔG_f°. Generally speaking, ΔH_f° for multiply charged ions is more negative than that of singly charged ions, and ΔH_f° for a given charge is more negative for smaller ions because of the stronger electrostatic attraction between the multiply charged or smaller ion and the water in the solvation shell.

Recall from Section 5.8 that the entropy of an atom or molecule was shown to be always positive. This is not the case for solvated ions because the entropy is measured relative to $\mathrm{H}^+(aq)$. The entropy decreases as the hydration shell is formed because liquid water molecules are converted to relatively immobile molecules. Ions with a negative value for the conventional standard entropy such as $\mathrm{Mg}^{2+}(aq)$, $\mathrm{Zn}^{2+}(aq)$, and $\mathrm{PO}_4^{3-}(aq)$ have a larger charge-to-size ratio than $\mathrm{H}^+(aq)$. For this reason, the solvation shell is more tightly bound. Conversely, ions with a positive value for the standard entropy such as $\mathrm{Na}^+(aq)$, $\mathrm{Cs}^+(aq)$, and $\mathrm{NO}_3^-(aq)$ have a smaller charge-to-size ratio than $\mathrm{H}^+(aq)$ and a less tightly bound solvation shell.

TABLE 10.1 Conventional Formation Enthalpies, Gibbs Energies, and Entropies of Selected Aqueous Anions and Cations

Ion	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S_m° (J K^{-1} mol^{-1})
$\mathrm{Ag}^+(aq)$	105.6	77.1	72.7
$\mathrm{Br}^-(aq)$	−121.6	−104.0	82.4
$\mathrm{Ca}^{2+}(aq)$	−542.8	−553.6	−53.1
$\mathrm{Cl}^-(aq)$	−167.2	−131.2	56.5
$\mathrm{Cs}^+(aq)$	−258.3	−292.0	133.1
$\mathrm{Cu}^+(aq)$	71.7	50.0	40.6
$\mathrm{Cu}^{2+}(aq)$	64.8	65.5	−99.6
$\mathrm{F}^-(aq)$	−332.6	−278.8	−13.8
$\mathrm{H}^+(aq)$	0	0	0
$\mathrm{I}^-(aq)$	−55.2	51.6	111.3
$\mathrm{K}^+(aq)$	−252.4	283.3	102.5
$\mathrm{Li}^+(aq)$	278.5	293.3	13.4
$\mathrm{Mg}^{2+}(aq)$	−466.9	454.8	−138.1
$\mathrm{NO}_3^-(aq)$	−207.4	−111.3	146.4
$\mathrm{Na}^+(aq)$	−240.1	−261.9	59.0
$\mathrm{OH}^-(aq)$	−230.0	−157.2	−10.9
$\mathrm{PO}_4^{3-}(aq)$	−1277.4	−1018.7	−220.5
$\mathrm{SO}_4^{2-}(aq)$	−909.3	−744.5	20.1
$\mathrm{Zn}^{2+}(aq)$	−153.9	−147.1	−112.1

Source: Lide, D. R., ed. *Handbook of Chemistry and Physics*. 83rd ed. Boca Raton, FL: CRC Press 2002.

conventional values relative to H^+

(of thermodyn. quantities ~~of~~ for ions)

G is state function

=) G is the same for the direct reaction pathway or for path around the direct one

Born equation:

$$\Delta G^0_{solvation} = \frac{z^2 e^2 N_A}{8\pi\varepsilon_0 r}\left(\frac{1}{\varepsilon_r} - 1\right)$$

ionic charge : ze

ε_r : relative permitivity of the solvent

$\varepsilon_r > 1 \Rightarrow \Delta G^0_{solvation} < 0 \rightarrow$ solution is ~~spontine~~ spontaneous

for absolute values, calculated absolute values for the smallest ion, H^+, can be used:

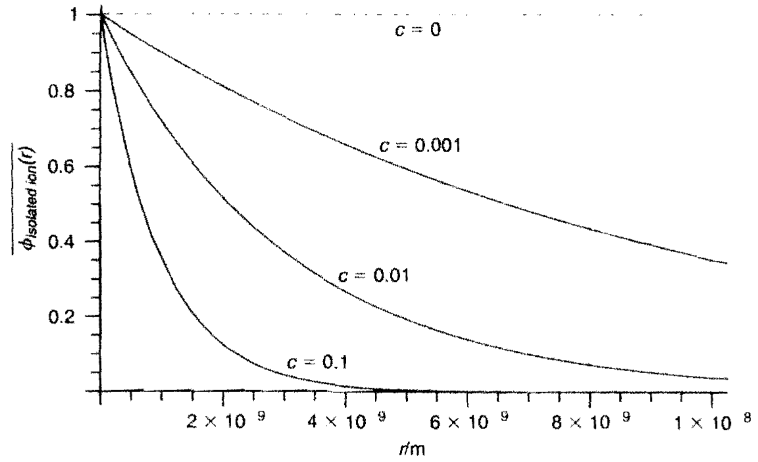
$$\Delta H^0_{solvation} \cancel{(H^+)} (H^+, aq) = -1090 \frac{kJ}{mol}$$

$$\Delta G^0_{solvation} (H^+, aq) = -1050 \ kJ/mol$$

$$\Delta S^0_{solvation} (H^+, aq) = -130 \frac{J}{K\,mol}$$

for absolute values, if the Born equation is correct: $\Delta G^0_{solvation}$ vs $\frac{z^2}{r}$ must be a straight line. if r for ions from the ~~cy~~ crystal structure $\rightarrow$ no agreement with effective radii r from center of ion to center of charge of H_2O, much better straight line

conventional values still used because in any Δ, ~~absolute~~ corrections cancel!



ɿE 10.3

o of the falloff in the electrostatic potential in the electrolyte solution to that for an iso-
ı is shown as a function of the radial distance for three different molarities of a 1–1 elec-
uch as NaCl.

ıtions (10.27) and (10.28). ε_0 and ε_r are the permittivity of free space and the permittivity (dielectric constant) of the dielectric medium or solvent, respec- ɜecause of the exponential term, $\phi_{solution}(r)$ falls off much more rapidly with r $_{solated\ ion}(r)$. We say that an individual ion experiences a **screened potential** ɜ other ions.

Debye–Hückel theory shows that κ is related to the individual charges on the l to the solute molality m by

$$\kappa^2 = e^2 N_A (1000\ \mathrm{L\ m^{-3}})\, m \left(\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\varepsilon_0 \varepsilon_r k_B T}\right) \rho_{solvent} \qquad \textbf{(10.29)}$$

s formula, we can see that screening becomes more effective as the concentra- ıe ionic species increases. Screening is also more effective for multiply charged for larger values of ν_+ and ν_-.

ʼatio

$$\frac{\phi_{solution}(r)}{\phi_{isolated\ ion}(r)} = e^{-\kappa r}$$

in Figure 10.3 for different values of m for an aqueous solution of a 1–1 elec- ʼote that the potential falls off much more rapidly with the radial distance r in olyte solution than in the uniform dielectric medium. Note also that the poten- ɔff more rapidly with increasing concentration of the electrolyte. The origin of is that ions of sign opposite to the central ion are more likely to be found close ıtral ion. These surrounding ions form a diffuse ion cloud around the central own pictorially in Figure 10.4. If a spherical surface is drawn centered at the ı, the net charge within the surface can be calculated. The results show that the : has the same sign as the central charge, falls off rapidly with distance, and is ɜro for $\kappa r \sim 8$. For larger values of κr, the central ion is completely screened ʼuse ion cloud, meaning that the net charge in the sphere around the central ion e net effect of the diffuse ion cloud is to screen the central ion from the rest of ɔn, and the quantity $1/\kappa$ is known as the **Debye–Hückel screening length.** ɹes of κ correspond to a smaller diffuse cloud, and a more effective screening. ɔnvenient to combine the concentration-dependent terms that contribute to κ ɛ **strength I**, which is defined by

$$I = \frac{m}{2} \sum_i (\nu_{i+} z_{i+}^2 + \nu_{i-} z_{i-}^2) = \frac{1}{2} \sum_i (m_{i+} z_{i+}^2 + m_{i-} z_{i-}^2) \qquad \textbf{(10.30)}$$

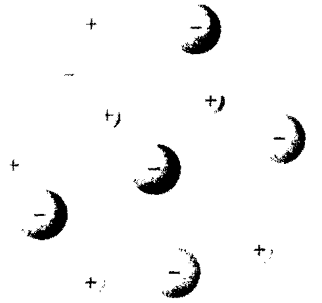


FIGURE 10.4

Pictorial rendering of the arrangement of ions about an arbitrary ion in an electrolyte solution. The central ion is more likely to have oppositely charged ions as neighbors. The large circle represents a sphere of radius $r \sim 8/\kappa$. From a point outside of this sphere, the charge on the central ion is essentially totally screened.

electrical potential around a sphere of radius r with the charge Q' is given by $'/4\pi\varepsilon r$. From electrostatics, the work in charging the sphere by the additional dQ is $\phi\, dQ$. Therefore, the work in charging a neutral sphere in vacuum to the Q is

$$w = \int_0^Q \frac{Q'dQ'}{4\pi\varepsilon_0 r} = \frac{1}{4\pi\varepsilon_0 r}\int_0^Q Q'dQ' = \frac{Q^2}{8\pi\varepsilon_0 r} \tag{10.8}$$

$_0$ is the permittivity of free space. The work of the same process in a solvent is $_0\varepsilon_r r$, where ε_r is the relative permittivity (dielectric constant) of the solvent. iently, $\Delta G^\circ_{solvation}$ for an ion of charge $Q = ze$ is given by

$$\Delta G^\circ_{solvation} = \frac{z^2e^2N_A}{8\pi\varepsilon_0 r}\left(\frac{1}{\varepsilon_r} - 1\right) \tag{10.9}$$

$\varepsilon_r > 1$, $\Delta G^\circ_{solvation} < 0$, showing that solvation is a spontaneous process. 'or ε_r for a number of solvents are listed in Table 10.2 (see Appendix B, oles).

st the Born model, we need to compare absolute values of $\Delta G^\circ_{solvation}$ for ions ent radii with the functional form proposed in Equation (10.9). However, this ion requires knowledge of $\Delta G^\circ_{solvation}(H^+, aq)$ to convert experimentally ed values of $\Delta G^\circ_{solvation}$ referenced to $H^+(aq)$ to absolute values. It turns out $_{olvation}(H^+, aq)$, and $\Delta H^\circ_{solvation}(H^+, aq)$, and $S^\circ_{solvation}(H^+, aq)$ can be calcu- cause the calculation is involved, the results are simply stated here.

$$\begin{aligned} \Delta H_{solvation}(H^+, aq) &= -1090\,\text{kJ mol}^{-1} \\ \Delta G_{solvation}(H^+, aq) &= -1050\,\text{kJ mol}^{-1} \\ S^\circ_{solvation}(H^+, aq) &= -130\,\text{J mol}^{-1}\,\text{K}^{-1} \end{aligned} \tag{10.10}$$

es listed in Equation (10.10) can be used to calculate absolute values of $_{on}$, $\Delta G^\circ_{solvation}$, and $S^\circ_{solvation}$ for other ions from the conventional values refer- $H^+(aq)$. These calculated absolute values can be used to test the validity of the lel. If the model is valid, a plot of $\Delta G^\circ_{solvation}$ versus z^2/r will give a straight own by Equation (10.9), and the data points for individual ions should lie on he results are shown in Figure 10.2, where r is the ionic radius obtained from ucture determinations.

'st and second clusters of data points in Figure 10.2 are for singly and doubly ons, respectively. The data are compared with the result predicted by 10.9) in Figure 10.2a. As can be seen from the figure, the trends are repro- t there is no quantitative agreement. The agreement can be considerably by using an effective radius for the solvated ion rather than the ionic radius al structure determinations. The effective radius is defined as the distance enter of the ion to the center of charge in the dipolar water molecule in the sol- l. Latimer, Pitzer, and Slansky [*J. Chemical Physics*, 7 (1939) 109] found the nent with the Born equation by adding 0.085 nm to the crystal radius of posi- nd 0.100 nm to the crystal radius for negative ions to account for the fact that olecule is not a point dipole. This difference is explained by the fact that the harge in the water molecule is closer to positive ions than to negative ions. 2b shows that the agreement obtained between the predictions of Equation experimental values is very good if this correction to the ionic radii is made.

0.2 shows good agreement between the predictions of the Born model and cal- ues for $\Delta G^\circ_{solvation}$, and justifies the approach used to calculate absolute Gibbs energies and entropies for solvated ions. However, because of uncertain- ne numerical values of the ionic radii and for the dielectric constant of the l water in the solvation shell of an ion, the uncertainty is ±50 kJ mol^{-1} for the vation enthalpy and Gibbs energy and ±10 J K^{-1} mol^{-1} for the absolute sol- py. Because these uncertainties are large compared to the uncertainty of the mic functions using the convention described in Equations (10.3) and (10.4),

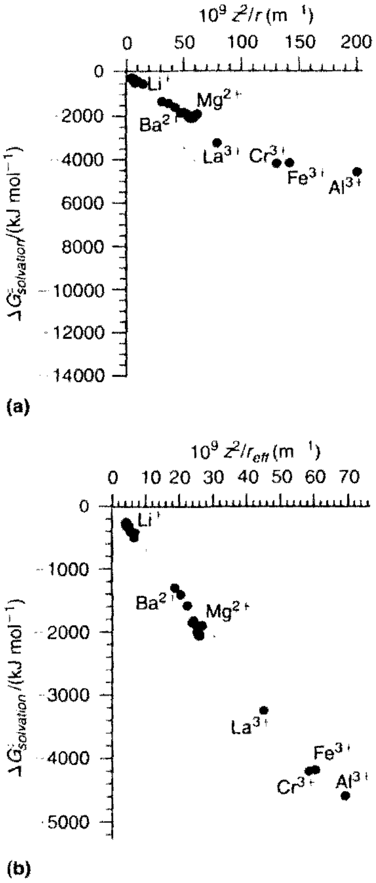


FIGURE 10.2

(a) The solvation energy calculated using the Born model is shown as a function of z^2/r. **(b)** The same results are shown as a function of z^2/r_{eff}. (See text.) The dashed line shows the behavior predicted by Equation (10.9).

electrolyte solutions:

$$G = n_{solvent}\mu_{solvent} + n_{solute}\mu_{solute}$$

n: mole numbers

μ: chemical potential, $\mu = \left(\frac{\partial G}{\partial n}\right)_{P,T}$

$$G = n_{solvent}\mu_{solvent} + \underset{cation}{n_+\mu_+} + \underset{anion}{n_-\mu_-}$$

$$= n_{solvent}\mu_{solvent} + n_{solute}(\nu_+\mu_+ + \nu_-\mu_-)$$

~~$n_{solute} = n_+$~~

ν_+, ν_- : stoichiometric numbers in formula

$$\mu_{solute} = \nu_+\mu_+ + \nu_-\mu_-$$

mean chemical potential $\mu_\pm$:

$$\mu_\pm = \frac{\mu_{solute}}{\nu} = \frac{\nu_+\mu_+ + \nu_-\mu_-}{\nu} \qquad \nu = \nu_+ + \nu_-$$

no. of ions in formula unit

experiment: μ_+, μ_- cannot be obtained
$\mu_\pm$ can be obtained

$$\mu_+ = \mu_+^\circ + RT\ln a_+$$

$$\mu_- = \mu_-^\circ + RT\ln a_-$$

based on Henry's law standard state

→ for ideal (dilute) solutions:

$$\mu_\pm = \mu_\pm^\circ + RT\ln a_\pm$$

$$a_\pm^\nu = a_+^{\nu_+} a_-^{\nu_-}, \quad a_\pm = (a_+^{\nu_+} a_-^{\nu_-})^{1/\nu}$$

is known as the **Davies equation.** As seen in Figure 10.8, this equation for $\gamma_\pm$ shows the correct limiting behavior for low I values, and the trend at higher values of I is in better agreement with the experimental results shown in Figures 10.6 and 10.7. However, unlike the Debye–Hückel limiting law, there is no theoretical basis for the Davies equation.

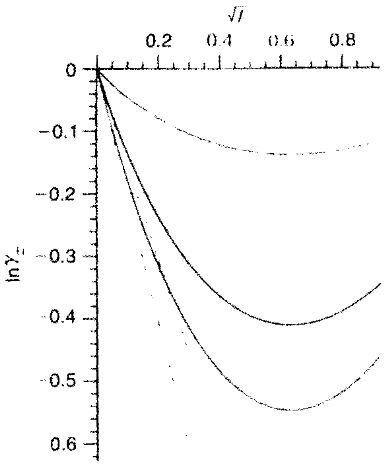


FIGURE 10.8
Comparison between the predictions of the Debye–Hückel limiting law (dashed lines) and the Davies equation (solid curves) for 1–1 (red), 1–2 (purple), and 1–3 (blue) electrolytes.

Chemical Equilibrium in Electrolyte Solutions

As discussed in Section 9.13, the equilibrium constant in terms of activities is given by Equation (9.66):

$$K = \prod_i (a_i^{eq})^{v_i} \tag{10.35}$$

It is convenient to define the activity of a species relative to its molarity. In this case,

$$a_i = \gamma_i \frac{c_i}{c^\circ} \tag{10.36}$$

where γ_i is the activity coefficient of species i. We next specifically consider chemical equilibrium in electrolyte solutions, illustrating that activities rather than concentrations must be taken into account to accurately model equilibrium concentrations. We first restrict our considerations to the range of ionic strengths for which the Debye–Hückel limiting law is valid. As an example, we calculate the degree of dissociation of MgF_2 in water. The equilibrium constant in terms of molarities for ionic salts is usually given the symbol K_{sp}, where the subscript refers to the solubility product. The equilibrium constant K_{sp} is unitless and has the value of 6.4×10^{-9} for the reaction shown in Equation (10.37). Values for K_{sp} are generally tabulated for reduced concentration units of molarity (c/c°) rather than molality (m/m°), and values for selected substances are listed in Table 10.4. Because the mass of 1 L of water is 0.998 kg, the numerical value of the concentration is the same on both scales for dilute solutions.

We next consider dissociation of MgF_2 in an aqueous solution:

$$MgF_2(s) \rightarrow Mg^{2+}(aq) + 2F^-(aq) \tag{10.37}$$

Because the activity of the pure solid can be set equal to one,

$$K_{sp} = a_{Mg^{2+}} a_{F^-}^2 = \left(\frac{c_{Mg^{2+}}}{c^\circ}\right)\left(\frac{c_{F^-}}{c^\circ}\right)^2 \gamma_\pm^3 = 6.4 \times 10^{-9} \tag{10.38}$$

From the stoichiometry of the overall equation, we know that $c_{F^-} = 2c_{Mg^{2+}}$, but Equation (10.38) still contains two unknowns, $\gamma_\pm$ and c_{F^-}, that we solve for iteratively as shown in Example Problem 10.3.

TABLE 10.4 Solubility Product Constants (Molarity Based) for Selected Salts

Salt	K_{sp}	Salt	K_{sp}
AgBr	4.9×10^{-13}	$CaSO_4$	4.9×10^{-6}
AgCl	1.8×10^{-10}	$Mg(OH)_2$	5.6×10^{-11}
AgI	8.5×10^{-17}	$Mn(OH)_2$	1.9×10^{-13}
$Ba(OH)_2$	5.0×10^{-3}	$PbCl_2$	1.6×10^{-5}
$BaSO_4$	1.1×10^{-10}	$PbSO_4$	1.8×10^{-8}
$CaCO_3$	3.4×10^{-9}	ZnS	1.6×10^{-23}

Source: Lide, D. R., ed. *Handbook of Chemistry and Physics.* 83rd ed. Boca Raton, FL: CRC Press 2002.

EXAMPLE PROBLEM 10.2

Calculate I for (a) a 0.050 molal solution of NaCl and for (b) a Na_2SO_4 solution of the same molality.

Solution

a. $$I_{NaCl} = \frac{m}{2}(\nu_+ z_+^2 + \nu_- z_-^2) = \frac{0.050\,\text{mol}\,\text{kg}^{-1}}{2} \times (1 + 1) = 0.050\,\text{mol}\,\text{kg}^{-1}$$

b. $$I_{Na_2SO_4} = \frac{m}{2}(\nu_+ z_+^2 + \nu_- z_-^2) = \frac{0.050\,\text{mol}\,\text{kg}^{-1}}{2} \times (2 + 4) = 0.15\,\text{mol}\,\text{kg}^{-1}$$

Using the definition of the ionic strength, Equation (10.29) can be written in the form

$$\kappa = \sqrt{\left(\frac{2e^2 N_A}{\varepsilon_0 k_B T}\right)(1000\text{L}\,\text{m}^{-3})}\sqrt{\left(\frac{I}{\varepsilon_r}\right)\rho_{solvent}}$$
$$= 2.91 \times 10^8 \sqrt{\frac{I/\text{mol}\,\text{kg}^{-1}}{\varepsilon_r}\frac{\rho_{solvent}}{\text{kg}\,\text{L}^{-1}}}\ \text{m}^{-1} \text{ at } 298\text{ K} \qquad \textbf{(10.31)}$$

The first factor in this equation contains only fundamental constants that are independent of the solvent and solute as well as the temperature. The second factor contains the ionic strength of the solution and the unitless relative permittivity of the solvent. For the more conventional units of mol L^{-1}, and for water, for which $\varepsilon_r = 78.5$, $\kappa = 3.29 \times 10^9 \sqrt{I}\ m^{-1}$ at 298 K.

By calculating the charge distribution of the ions around the central ion and the work needed to charge these ions up to their charges z_+ and z_- from an initially neutral state, Debye and Hückel were able to obtain an expression for the mean ionic activity coefficient. It is given by

$$\ln \gamma_\pm = -|z_+ z_-|\frac{e^2\kappa}{8\pi\varepsilon_0\varepsilon_r k_B T} \qquad \textbf{(10.32)}$$

This equation is known as the **Debye–Hückel limiting law.** It is called a limiting law because Equation (10.32) is only obeyed for small values of the ionic strength. Note that because of the negative sign in Equation (10.32), $\gamma_\pm < 1$. From the concentration dependence of κ shown in Equation (10.31), the model predicts that $\ln \gamma_\pm$ decreases with the ionic strength as $\sqrt{I}$. This dependence is shown in Figure 10.5. Although all three solutions have the same solute concentration, they have different values for z^+ and z^-. For this reason, the three lines have a different slope.

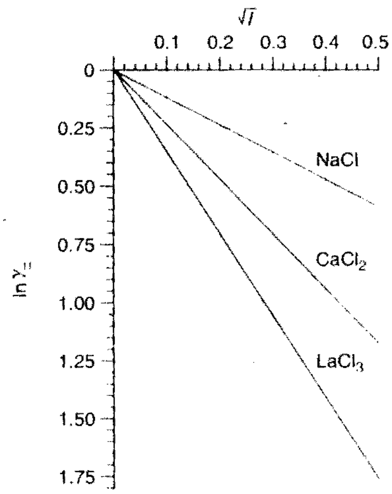


FIGURE 10.5
The decrease in the Debye–Hückel mean activity coefficient with the square root of the ionic strength is shown for a 1–1, a 1–2, and a 1–3 electrolyte, all of the same molality in the solute.

Equation (10.32) can be simplified for a particular choice of solvent and temperature. For aqueous solutions at 298.15 K, the result is

$$\log \gamma_\pm = -0.5092|z_+ z_-|\sqrt{I} \text{ or } \ln \gamma_\pm = -1.173|z_+ z_-|\sqrt{I} \qquad \textbf{(10.33)}$$

How well does the Debye–Hückel limiting law agree with experimental data? Figure 10.6 shows a comparison of the model with data for aqueous solutions of $AgNO_3$ and $CaCl_2$. In each case, $\ln \gamma_\pm$ is plotted versus $\sqrt{I}$. The Debye–Hückel limiting law predicts that the data will fall on the line indicated in each figure. The data points deviate from the predicted behavior above $\sqrt{I} = 0.1$ for $AgNO_3$ ($m = 0.01$), and above $\sqrt{I} = 0.006$ for $CaCl_2$ ($m = 0.004$). In the limit that $I \rightarrow 0$, the limiting law is obeyed. However, the deviations are significant at a concentration for which a neutral solute would exhibit ideal behavior.

The deviations continue to increase with increasing ionic strength. Figure 10.7 shows experimental data for $ZnBr_2$ out to $\sqrt{I} = 5.5$, corresponding to $m = 10$. Note that, although the Debye–Hückel limiting law is obeyed as $I \rightarrow 0$, $\ln \gamma_\pm$ goes through a minimum and begins to increase with increasing ionic strength. At the highest value of the ionic strength, $\gamma_\pm = 2.32$, which is significantly greater than one. Although the deviations from ideal behavior are less pronounced in Figure 10.6, the trend is the same for all the solutes. The mean ionic activity coefficient $\gamma_\pm$ falls off more slowly with the ionic strength than predicted by the Debye–Hückel limiting law. The behavior shown in Figure 10.7 is typical for most electrolytes: after passing through a minimum, $\gamma_\pm$ rises

$$a^2_{NaCl} = a_{Na^+} a_{Cl^-} \Rightarrow a_{NaCl} = \sqrt{a_{Na^+} a_{Cl^-}}$$

$$a_{NaCl} = a_\pm$$

$$a^3_{K_2SO_4} = a^2_{K^+} a_{SO_4^{2-}} \Rightarrow a_{K_2SO_4} = \sqrt[3]{a^2_{K^+} a_{SO_4^{2-}}}$$

$$a^4_{H_3PO_4} = a^3_{H} a_{PO_4^{3-}} \Rightarrow a_{H_3PO_4} = \sqrt[4]{a^3_{H^+} a_{PO_4^{3-}}}$$

$m_+ = \nu_+ m$, $m_- = \nu_- m$ m for solute

$$\Rightarrow a_+ = \frac{m_+}{m_0} \gamma_+ \qquad a_- = \frac{m_-}{m_0} \gamma_-$$

$m_0 = 1 \frac{mol}{kg}$, γ activity coefficients

$\Rightarrow$ a-s have no units

Henry's law standard states (not real)

Henry's law is ok (not only for $m \to 0$) but up to $m_0 = 1 \frac{mol}{kg}$

$$\Rightarrow a_\pm^\nu = \left(\frac{m_+}{m_0}\right)^{\nu_+} \left(\frac{m_-}{m_0}\right)^{\nu_-} \gamma_+^{\nu_+} \gamma_-^{\nu_-}$$

mean ionic molality, $m_\pm$, mean ionic activity coefficient; $\gamma_\pm$:

$$m_\pm^\nu = m_+^{\nu_+} m_-^{\nu_-} , \quad m_\pm = (\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu} m$$

$$\gamma_\pm^\nu = \gamma_+^{\nu_+} \gamma_-^{\nu_-} ; \quad \gamma_\pm = (\gamma_+^{\nu_+} \gamma_-^{\nu_-})^{1/\nu}$$

$$\Rightarrow a_\pm^\nu = \left(\frac{m_\pm}{m_0}\right)^\nu \gamma_\pm^\nu \to a_\pm = \left(\frac{m_\pm}{m_0}\right) \gamma_\pm$$

$$\Rightarrow \mu_{solute} = \mu^\circ_{solute} + RT \ln a_\pm^\nu$$

$$\mu_{solute} = \mu_\pm = \left[\nu \mu^\circ_\pm + RT \ln (\nu_+^{\nu_+} \nu_-^{\nu_-})\right] + RT \ln \left(\frac{m_+}{m_0}\right) + \\ + \nu RT \ln \gamma_\pm$$

with $\mu_\pm^{\infty} = \nu\mu_\pm^{0} + RT\ln\left(\nu_+^{\nu_+}\nu_-^{\nu_-}\right)$

$$\Rightarrow \mu_{solute} = \mu_\pm = \underbrace{\mu_\pm^{\infty} + \nu RT\ln\left(\frac{m_\pm}{m_0}\right)}_{\text{ideal ionic solution } (\gamma_\pm = 1)} + \nu RT\ln\gamma_\pm$$

$\nu RT\ln\gamma_\pm$ describes ~~behavior~~ deviations from ideal behavior

$$\phi_{\text{isolated ion}} = \frac{\pm ze}{4\pi\varepsilon_r\varepsilon_0\cdot r}$$

$$\phi_{\text{solution}}^{\text{ion in}} = \frac{\pm ze}{4\pi\varepsilon_r\varepsilon_0}\exp(-\kappa r)$$

$\frac{1}{\kappa}$: screening length

Debye-Hückel limiting law (DHLL):

$$\kappa^2 = e^2 N_A \left(1000\frac{L}{m^3}\right) m \, \frac{\nu_+ z_+^2 + \nu_- z_-^2}{\varepsilon_0\varepsilon_r k_B T} \, d_{solvent}$$

molality

solvent density

ionic strength, I:

$$I = \frac{1}{2} m \sum_i \left(\nu_{i,+} z_{i,+}^2 + \nu_{i,-} z_{i,-}^2\right)$$

i runs over all ion types in solution

NaCl: 2 terms

NaCl/NaBr mixture: 4 terms (2 for Na^+)

0.050 m ~~NaCl~~ NaCl solutions

$$I_{NaCl} = \frac{1}{2} 0{,}050 \frac{mol}{kg} (1+1) = 0{,}050 \frac{mol}{kg}$$

0.050 m Na_2SO_4 solution

$$I_{Na_2SO_4} = \frac{1}{2} \cdot 0{,}050 \frac{mol}{kg} (2+4) = 0.15 \frac{mol}{kg}$$

$\nu_+ = 2$, $z_+ = 1$, $\nu_- = 1$, $z_- = -2$

$$\kappa = \sqrt{\frac{2e^2N_A}{\varepsilon_0 k_BT}\cdot 1000\,\frac{L}{m^3}\cdot\sqrt{\frac{I}{\varepsilon_r}\,d_{solvent}}}$$

$$= 2.91\cdot 10^{8}\,\frac{1}{m}\sqrt{\frac{I/(mol/kg)}{\varepsilon_r}\,\frac{d_{solvent}}{kg/L}} \quad \text{at } 298K$$

↑ 1/meter

DHLL:

$$\ln\gamma_\pm = -|z_+z_-|\,\frac{\kappa e^2}{8\pi\varepsilon_0\varepsilon_r k_BT}$$

for water and 298.15K:

$$\ln\gamma_\pm = -1.173\,|z_+z_-|\,\sqrt{I/M}$$

$$\log_{10}\gamma_\pm = -0.5092\,|z_+z_-|\,\sqrt{I/M}$$

only good for small concentration,
then also $I/M = I/m$

in 1M H_2SO_4 (1L)
9 H_2O bound to each H_2SO_4
pure H_2O: 55 mol H_2O in 1L
H_2SO_4: 46 mol free H_2O

better: Davies equation (empirical)

$$\log_{10}\gamma_\pm = -0.51\,|z_+z_-|\left[\frac{\sqrt{I/m_0}}{1+\sqrt{I/m_0}} - 0.30\,(I/m_0)\right]$$

Equilibrium

constant at $T=$ const., $K = \prod_i (a_i^{eq})^{\nu_i}$
$p =$ const.
(gases)

products: $\nu_i > 0$

reactants: $\nu_i < 0$

$$a_i = \frac{c_i}{c_0}\gamma_i \, , \quad c_0 = 1M$$

solubility constants K_{sp} usuall tabulated in terms of c_i/c_0

$$MgF_2(s) \xrightarrow{H_2O} Mg^{2+}(aq) + 2F^-(aq)$$

$$K_{sp} = a_{Mg^{2+}} a_{F^-}^2 = \left(\frac{c_{Mg^{2+}}}{c_0}\right)\left(\frac{c_{F^-}}{c_0}\right)^2 \gamma_\pm^3$$

$$= 6{,}4 \cdot 10^{-9} \quad \text{for } MgF_2$$

solubility s of MgF_2, using DHLL and $K_{sp} = 6.4 \cdot 10^{-9}$

$$s = \frac{c_{Mg^{2+}}}{c_0} \quad \text{in saturated solutions}$$

$$K_{sp} = a_{Mg^{2+}} a_{F^-}^2 = \left(\frac{c_{Mg^{2+}}}{c_0}\right)\left(\frac{c_{F^-}}{c_0}\right)^2 \gamma_\pm^3 = 6.4 \cdot 10^{-9}$$

$$c_{Mg^{2+}}/c_0 = s = \frac{1}{2} c_{F^-}/c_0$$

$$K_{sp} = s \cdot (2s)^2 \gamma_\pm^3 = 4s^3 \gamma_\pm^3 \qquad c_{F^-} = 2c_{Mg^{2+}}$$

1. step assume $\gamma_\pm = 1$ (0 iteration)

$$\Rightarrow 4s^3 = 6{,}4 \cdot 10^{-9} \quad \Rightarrow s = 1.17 \cdot 10^{-3}$$

$$\Rightarrow m = 1.17 \cdot 10^{-3} \cdot m$$

2. step (iteration 1)

$$I = \frac{m}{2}\left(\nu_+ z_+^2 + \nu_- z_-^2\right) = \frac{1}{2}\, 1.17\cdot 10^{-3}\, \frac{mol}{kg}\,(2^2 + 2)$$

$\nu_+ = 1$, $z_+ = 2$, $\nu_- = 2$, $z_- = -1$

$$I = 3{,}51\cdot 10^{-3}\, \frac{mol}{kg}$$

DHLL: $\ln \gamma_\pm = -1{,}173\,|1\cdot(-2)|\,\sqrt{I/m_0}$

$$= -1{,}173\cdot 2\cdot \sqrt{3{,}51\cdot 10^{-3}} = -0{,}1390$$

$$\gamma_\pm = \exp(-0{,}1390) = 0{,}870$$

3. step (iteration 2)

~~I with~~ ~~$m = \frac{1}{3} I$~~

$$s = \sqrt[3]{\frac{K_{sp}}{4\cdot\cancel{\gamma}}}\cdot \frac{1}{\gamma_\pm} = 1{,}34\cdot 10^{-3}\, m$$

new I from s → new $\gamma_\pm$

$\gamma_\pm = 0{,}862$, $s = 1{,}36\cdot 10^{-3}\, m$

4. step (iteration 3)

$\gamma_\pm = 0{,}861$, $s = 1{,}36\cdot 10^{-3}\, m$

⇒ iteration converged

salting in adding electrolyte

⇒ I increases ⇒ $\gamma_\pm$ decreases

(at small s → DHLL)

then: $K_{sp} = 4 s^3 \gamma_\pm^3 = const.$

⇒ when $\gamma_\pm$ decreases then s must increase

to have K_{sp} constant

increasing s = salting in

<u>salting out</u>

when I is <u>large</u>, then $\gamma_\pm$ increases

when I increases ⇒ s decreases

= salting out

because $\gamma_\pm$ increases

buffer: 0.1 M HAc (acetic acid) + 0.1 M NaAc

for $HAc \xrightarrow{H_2O} H^+ + Ac^-$ $K_a = 1.75 \cdot 10^{-5}$ pH?

$$K_a = \frac{a_{H^+}\, a_{Ac^-}}{a_{HAc}}$$

for H^+ and Ac^- : $\gamma_\pm$

for neutral HAc $\gamma = 1$

$$K_a = \frac{\gamma_\pm\, m_{H^+}\, \gamma_\pm\, m_{Ac^-}}{m_{HAc}}$$

x ~~HA~~ HAc dissociate

$\rightarrow$ $m_{H^+} = x$

$m_{Ac^-} = x + 0.1$

$m_{HAc} = \cancel{x}\, 0.1 - ($

$$\Rightarrow K_a = \frac{\gamma_\pm^2\, x\, (0.1 + x)}{0.1 - x}$$

K_a very small ⇒ $x \ll 0.1$

$$\rightarrow K_a \approx \gamma_\pm^2 \frac{x \cdot 0.1}{0.1} = x\gamma_\pm^2$$

$$x = m_{H^+} = \frac{K_a}{\gamma_\pm^2} = \frac{1.75 \cdot 10^{-5}}{\gamma_\pm^2}$$

with $\gamma_\pm = 1$ assumptions

$$m_{H^+} = 1.75\cdot 10^{-5}$$

$$pH = -\log_{10}(1.75\cdot 10^{-5}) = 4.76$$

ionic strength from NaAc alone (Ka small)

$$I = \frac{0.1}{2}\,\frac{mol}{kg}\cdot(1+1) = 0.1\,\frac{mol}{kg}$$

I large → Davies equation:

$$\log_{10}\gamma_\pm = -0.51\left[\frac{\sqrt{0.1}}{1+\sqrt{01}} - 0.3\cdot 0.1\right] = -0.1270$$

$$\gamma_\pm = \cancel{ex}\ 10^{-0.1270} = 0.746$$

$$m_{H^+} = \frac{1.75\cdot 10^{-5}}{(0.746)^2} = 3.14\cdot 10^{-5}\,\frac{mol}{kg}$$

$$pH = -\log_{10}(3.14\cdot 10^{-5}) = 4.50$$

much smaller than with $\gamma_\pm = 1$

Chapter 10: discussion of electrolysis

Chapter 11; Electrochem. cells used as batteries

equilibrium conditions

for every chemical the electrochemical potential $\tilde{\mu}$ must be the same ~~av~~ everywhere in the cell

$$\tilde{\mu} = \mu + z\phi\cancel{\Phi}F$$

electrical potential in the cell

Faraday's constant

chem. potential

charge number of the ion transported ~~th~~ through ϕ

with increasing ionic strength, and for high values of I, $\gamma_\pm > 1$. Experimental values for $\gamma_\pm$ for a number of solutes at different concentrations in aqueous solution are listed in Table 10.3 (see Appendix B, Data Tables).

There are a number of reasons why the experimental values of $\gamma_\pm$ differ at high ionic strength from those calculated from the Debye–Hückel limiting law. They mainly involve the assumptions made in the model. It has been assumed that the ions can be treated as point charges with zero volume, whereas ions and their associated solvation shells occupy a finite volume. As a result, there is an increase in the repulsive interaction among ions in an electrolyte over that predicted for point charges, which becomes more important as the concentration increases. Repulsive interactions raise the energy of the solution and, therefore, increase $\gamma_\pm$. The Debye–Hückel model also assumes that the solvent can be treated as a structureless dielectric medium. However, the ion is surrounded by a relatively ordered primary solvation shell, as well as by more loosely bound water molecules. The atomic level structure of the solvation shell is not adequately represented by using the dielectric strength of bulk solvent. Another factor that has not been taken into account is that as the concentration increases, some ion pairing occurs such that the concentration of ionic species is less than would be calculated assuming complete dissociation.

Additionally, consider the fact that the water molecules in the solvation shell have effectively been removed from the solvent. For example, in an aqueous solution of H_2SO_4, approximately nine H_2O molecules are tightly bound per dissolved H_2SO_4 formula unit. Therefore, the number of moles of H_2O as solvent in 1 L of a one molar H_2SO_4 solution is reduced from 55 for pure H_2O to 46 in the solution. Consequently, the actual solute molarity is larger than that calculated by assuming that all the H_2O is in the form of solvent. Because the activity increases linearly with the actual molarity, $\gamma_\pm$ increases as the solute concentration increases. If there were no change in the enthalpy of solvation with concentration, all the H_2O molecules would be removed from the solvent at a concentration of six molar H_2SO_4. Clearly, this assumption is unreasonable. What actually happens is that solvation becomes energetically less favorable as the H_2SO_4 concentration increases. This corresponds to a less negative value of $\ln \gamma_\pm$, or equivalently to an increase in $\gamma_\pm$. Summing up, many factors explain why the Debye–Hückel limiting law is only valid for small concentrations. Because of the complexity of these different factors, there is no simple formula based on theory that can replace the Debye–Hückel limiting law. However, the main trends exhibited in Figures 10.6 and 10.7 are reproduced in more sophisticated theories of electrolyte solutions.

Because none of the usual models are valid at high concentrations, empirical models that "improve" on the Debye–Hückel model by predicting an increase in $\gamma_\pm$ for high concentrations are in widespread use. An empirical modification of the Debye–Hückel limiting law that has the form

$$\log_{10}\gamma_\pm = -0.51|z_+z_-|\left[\frac{\left(\dfrac{I}{m^\circ}\right)^{1/2}}{1+\left(\dfrac{I}{m^\circ}\right)^{1/2}} - 0.30\left(\frac{I}{m^\circ}\right)\right] \qquad (10.34)$$

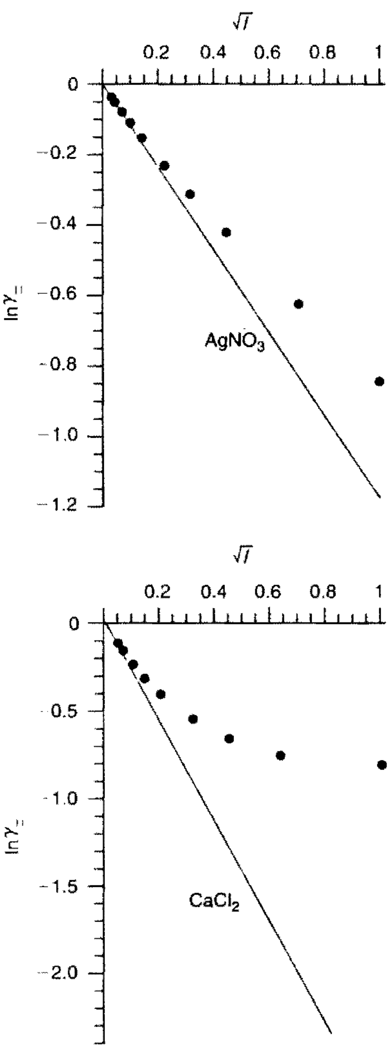


FIGURE 10.6
The experimentally determined activity coefficients for $AgNO_3$ and $CaCl_2$ are shown as a function of the square root of the ionic strength. The solid lines are the prediction of the Debye–Hückel theory.

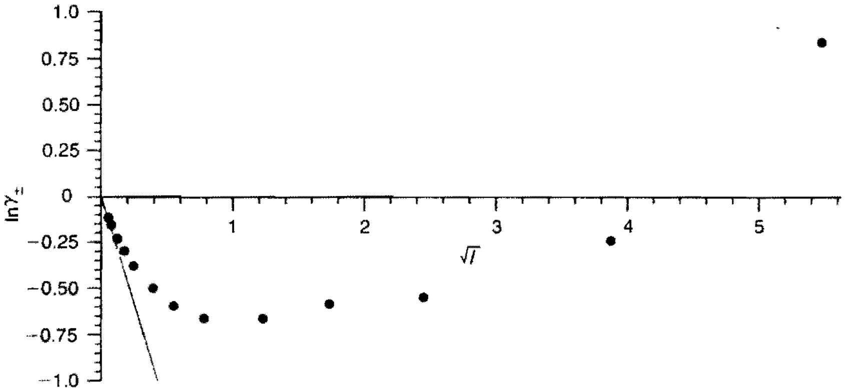


FIGURE 10.7
Experimentally determined values for the mean activity coefficient for $ZnBr_2$ are shown as a function of the square root of the ionic strength. The solid line is the prediction of the Debye–Hückel theory.

is known as the **Davies equation.** As seen in Figure 10.8, this equation for $\gamma_\pm$ shows the correct limiting behavior for low I values, and the trend at higher values of I is in better agreement with the experimental results shown in Figures 10.6 and 10.7. However, unlike the Debye–Hückel limiting law, there is no theoretical basis for the Davies equation.

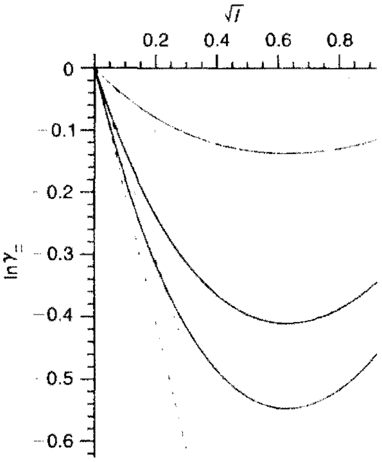


FIGURE 10.8
Comparison between the predictions of the Debye–Hückel limiting law (dashed lines) and the Davies equation (solid curves) for 1–1 (red), 1–2 (purple), and 1–3 (blue) electrolytes.

Chemical Equilibrium in Electrolyte Solutions

As discussed in Section 9.13, the equilibrium constant in terms of activities is given by Equation (9.66):

$$K = \prod_i \left(a_i^{eq}\right)^{\nu_i} \tag{10.35}$$

It is convenient to define the activity of a species relative to its molarity. In this case,

$$a_i = \gamma_i \frac{c_i}{c^\circ} \tag{10.36}$$

where γ_i is the activity coefficient of species i. We next specifically consider chemical equilibrium in electrolyte solutions, illustrating that activities rather than concentrations must be taken into account to accurately model equilibrium concentrations. We first restrict our considerations to the range of ionic strengths for which the Debye–Hückel limiting law is valid. As an example, we calculate the degree of dissociation of MgF_2 in water. The equilibrium constant in terms of molarities for ionic salts is usually given the symbol K_{sp}, where the subscript refers to the solubility product. The equilibrium constant K_{sp} is unitless and has the value of 6.4×10^{-9} for the reaction shown in Equation (10.37). Values for K_{sp} are generally tabulated for reduced concentration units of molarity (c/c°) rather than molality (m/m°), and values for selected substances are listed in Table 10.4. Because the mass of 1 L of water is 0.998 kg, the numerical value of the concentration is the same on both scales for dilute solutions.

We next consider dissociation of MgF_2 in an aqueous solution:

$$MgF_2(s) \longrightarrow Mg^{2+}(aq) + 2F^-(aq) \tag{10.37}$$

Because the activity of the pure solid can be set equal to one,

$$K_{sp} = a_{Mg^{2+}}\, a_{F^-}^2 = \left(\frac{c_{Mg^{2+}}}{c^\circ}\right)\left(\frac{c_{F^-}}{c^\circ}\right)^2 \gamma_\pm^3 = 6.4 \times 10^{-9} \tag{10.38}$$

From the stoichiometry of the overall equation, we know that $c_{F^-} = 2c_{Mg^{2+}}$, but Equation (10.38) still contains two unknowns, $\gamma_\pm$ and c_{F^-}, that we solve for iteratively as shown in Example Problem 10.3.

TABLE 10.4 Solubility Product Constants (Molarity Based) for Selected Salts

Salt	K_{sp}	Salt	K_{sp}
AgBr	4.9×10^{-13}	$CaSO_4$	4.9×10^{-6}
AgCl	1.8×10^{-10}	$Mg(OH)_2$	5.6×10^{-11}
AgI	8.5×10^{-17}	$Mn(OH)_2$	1.9×10^{-13}
$Ba(OH)_2$	5.0×10^{-3}	$PbCl_2$	1.6×10^{-5}
$BaSO_4$	1.1×10^{-10}	Pb SO_4	1.8×10^{-8}
$CaCO_3$	3.4×10^{-9}	ZnS	1.6×10^{-23}

Source: Lide, D. R., ed. *Handbook of Chemistry and Physics.* 83rd ed. Boca Raton, FL: CRC Press 2002.

$Zn(s) / ZnSO_4(aq)$ half-cell :

a Zn electrode is immersed in a $ZnSO_4(aq)$ solution.

Then : $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$

⇒ a negative potential buildsup in the Zn(s) and
a positive potential ~~but~~ builds up in the solution.
because Zn atoms dissolving leave 2e- in the Zn(s) and $Zn^{2+}(aq)$ ions appear in the solution.

However, equilibrium is far on the left.

$< 10^{-4}$ mol on Zn(s) dissolves in 1 L solution but building a potential difference between Zn(s) and the solution of ≈ 1V

equilibrium constant different for different metals ⇒ also potential different

Pt wire connected to Zn(s) and the other end immersed in the $ZnSO_4$ ~~solut~~ solution.
~~to~~ but then $\Delta\phi$ between the Pt / Zn(s) and the Pt / $ZnSO_4(aq)$ contacts is measured, not $\phi_{Zn / ZnSO_4(aq)}$ which cannot be directly measured.

half-cell potentials cannot be measured alone, but relative to another half-cell rev. work $\text{đ}w_{rev}$ that must be done to move a charge from a phase with ϕ_1 to another <u>identical</u> phase, but with ϕ_2:

$$\text{đ}w_{rev} = (\phi_2 - \phi_1)\, dQ$$

$dQ = -zF\,dn$ is the charge transferred through the potential difference

z: charge number in terms of electron charges, e

F: Faraday's constant

$$F = 96\,485 \, \frac{\overset{\swarrow \text{ Coulomb}}{C}}{mol} = 96\,485 \, \frac{As}{mol}$$

unit of charge: 1 Coulomb, 1C = 1 As

charge transport: only non-expansion work

$$\Rightarrow \text{đ}w_{rev} = \cancel{dQ}\, dG$$

dG: Gibb's ~~di~~ energy difference = difference between the electrochemical potential ($\tilde{\mu}$ between the two phases

$$dG = \tilde{\mu}_2\, dn - \tilde{\mu}_1\, dn$$

$$\tilde{\mu} = \underset{\substack{\uparrow \\ \text{chemical potential}}}{\mu} + z\phi F$$

$$\tilde{\mu} \rightarrow \mu \quad \text{if } \phi \rightarrow 0$$

$$\Rightarrow \tilde{\mu}_2 - \tilde{\mu}_1 = z(\phi_2 - \phi_1)F$$

<u>or</u> $\tilde{\mu}_2 = \tilde{\mu}_1 + z(\phi_2 - \phi_1)F$

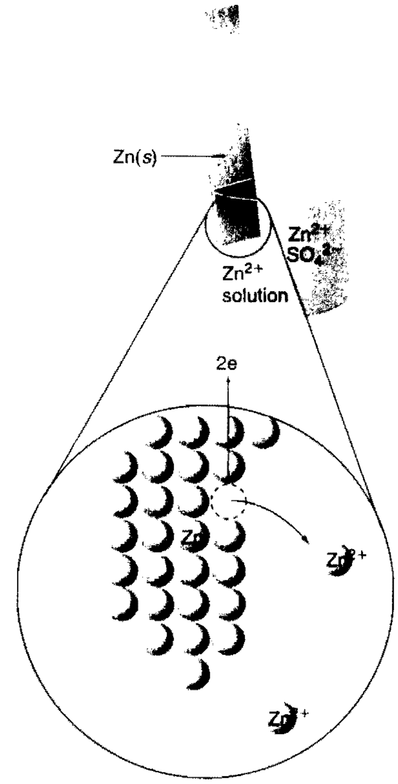


FIGURE 11.1
When a Zn electrode is immersed in an aqueous solution containing $Zn^{2+}(aq)$ ions, a very small amount of the Zn goes into solution as $Zn^{2+}(aq)$, leaving two electrons behind on the Zn electrode per ion formed.

The equilibrium position in this reaction lies far toward Zn(*s*). At equilibrium, fewer than 10^{-14} mol of the Zn(*s*) dissolves in 1 liter of solution to form $Zn^{2+}(aq)$. However, this minuscule amount of charge transfer between the electrode and the solution is sufficient to create a difference of approximately 1 V in the electrical potential between the Zn electrode and the electrolyte solution. A similar dissociation equilibrium is established for other metal electrodes. Because the value of the equilibrium constant depends on ΔG_f° of the solvated metal ion, the equilibrium constant for the dissociation reaction and ϕ depends on the identity of the metal.

Can ϕ be measured directly? Let us assume that we can carry out the measurement using two chemically inert Pt wires as probes. One Pt wire is placed on the Zn electrode, and the second Pt wire is placed in the $ZnSO_4$ solution. However, the measured voltage is the difference in electrical potential between a Pt wire connected to a Zn electrode in a $ZnSO_4$ solution and a Pt electrode in a $ZnSO_4$ solution, which is not what we want. A difference in electrical potential can only be measured between one phase and a second phase *of identical composition*. For example, the difference in electrical potential across a resistor is measured by contacting the metal wire at each end of the resistor with two metal probes of identical composition connected to the terminals of a voltmeter. Although we can not measure the half-cell potential ϕ directly, half-cell potentials can be determined relative to a reference half-cell as will be shown in Section 11.2.

How are chemical species affected by the electrical potential ϕ? To a very good approximation, the chemical potential of a **neutral** atom or molecule is not affected if a small electrical potential is applied to the environment containing the species. However, this is not the case for a **charged** species such as an Na^+ ion in an electrolyte solution. The work required to transfer *dn* moles of charge reversibly from a chemically uniform phase at an electrical potential ϕ_1 to a second, otherwise identical phase at an electrical potential ϕ_2 is equal to the product of the charge and the difference in the electrical potential between the two locations:

$$dw_{rev} = (\phi_2 - \phi_1)\,dQ \tag{11.2}$$

In this equation, $dQ = -zF\,dn$ is the charge transferred through the potential, z is the charge in units of the electron charge (+1, −1, +2, −2, ...), and the **Faraday constant** F is the absolute magnitude of the charge associated with 1 mol of a singly charged species. The Faraday constant has the numerical value $F = 96{,}485$ Coulombs mole^{-1} (C mol^{-1}).

Because the work being carried out in this reversible process is nonexpansion work, $dw_{rev} = dG$, which is the difference in the **electrochemical potential** $\widetilde{\mu}$ of the charged particle in the two phases:

$$dG = \widetilde{\mu}_2\,dn - \widetilde{\mu}_1\,dn \tag{11.3}$$

The electrochemical potential is a generalization of the chemical potential to include the effect of an electrical potential on a charged particle. It is the sum of the normal chemical potential μ and a term that results from the nonzero value of the electrical potential:

$$\widetilde{\mu} = \mu + z\phi F \tag{11.4}$$

Note that with this definition $\widetilde{\mu} \rightarrow \mu$ as $\phi \rightarrow 0$.

Combining Equations (11.2) and (11.4) gives

$$\widetilde{\mu}_2 - \widetilde{\mu}_1 = +z(\phi_2 - \phi_1)F \quad \text{or} \quad \widetilde{\mu}_2 = \widetilde{\mu}_1 + z(\phi_2 - \phi_1)F \tag{11.5}$$

Because only the difference in the electrical potential between two points can be measured, one can set $\phi_1 = 0$ in Equation (11.5) to obtain the result

$$\widetilde{\mu}_2 = \widetilde{\mu}_1 + z\phi F \tag{11.6}$$

This result shows that charged particles in two otherwise identical phases have different values for the electrochemical potential if the phases are at different electrical only $\Delta\phi$ between two points can be measured

thus $\phi_1 = 0$ can be set!

$$\Rightarrow \tilde{\mu}_2 = \tilde{\mu}_1 + z\phi F$$

normal equilibrium conditions:

$$\Delta G_R = \sum_i \nu_i \mu_i = 0$$

but equilibrium condition in electrochemical cell: $\Delta G_R = \sum_i \nu_i \tilde{\mu}_i = 0$

difficult to change ΔG_R by changing P, T or concentration

but easy to change ΔG_R (even change sign and reverse ~~sign~~ reaction) by applying an electrical potential ϕ

example of sign change of ΔG_R: recharging of batteries with a potential ϕ.

Zn(s) is in standard state and uncharged

$$\Rightarrow \tilde{\mu}(Zn(s)) = \mu(Zn(s)) = \Delta G_f(Zn(s)) = 0$$

if overall reaction in a cell happens in single phase, then ϕ is the same for all ionic reactants and products:

$$\Delta G_R = \sum_i \nu_i \tilde{\mu}_i = \sum_i \nu_i \mu_i + F\phi \underbrace{\sum_i \nu_i z_i}_{0} = \sum_i \nu_i \mu_i = 0$$

equil. condition

i runs over all ions in the cell reaction

$\sum \nu_i z_i = 0$

ν_i: stoichiometric coefficient of ion i in the cell reaction

$\rightarrow \sum_i \nu_i z_i$ = total charge (right side of equation)

− " " (left " " ")

= 0

$\nu_i > 0$ for products, $\nu_i < 0$ for reactants,

z_i charge number of ion i

since $\sum_i \nu_i z_i = 0$ one can ~~#~~ set $\phi = 0$

$\Rightarrow \tilde{\mu}_i = \mu_i$ for ions in solution

μ_i can be calculated at low concentrations with γ from DHLL or at higher conc. e.g. with the ~~Davi~~ Davies equation for γ

standard state definition: $\mu_i(e^- \text{ in electrode}) = 0$

$\Rightarrow \tilde{\mu}_e = -\phi F$ for e^- in metal electrode

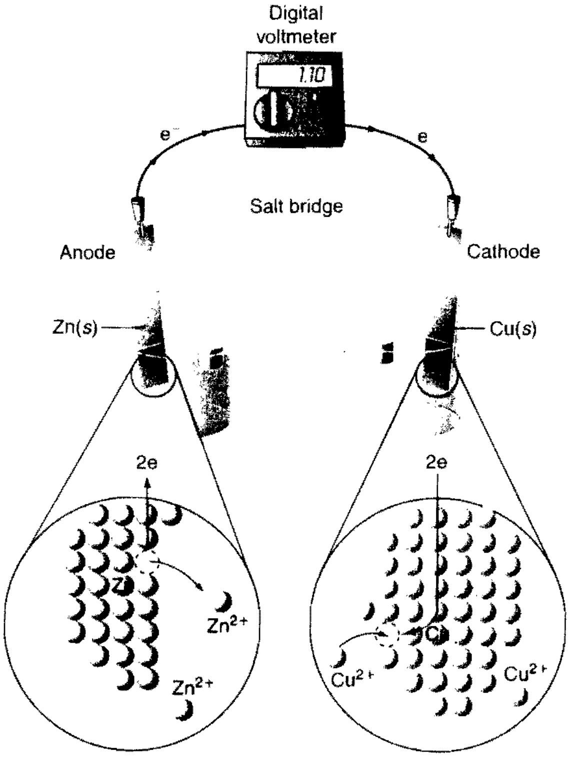
Daniell cell

$Zn(s) | ZnSO_4(aq)$ half-cell connected with a $Cu(s) | CuSO_4(aq)$ half-cell

1) by a Pt wire between $Zn(s)$ and $Cu(s)$ and
2) by a salt-bridge between the solutions

salt bridge: KCl suspended in a gel prevents direct mixing of the solutions because of the gel, but conducts current because of the ~~KCl~~ KCl in the gel

Daniell cell.
lf-cells are con-
e in the internal
wn in the external
e atomic level
h electrode.



is immersed in a solution of $CuSO_4$, which is completely dissociated to form Cu^{2+} (aq) and SO_4^{2-} (aq). The two half-cells are connected by an ionic conductor known as a salt bridge. The **salt bridge** consists of an electrolyte such as KCl suspended in a gel. A salt bridge allows current to flow between the half-cells while preventing the mixing of the solutions. A metal wire fastened to each electrode allows the electron current to flow through the external part of the circuit. Note that because the wire is connected on one end to a Cu electrode and on the other end to a Zn electrode, the two phases between which we are measuring the electrical potential are not identical.

Using the experimental setup of Figure 11.2, the electrical potential difference between two half-cells can be measured, rather than the absolute electrical potential of each half-cell. However, we need potentials of individual half-cells. Therefore, it is convenient to choose one half-cell as a reference and arbitrarily assign an electrical potential of zero to this half-cell. Once this is done, the electrical potential associated with any other half-cell can be determined by combining it with the reference half-cell. The measured potential difference across the cell is associated with the half-cell of interest. It is next shown that the standard hydrogen electrode fulfills the role of a reference half-cell of zero potential. The measurement of electrical potentials is discussed using this cell. The reaction in the standard hydrogen electrode is

$$H^+(aq) + e^- \rightarrow \frac{1}{2} H_2(g) \tag{11.10}$$

and the equilibrium in the half-cell is described by

$$\mu_{H^+}(aq) + \widetilde{\mu}_e = \frac{1}{2}\mu_{H_2(g)} \tag{11.11}$$

Half-cell reactions such as Equation (11.10) are generally written as reduction reactions by convention as is done in Tables 11.1 and 11.2 (see Appendix B, Data Tables) even though equilibrium is established in the half-cell. It is useful to separate $\mu_{H_2(g)}$ and $\mu_{H^+}(aq)$ into a standard state portion and a portion that depends on the

activity and use Equation (11.9) f
preceding equation then takes the

$$\mu^{\circ}_{H^+} + RT \ln a_{H^+}$$

where f_{H_2} is the fugacity of the hy

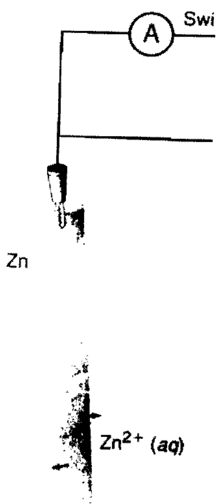
$$\phi_{H^+/H_2} =$$

For unit activities of all species,
$\phi^{\circ}_{H^+/H_2}$. Because $\mu^{\circ}_{H_2} = \Delta G^{\circ}_f(H_2,$

In Section 10.1 the convention
Therefore, we find that

We have shown that the standard hy
with zero potential against which th
schematic drawing of this electrode
short timescale, this reaction $H^+(aq$
alyst electrode. It is also necessary t
It is customary to use a Henry's law
and $\gamma_i \rightarrow 1$ as $c_i \rightarrow 0$. The standard
that shows ideal solution behavior at

The usefulness of the result $\phi^{\circ}_{H^+}$
be assigned to individual half-cells b
cell. For example, the cell potential o
the Zn/Zn^{2+} half-cell if the $H^+(aq)$
not directly measurable, absolute v
Supplemental Section 11.16 it is sho
gen electrode is −4.44 ± 0.02 V. F
energies can be measured, chemists
dard hydrogen electrode assuming th



wire connected with a voltmeter and to Cu(s) and Zn(s)

→ ϕ is measured between two different phases, Cu(s) and Zn(s)

⇒ ϕ between two connected half-cells can be measured but not the needed potential of one half-cell alone

⇒ one special half-cell is used as a reference with a half-cell potential defined as 0

then absolute half-cell potential for each half-cell can be measured by connecting it to the reference half-cell

reference: standard hydrogen electrode:

H_2 of 1 bar bubbles over a Pt electrode (catalyst) and immersed in an acid (HCl) at $a_{H^+} = 1$, H_2-fugacity also $f_{H_2} = 1$

reduction in the standard H_2 half-cells

$$H^+ + e^- \rightarrow \frac{1}{2} H_2$$

⇒ equilibrium condition in the half-cell:

$$\mu_{H^+(aq)} + \tilde{\mu}_{e^-} = \frac{1}{2}\mu_{H_2(g)}$$

half-cell reactions always written as reductions

also standard state potentials in tables are always for reduction

μ_i separated into a standard part and an activity dependent part

$\Rightarrow \mu^\circ_{H^+} + RT\ln a_{H^+} - F\phi_{H^+/H_2} = \frac{1}{2}\mu^\circ_{H_2} + \frac{1}{2}RT\ln f_{H_2}$

f_{H_2} : fugacity of the H_2 gas

solving ~~of~~ for ϕ_{H^+/H_2}:

$$\rightarrow \phi_{H^+/H_2} = \frac{\mu^\circ_{H^+} - \frac{1}{2}\mu^\circ_{H_2}}{F} - \frac{RT}{F}\ln\frac{\sqrt{f_{H_2}}}{a_{H^+}}$$

standard half-cell $\Rightarrow \ln\frac{\sqrt{f_{H_2}}}{a_{H^+}} = \ln 1 = 0$

and $\mu^\circ_{H_2} = \Delta G^\circ_f(H_2, g) = 0$ since H_2 is element

$$\rightarrow \phi^\circ_{H^+/H_2} = \frac{\mu^\circ_{H^+}}{F}$$

convention from 10.1 : $\cancel{\mu^\circ_{H_2}}$

$\Delta G^\circ_f(H^+, aq) = \mu^\circ_{H^+} = 0$

$\rightarrow \phi^\circ_{H^+/H_2} = 0$ with our conventions

$\Rightarrow$ standard H_2 can be used as reference with $\phi^\circ_{H^+/H_2} = 0$

Pt catalyst as electrode for fast equilibrium of $H^+ + e^- \rightleftharpoons \frac{1}{2}H_2$

standard state for a_{H^+}:

Henry's law standard state based on molarity: a solution of $H^+(aq)$ which behaves as ideal solution at $c^\circ = 1M$ (hypothetical, not real standard state)

half-cell potential of $Zn/ZnSO_4(aq)$ is assigned to measurement of ϕ together with standard hydrogen half-cell. in which $a_{H^+} = f_{H_2} = 1$

d use Equation (11.9) for the electrochemical potential of the electron. The equation then takes the form

$$\mu^{\circ}_{H^+} + RT \ln a_{H^+} - F\phi_{H^+/H_2} = \frac{1}{2}\mu^{\circ}_{H_2} + \frac{1}{2}RT \ln f_{H_2} \qquad \textbf{(11.12)}$$

is the fugacity of the hydrogen gas. Solving Equation (11.12) for ϕ_{H^+/H_2}

$$\phi_{H^+/H_2} = \frac{\mu^{\circ}_{H^+} - \frac{1}{2}\mu^{\circ}_{H_2}}{F} - \frac{RT}{F} \ln \frac{f^{1/2}_{H_2}}{a_{H^+}} \qquad \textbf{(11.13)}$$

ctivities of all species, the cell has its standard state potential, designated ecause $\mu^{\circ}_{H_2} = \Delta G^{\circ}_f(\mathrm{H_2}, g) = 0$,

$$\phi^{\circ}_{H^+/H_2} = \frac{\mu^{\circ}_{H^+}}{F} \qquad \textbf{(11.14)}$$

n 10.1 the convention that $\Delta G^{\circ}_f(H^+, aq) = \mu^{\circ}_{H^+} = 0$ was introduced. we find that

$$\phi^{\circ}_{H^+/H_2} = 0 \qquad \textbf{(11.15)}$$

hown that the standard hydrogen electrode is a convenient **reference electrode** otential against which the potentials of all other half-cells can be measured. A drawing of this electrode is shown in Figure 11.3. To achieve equilibrium on a cale, this reaction $\mathrm{H^+}(aq) + \mathrm{e^-} \rightleftharpoons 1/2\ \mathrm{H_2}(g)$ is carried out over a Pt catode. It is also necessary to establish a standard state for the activity of $\mathrm{H^+}(aq)$. nary to use a Henry's law standard state based on molarity. Therefore, $a_i \to c_i$ 1 as $c_i \to 0$. The standard state is a (hypothetical) aqueous solution of $\mathrm{H^+}(aq)$ ideal solution behavior at a concentration of $c^{\circ} = 1 \text{ mol L}^{-1}$.

efulness of the result $\phi^{\circ}_{H^+/H_2} = 0$ is that values for the electrical potential can d to individual half-cells by measuring their potential relative to the $\mathrm{H^+/H_2}$ half-ample, the cell potential of the electrochemical cell in Figure 11.4 is assigned to $^{2+}$ half-cell if the $\mathrm{H^+}(aq)$ and $\mathrm{H_2}(g)$ activities both have the value 1. Although y measurable, absolute values for half-cell potentials can be determined. In tal Section 11.16 it is shown that the absolute potential of the standard hydrode is −4.44 ± 0.02 V. Because only changes in energy rather than absolute n be measured, chemists generally use half-cell potentials relative to the stangen electrode assuming that $\phi^{\circ}_{H^+/H_2} = 0$.

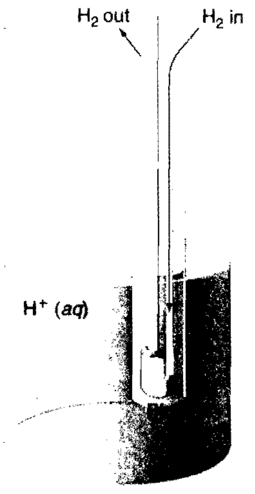


FIGURE 11.3
The standard hydrogen electrode consists of a solution of an acid such as HCl, $\mathrm{H_2}$ gas, and a Pt catalyst electrode that allows the equilibrium in the half-cell reaction to be established rapidly. The activities of $\mathrm{H_2}$ and $\mathrm{H^+}$ are equal to one.

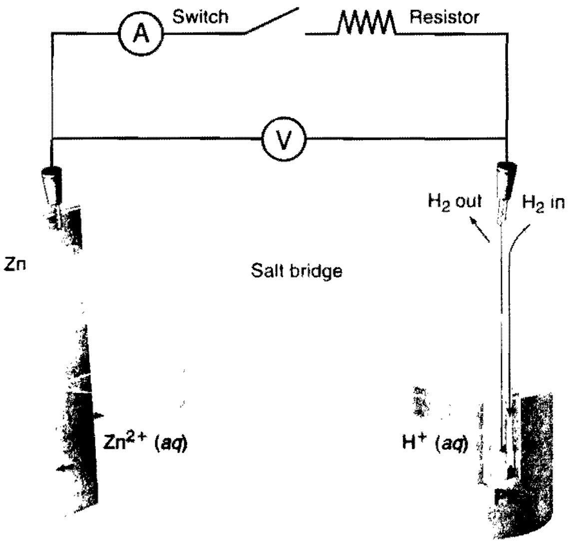


FIGURE 11.4
In a cell consisting of a half-cell and the standard hydrogen electrode, the entire cell voltage is assigned to the half-cell.

in 11.16 (not in our course) the ⑭-17 absolute half-cell potential of a standard hydrogen electrode is shown to be

$(-4.44 \pm 0.02)\,V$

emf: reversible cell potential

for a cell working reversible the current I must be $I = 0$

flowing $I \neq 0$: heat is produced

$\rightarrow$ cell working irreversibly when a current $I \neq 0$ flows

$\rightarrow$ for reversibly working cell current $\underline{I}$ must be $I = 0$!

put a dc source (battery) to a cell and change the dc-voltage until an ampere-meter show $I = 0$

then the dc voltage for this is the emf!

Daniell cell: Zn is dissolved leaving $2e$ at the $Zn(s)$ electrode for each dissolved Zn^{2+}

Cu^{2+} is deposited at the Cu electrode, taking up $2e^-$ for each deposited Cu^{2+}

$\rightarrow$ electrons flow through the wire from Zn to Cu

$\Rightarrow$ cell reactions:

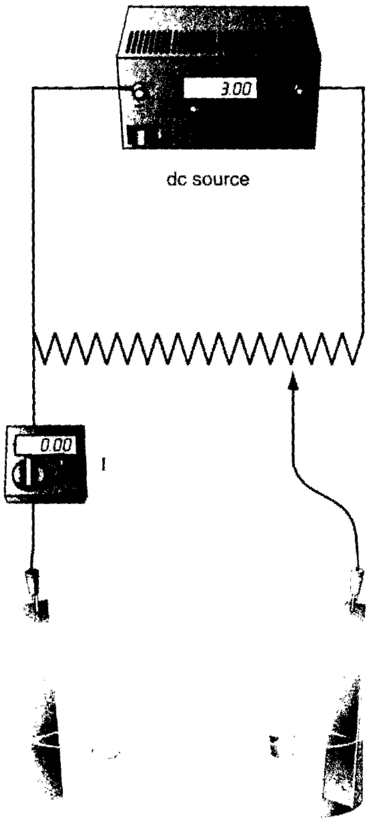


FIGURE 11.5
Schematic diagram showing how the reversible cell potential is measured.

Measurement of the Reversible Cell Potential

The cell potential measured under reversible conditions is directly related to the state functions *G*, *H*, and *S*. The reversible cell potential, also called **electromotive force (emf)**, is determined in an experiment depicted in Figure 11.5. The dc source provides a voltage to a potentiometer circuit with a sliding contact. The sliding contact is attached to the positive cell terminal as shown, and the slider is adjusted until the current-sensing device labeled *I* shows a null current. At this position of the potentiometer, the voltage applied through the potentiometer exactly opposes the cell potential. The voltage measured in this way is the reversible cell potential. If the sliding contact is moved to a position slightly to the left of this position, the electron current will flow through the external circuit in one direction. However, if the sliding contact is moved to a position slightly to the right of this position, the electron current will flow through the external circuit in the opposite direction, showing that the direction of the cell reaction has been reversed. Because a small variation of the applied voltage can reverse the direction of spontaneous change, the criterion for reversibility is established. This discussion also demonstrates that the direction of spontaneous change in the cell can be reversed by changing the electrochemical potential of the electrons in one of the electrodes relative to that in the other electrode using an external voltage source.

11.4 Chemical Reactions in Electrochemical Cells and the Nernst Equation

What reactions occur in the Daniell cell shown in Figure 11.2? If the half-cells are connected through the external circuit, Zn atoms leave the Zn electrode to form Zn^{2+} in solution, and Cu^{2+} ions are deposited as Cu atoms on the Cu electrode. In the external circuit, it is observed that electrons flow through the wires and the resistor in the direction from the Zn electrode to the Cu electrode. These observations are consistent with the following electrochemical reactions:

$$\text{Left half-cell: } Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \tag{11.16}$$

$$\text{Right half-cell: } Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \tag{11.17}$$

$$\text{Overall: } Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s) \tag{11.18}$$

In the left half-cell, Zn is being oxidized to Zn^{2+}, and in the right half-cell, Cu^{2+} is being reduced to Cu. By convention, the electrode at which oxidation occurs is called the **anode,** and the electrode at which reduction occurs is called the **cathode.** Each half-cell in an electrochemical cell must contain a species that can exist in an oxidized and a reduced form. For a general redox reaction, the reactions at the anode and cathode and the overall reaction can be written as follows:

$$\text{Anode: } Red_1 \rightarrow \mathrm{Ox}_1^{n_1+} + n_1e^- \tag{11.19}$$

$$\text{Cathode: } Ox_2 + n_2e^- \rightarrow \mathrm{Red}_2^{n_2-} \tag{11.20}$$

$$\text{Overall: } n_2\mathrm{Red}_1 + n_1\mathrm{Ox}_2 \rightleftharpoons n_2\mathrm{Ox}_1^{n_1+} + n_1\mathrm{Red}_2^{n_2-} \tag{11.21}$$

Note that electrons do not appear in the overall reaction because the electrons produced at the anode are consumed at the cathode.

How are the cell voltage and ΔG_R for the overall reaction related? This important relationship can be determined from the electrochemical potentials of the species involved in the overall reaction of the Daniell cell:

$$\begin{aligned} \Delta G_R &= \widetilde{\mu}_{Zn^{2+}} + \widetilde{\mu}_{Cu} - \widetilde{\mu}_{Cu^{2+}} - \widetilde{\mu}_{Zn} = \mu^{\circ}{}_{Zn^{2+}} - \mu^{\circ}{}_{Cu^{2+}} + RT\ln\frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \\ &= \Delta G_R^{\circ} + RT\ln\frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \end{aligned} \tag{11.22}$$

left: $Zn(s) \rightarrow Zn^{2+}_{(aq)} + 2e^-$ half-cell reaction

right: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

overall cell reactions: $Zn(s) + Cu^{2+}(aq) \rightleftarrows Zn^{2+}(aq) + Cu(s)$

left: Zn oxidized to Zn^{2+}

rights: Cu^{2+} reduced to Cu

Zn electrode in which oxidation occurs is called the anode

Cu electrode in which reduction occurs is called the cathode

anode: $Zn \,|\, ZnSO_4(aq)$ electrode

cathode: $Cu \,|\, CuSO_4(aq)$ electrode

general:

anode $Red_1 \rightarrow Ox_1^{n_1+} + n_1 e^-$

cathode $Ox_2 + n_2 e^- \rightarrow \cancel{n_2} Red_2^{n_2-}$

overall: n_2 · anode + n_1 cathode to cancel all $n_1 n_2$ electrons:

$$n_2 Red_1 + n_1 Ox_2 \rightleftarrows n_2 Ox_1^{n_1+} + n_1 Red^{n_2-}$$

in overall cell reactions if correct never free electrons occur;

e^- produced in anode are consumed in cathode!

$$\Delta G_R = \tilde{\mu}_{Zn^{2+}} + \tilde{\mu}_{Cu} - \tilde{\mu}_{Cu^{2+}} - \tilde{\mu}_{Zn}$$

(products - reactants)

$$= \mu^{\circ}_{Zn^{2+}} - \mu^{\circ}_{Cu^{2+}} + RT \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

$$= \Delta G^{\circ}_R + RT \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

$Q = \dfrac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$, $\underline{\text{no solids}}$ in Q

$$\Delta G_R = -\underset{\substack{\downarrow \\ \text{no. of } e^- \text{ exchanged} \\ \text{in the Redox reaction}}}{n} F \Delta\phi \leftarrow \text{measured cell potential}$$

if the cell works reversible then $\Delta\phi = E$

E; electromotrive force (emf)

$$\Rightarrow (n=2) \quad -2FE = \Delta G^{\circ}_R + RT \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

standard state $a_{Zn^{2+}} = a_{Cu^{2+}} = 1$, $\ln Q = \ln 1 = 0$

and $\Delta G^{\circ}_R = -2FE^{\circ}$

$$\Rightarrow E = E^{\circ} - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

since $\quad -2FE = -2FE^{\circ} + RT \ln \dfrac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$

divide by $-2F$

general: n electrons exchanged:

$$E = E^{\circ} - \frac{RT}{nF} \ln Q \quad \text{Nernst equation}$$

Q like equilibrium constant but with concentrations as they are in the cell not equilibrium concentrations

in Q: activities of product ions over activities of reactant ions each to the power of its stoichiometric coefficient in the reaction equation

no solids in Q

liquids are only in Q if the are dissolved, pure liquids are not in Q

gases are in Q as fucacities

for a half-cell: $Ox^{n+} + ne^- \rightleftharpoons Red$

$$E_{Ox/Red} = \underset{\substack{\uparrow \\ \text{always for reduction}}}{E^\circ_{Ox/Red}} - \frac{RT}{nF} \ln \frac{a_{Red}}{a_{Ox^{n+}}}$$

what is E_{H^+/H_2} if $a_{H^+} = 0.770$, $f_{H_2} = 1.13$

half cell reaction: $H^+ + e^- \rightleftharpoons \frac{1}{2} H_2$

$$E = E^\circ - \frac{0.05916\ V}{n} \log_{10} \frac{\sqrt{f_{H_2}}}{a_{H^+}}$$ error in book!

$\frac{RT}{F} = 59.16$ mV ~~in~~ at 298.15 K for $\log_{10}$!

$E^\circ_{H^+/H_2} = 0$ by definition!

$n = 1$

$$E = -0.05916\ V \log_{10} \frac{\sqrt{\cancel{f_{H_2}}}\ \sqrt{1.13}}{0.770} = -0.0083\ V$$

If this reaction is carried out reversibly, the electrical work done is equal to the product of the charge and the potential difference through which the charge is moved. However, the reversible work at constant pressure is also equal to ΔG. Therefore, we can write the following equation:

$$\Delta G_R = -nF\Delta\phi \qquad \textbf{(11.23)}$$

In Equation (11.23), $\Delta\phi$ is the measured potential difference generated by the spontaneous chemical reaction for particular values of $a_{Zn^{2+}}$ and $a_{Cu^{2+}}$, and n is the number of moles of electrons involved in the redox reaction. The measured cell voltage is directly proportional to ΔG. For a reversible reaction, the symbol E is used in place of $\Delta\phi$, and E is referred to as the **electromotive force (emf).** Using this definition, we rewrite Equation (11.23) as follows:

$$-2FE = \Delta G_R^\circ + RT \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \qquad \textbf{(11.24)}$$

For standard state conditions, $a_{Zn^{2+}} = a_{Cu^{2+}} = 1$, and Equation (11.24) takes the form $\Delta G_R^\circ = -2FE^\circ$. This definition of E° allows Equation (11.24) to be rewritten as

$$E = E^\circ - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \qquad \textbf{(11.25)}$$

For a general overall electrochemical reaction involving the transfer of n moles of electrons,

$$E = E^\circ - \frac{RT}{nF} \ln Q \qquad \textbf{(11.26)}$$

where Q is the familiar reaction quotient. The preceding equation is known as the **Nernst equation.** At 298.15 K, the Nernst equation can be written in the form

$$E = E^\circ - \frac{0.05916 \text{ V}}{n} \log_{10} Q \qquad \textbf{(11.27)}$$

This function is graphed in Figure 11.6. The Nernst equation allows the emf for an electrochemical cell to be calculated if the activity is known for each species and if E° is known.

The Nernst equation has been derived on the basis of the overall cell reaction. For a half-cell, an equation of a similar form can be derived. The equilibrium condition for the half-cell reaction

$$\text{Ox}^{n+} + ne^- \rightleftharpoons \text{Red} \qquad \textbf{(11.28)}$$

s given by

$$\mu_{Ox^{n+}} + n\tilde{\mu}_{e^-} = \mu_{Red} \qquad \textbf{(11.29)}$$

Using the convention for the electrochemical potential of an electron in a metal electrode [Equation (11.9)], Equation (11.29) can be written in the form

$$\mu^\circ_{Ox^{n+}} + RT \ln a_{Ox^{n+}} - nF\phi_{Ox/Red} = \mu^\circ_{Red} + RT \ln a_{Red}$$

$$\phi_{Ox/Red} = -\frac{\mu^\circ_{Red} - \mu^\circ_{Ox^{n+}}}{nF} - \frac{RT}{nF} \ln \frac{a_{Red}}{a_{Ox^{n+}}}$$

$$E_{Ox/Red} = E^\circ_{Ox/Red} - \frac{RT}{nF} \ln \frac{a_{Red}}{a_{Ox^{n+}}} \qquad \textbf{(11.30)}$$

The last line in Equation (11.30) has the same form as the Nernst equation, but the ctivity of the electrons does not appear in Q. An example of the application of Equation (11.30) to a half-cell reaction is shown in Example Problem 11.1.

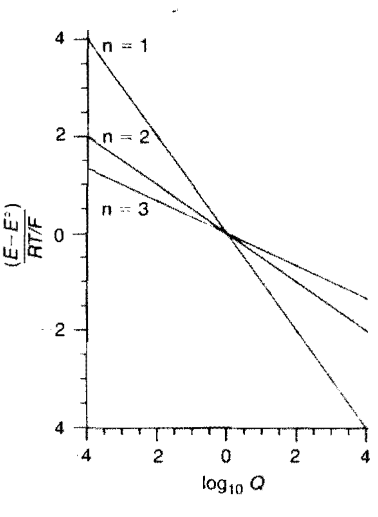


FIGURE 11.6
The cell potential E varies linearly with log Q. The slope of a plot of $(E - E^\circ)/(RT/F)$ is inversely proportional to the number of electrons transferred in the redox reaction.

EXAMPLE PROBLEM 11.1

Calculate the potential of the H^+/H_2 half-cell when $a_{H^+} = 0.770$ and $f_{H_2} = 1.13$.

Solution

$$E = E^\circ - \frac{0.05916 \text{ V}}{n} \log_{10} \frac{a_{H^+}}{\sqrt{f_{H_2}}} = 0 - \frac{0.05916 \text{ V}}{1} \log_{10} \frac{0.770}{\sqrt{1.13}} = 0.0083 \text{ V}$$

App. B Tables 11.1 and 11.2:
half-cell standard potentials are listed, as always the reduction potentials

$$E^\circ(\text{reduction}) = -E^\circ(\text{oxidation})$$

half-cell standard potential is intensive and does not change if reaction is multiplied by an integer

ΔG_R°, n are both ~~intensive~~ extensive, but their ratio $\frac{\Delta G_R^\circ}{nF} = -E^\circ$ is intensive

$$E^\circ_{cell} = E^\circ_{reduction} + E^\circ_{oxidation}$$

$$= E^\circ_{reduction_1} - E^\circ_{reduction_2}$$

E or also half-cell potentials do not change when the reaction (cell or half-cell reaction) is multiplied with an integer

Given (i) $Fe(OH)_2(s) + 2e^- \rightarrow Fe(s) + 2OH^-(aq)$

$E^\circ = -0.877$ V

combined with half-cells

(a) $Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ $E^\circ = -1.66V$

or (b) $AgBr(s) + e^- \rightarrow Ag(s) + Br^-(aq)$ $E^\circ = 0.071V$

what are the spontaneous cell reactions for the cells (a) and (b)?

(a) one reaction must be reversed ⑭-22
to oxidation, for example reaction (a)

half-cell$_1$: $Fe(OH)_2(s) + 2e^- \rightarrow Fe(s) + 2OH^-(aq)$ | · 3
half-cell$_2$: $Al(s)$ ~~+3e~~ $\rightarrow Al^{3+}(aq) + 3e^-$ | · 2
cell reaction (cancel 6 electrons)

$$3Fe(OH)_2(s) + 2Al(s) \rightarrow 3Fe(s) + 6OH^-(aq) + 2Al^{3+}(aq)$$

$E^\circ = E^\circ_1(\text{reduction}) - E^\circ_2(\text{reduction})$
$= (\cancel{-0.087} -0.877 - (-1.66))\ V$
$= -0.877\ V + 1.66\ V = 0.783\ V$

E° positive ⇒ the above cell reaction is spontaneous and in the cell $Fe(OH)_2$ is reduced and Al oxidized

(b) for example reaction (b) is reversed to oxidations

half-cell$_1$: $Fe(OH)_2(s) + 2e^- \rightarrow Fe(s) + 2OH^-(aq)$
half-cell$_2$: ~~$AgBr(s) + e^- + e^- \rightarrow Ag(s) + Br^-$~~ (aq)
$Ag(s) + Br^-(aq) \rightarrow AgBr(s) + e^-$ | · 2

overall cell reaction (cancel $2e^-$)
$$Fe(OH)_2(s) + 2Ag(s) + 2Br^-(aq) \rightarrow Fe(s) + 2OH^- + 2AgBr(s)$$

$E^\circ = E^\circ_1(\text{reduction}) - E^\circ_2(\text{reduction})$
$= -0.877\ V - (\cancel{0} -0.071)\ V$
$= -0.877\ V + 0.071\ V$
$= -0.95 V$

⇒ The $\overset{E^\circ<0}{\text{above}}$ reaction happens reversed in the cell

⇒ real cell reaction:

$$Fe(s) + 2OH^-(aq) + 2AgBr(s) \rightleftharpoons Fe(OH)_2(s) + 2Ag(s) + 2Br^-(aq)$$

⇒ in cell b Fe is oxidized ~~an~~ to $Fe(OH)_2$ and AgBr is reduced to Ag

ΔG is state function ⇒ E° for a half-cell can be calculated from the E° values of 2 other halfcell if they have a reaction in common (Hess's law). only extensive ΔG° values can be directly combined, not intensive E° values!

given: (1) $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $E^\circ_1 = 0.771\,V$

(2) $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $E^\circ_2 = -0.447\,V$

what is E° for (3) $Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$

step 1

combine the given reaction equation such that the asked one comes out

to have $Fe^{3+}(aq)$ on the right side (1) should be used as it is

to get Fe(s) on the right side, also (2) should be used as it is.

check if (1) + (2) $\overset{?}{=}$ (3)

(1) + (2): ✓

$Fe^{3+}(aq) + e^- + Fe^{2+}(aq) + 2e^-$ ✓

$\rightarrow Fe^{2+}(aq) + Fe(s)$

$Fe^{2+}(aq)$ cancels

(1) + (2): $Fe^{3+}(aq) + 3e^- + Fe(s) = (3)$

step 2

combine ΔG^0_R in the same way as you combined the equations:

$$\Delta G^0_3 = \Delta G^0_1 + \Delta G^0_2$$

$$-n_3 F E^0_3 = -n_1 F E^0_1 - n_2 F E^0_2$$

$$E^0_3 = \frac{1}{n_3}(n_1 E^0_1 + n_2 E^0_2) \qquad n_1 = 1, \; n_2 = 2$$

$$= \frac{1}{3}(0.771 - 2 \cdot 0.447)\,V$$

$$= \frac{1}{3}(-0.123)\,V = -0.041\,V$$

$$= -41\,mV$$

given

(1) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad E^0_1 = 1.507\,V$

(2) $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \quad E^0_2 = 1.679\,V$

What is E^0_3 for

(3) $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$

step 1 to get MnO_2 on the left side we have to reverse (2) then MnO_4^- is cancelled and Mn^{2+} is on the right

$\Rightarrow$ trial: is (3) $\overset{?}{=}$ (1) − (2) ? :

(1) − (2):

$$\cancel{MnO_4^-} + \underset{4H^+}{8\cancel{H^+}} + \underset{2e^-}{\cancel{5e^-}} + MnO_2 + 2\cancel{H_2O}$$

$$\longrightarrow Mn^{2+} + \underset{2H_2O}{4\cancel{H_2O}} + \cancel{MnO_4^-} + 4\cancel{H^+} + 3\cancel{e^-}$$

$$= MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O \quad = (3)$$

$$\Rightarrow \Delta G_3^\circ = \Delta G_1^\circ - \Delta G^\circ(2)$$

$$-n_3 F E_3^\circ = -n_1 F E_1^\circ - (-n_2 F E_2^\circ)$$

$$-n_3 F E_3^\circ = -n_1 F E_1^\circ + n_2 F E_2^\circ$$

$$E_3^\circ = \frac{1}{n_3}(\cancel{E^\circ}\, n_1 E_1^\circ - n_2 E_2^\circ)$$

$$= \frac{1}{2}(5 \cdot 1.507 - 3 \cdot 1.679)\ V$$

$$= 1.249\ V$$

ΔG_R° and ΔS_R° from emf

$$\Delta G_R = -nF\Delta\phi$$

→ standard conditions, reversible:

$$\Delta G_R^\circ = -nFE^\circ$$

Daniell cell: $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$

$E^\circ = 1.10\,V$

$$\Rightarrow \Delta G_R^\circ = -nFE^\circ = 2 \cdot 96485 \frac{As}{mol} \cdot 1.10\,V = -212 \frac{kJ}{mol}$$

$1\,VAs = 1\,J$

measure E° as $f(T)$, then $\left(\frac{\partial E^\circ}{\partial T}\right)_p$ is slope if E° vs T is linear, if not, the slope ~~at~~ of the tangent at the $E^\circ(T)$ curve at desired T

cell: $Cl_2(g)|Cl^-(aq)$ half-cell + standard hydrogen electrode (SHE)

SHE: H_2 of 1 bar fugacity bubbles over Pt electrode in $a_{H^+} = 1$ acid solution

$$E^\circ_{Cl_2|Cl^-} = 1.36\,V$$

further $\left(\frac{\partial E^\circ}{\partial T}\right)_p = -1.20 \cdot 10^{3}\,\frac{V}{K}$

cell reaction: $H_2(g) + Cl_2(g) \rightleftharpoons 2H^+(aq) + 2Cl^-(aq)$

$n = 2$

$\Delta S_R^\circ = ?$ compare with Table 10.1 in App B

$$\Delta S_R^\circ = -\left(\frac{\partial \Delta G_R^\circ}{\partial T}\right)_p = nF\left(\frac{\partial E^\circ}{\partial T}\right)_p$$

$$= 2 \cdot 96485 \frac{As}{mol} \cdot \left(-1.2 \cdot 10^{3} \frac{V}{K}\right)$$

$$= -2.3 \cdot 10^{2} \frac{J}{K\,mol} = -0.23 \frac{kJ}{K\,mol}$$

Table 10.1 App. B ⑭ - 27

$$\Delta S_R^\circ = \underset{\text{products}}{\sum_i \nu_i S^\circ_{m,i}} - \underset{\text{reactants}}{\sum_i \nu_i S^\circ_{m,i}}$$ here: all $\nu_i > 0$

$$\Delta S_R^\circ = 2\,\underbrace{S_m^\circ(H^+,aq)}_{=0 \text{ by convention}} + 2\,S_m^\circ(Cl^-,aq) - S_m^\circ(H_2,g) - S_m^\circ(Cl_2,g)$$

$$= (2\cdot 0 + 2\cdot 56{,}5 - 130{,}7 - 223{,}1)\,\frac{J}{K\,mol}$$

$$= -2.408\cdot 10^2\,\frac{J}{K\,mol} = -0{,}2408\,\frac{kJ}{K\,mol}$$

error because $E^\circ(T)$ measurement not too precise

if $\Delta G = 0$ and thus $E = 0$ the cell reaction is in equilibrium $\Rightarrow Q = K$ in equilibrium

$$\Rightarrow E^\circ = \frac{RT}{nF}\ln K \text{ in equilibrium}$$

$\Rightarrow E^\circ$ measured at all $a_i = 1 \rightarrow K$

usually other way used, since to prepare all $a_i = 1$ not so easy

to use table values of E°, n must be determined:

$$2MnO_4^-(aq) + 6H^+(aq) + 5(COOH)_2 \text{ (oxalic acid) } (3)$$

$$\rightleftharpoons 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g) \quad 25°C$$

half-reactions (to get n):

red. $\overset{+7}{Mn}O_4^- + 8H^+ + 5e^- \longrightarrow \overset{+2}{Mn}{}^{2+} + 4H_2O$ $\quad n_1 = 5$, $E^\circ = 1.51V$ (1)

ox. $(COOH)_2 \longrightarrow 2H^+ + 2\overset{+4}{C}O_2 + 2e^-$ $\quad n_2 = 2$, $E^\circ = 0{,}49V$ (2)

charge 0 on both sides $\Rightarrow 2e^-$ right

to cancel electrons: $(1)\cdot 2 + (2)\cdot 5 = (3)$

$$\Rightarrow n = 2\cdot 5 = 10$$

E° unchanged by $n=10$ multiplication

but ΔG° ⑭-28

$$\Delta G^\circ = -nFE^\circ = -10 \cdot 96485 \frac{As}{mol} \cdot (1{,}51 V + 0{,}49 V)$$

E° unchanged by $2 \cdot (1)$ and $5 \cdot (2)$

$$= -1{,}93 \cdot 10^2 \frac{kJ}{mol}$$

$$\Delta G^\circ = -RT \ln K$$

$$\Rightarrow \ln K = -\frac{\Delta G^\circ}{RT} = \frac{1{,}93 \cdot 10^2 \, kJ/mol}{8{,}314 \frac{J}{K\,mol} \cdot 298{,}15\,K} = 778$$

⇒ Equilibrium = 100% conversion reactants → products

~~Daniell~~ Daniell cell $E^\circ = 1{,}10\,V$ K at 25°C

$$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$$

$$\Rightarrow \ln K = -\frac{\Delta G_R^\circ}{RT} = \frac{\cancel{2 \cdot 96}\; 2 \cdot 96485 \frac{As}{mol} \cdot 1.10\,V}{8{,}314 \frac{J}{K\,mol} \cdot 298.15\,K}$$

$$= 85{,}63$$

$$\rightarrow K = exp(85{,}63) = 1.55 \cdot 10^{37}$$

→ ~~so~~ spectroscopic methods not accurate enough to measure $a_{Zn^{2+}}$ and $a_{Cu^{2+}}$

measurement must be accurate over 30 orders

However, in electrochem. cells only voltmeter accurate for 1.10 V is needed

$AgBr(s) + e^- \rightarrow Ag(s) + Br^-(aq)$ $E^\circ = 0{,}07133\,V$

$Ag(s) \rightarrow Ag^+(aq) + e^-$ $E^\circ = -0{,}7996\,V$

---

overall: $AgBr(s) \rightleftharpoons$ ~~Ag + Br~~ $Ag^+(aq) + Br^-(aq)$

$$E^\circ_{cell} = (0.07133 - 0.7996)V = -0.7283\,V$$

$Ag(s)\,|\,AgNO_3(aq)\,|\,AgBr(s)\,|\,Ag(s)$ 25°C

$\Delta G^\circ = -RT\ln K_{sp}$ equil.: $Q = K_{sp}$, $E = 0$

$E = 0 = E^\circ - \frac{RT}{nF}\ln K_{sp}$ ⑲ − 29

$n=1$ $\ln K_{sp} = \frac{nFE^\circ}{RT}$

$$= \frac{1.96485\,\frac{As}{mol}\,(-0{,}7283\,V)}{8{,}314\,\frac{J}{K\,mol}\cdot 298.15\,K}$$

$= -28{,}35$

$\rightarrow K_{sp} = \exp(-28{,}35) = 4.88\cdot 10^{-13}$

concentration cell:

2 half-cells, identical, but different a values

$Ag(s)|\,AgNO_3\,(aq,\,a=1)\,||\,Ag(NO_3)\,(aq,\,a_\pm=1) + NaCl\,(aq)\overbrace{)\,||}^{|AgCl(s)}Ag(s)$

just enough NaCl(aq) added in the right half-cell that all $Ag^+(aq)$ is precipitated as AgCl(s)

overall cell reaction?

$E = 0{,}29\,V$, $K_{sp} = ?$ for AgCl?

cell reaction: $AgCl(s) \rightleftharpoons Ag^+(aq,\,a_\pm) + Cl^-(aq,\,a_\pm)$

$\Rightarrow K_{sp} = a_{Ag^+}\,a_{Cl^-} = a_\pm^2$, $n=1$

$E^\circ = 0$ since in both half-cells it is $E^\circ_{Ag^+|Ag}$

when $E = 0{,}29\,V$:

$$E = -\frac{59.16\cdot 10^{-3}\,V}{n}\log_{10}\frac{a_\pm}{1}\begin{matrix}\leftarrow \text{right}\\ \leftarrow \text{left}\end{matrix}$$

$K_{sp} = a_\pm^2 \Rightarrow a_\pm = \sqrt{K_{sp}}$

$$E = -\frac{59.16\cdot 10^{-3}\,V}{1}\log_{10}\sqrt{K_{sp}}$$

$\log_{10}\sqrt{K_{sp}} = \frac{1}{2}\log_{10}K_{sp}$ ⑭-30

$E = -\frac{59.16\cdot10^{-3}\,V}{2}\log_{10}K_{sp}$

$\log_{10}K_{sp} = -\frac{2E}{0.05916\,V} = -\frac{2\cdot0.29\,V}{0.05916\,V}$

$= -9.804$

$\rightarrow K_{sp} = 1.57\cdot10^{-10}$

problem for E° measurement: $\gamma_\pm = f(c_{solute})$

measure at c so low, that $\gamma_\pm \rightarrow 1$, not at 1M

example: cell: Ag^+/Ag vs SHE at 25°C

reaction: $Ag^+(aq) + \frac{1}{2}H_2(g) \rightleftharpoons Ag(s) + H^+(aq)$

$\Rightarrow Q = \frac{1}{a_{Ag^+}}$

$f_{H_2} = 1,\ a_{H^+} = 1$ (SHE), so not in Q!

Ag^+ from dissociation of $AgNO_3$

$a_\pm^{\nu} = a_+^{\nu_+}a_-^{\nu_-}$

with ~~Ag~~ $AgNO_3$, $a_\pm^2 = a_{Ag^+}a_{NO_3^-}$

thus $a_\pm = a_{Ag^+} = a_{NO_3^-}$

Further $\gamma_\pm = \gamma_{Ag^+} = \gamma_{NO_3^-}$

and $m_{Ag^+} = m_{NO_3^-} = m_\pm = m$

$\Rightarrow E - E^\circ_{Ag^+/Ag} + \frac{RT}{F}\ln a_{Ag^+} = E^\circ_{Ag^+/Ag} + \frac{RT}{F}\ln\frac{m}{m^\circ} + \frac{RT}{F}\ln\gamma_\pm$

$\uparrow$ $a_{H^+} = 1$

not $-$, since $\ln\frac{1}{a_{Ag^+}} = -\ln a_{Ag^+}$

and $a_{H^+} = 1$

if c is small enough that DHLL is ok

$\rightarrow \log_{10}\gamma_\pm = -0.509$ ~~$\log_{10}$~~ $\sqrt{\frac{m_\pm}{m^\circ}}$ at 25°C

⑤

$$\Rightarrow E - \frac{RT}{F} \ln \frac{m}{m^\circ} = E - \overset{0.05916\,V}{\cancel{0.59}} \log_{10}\left(\frac{m}{m^\circ}\right)$$

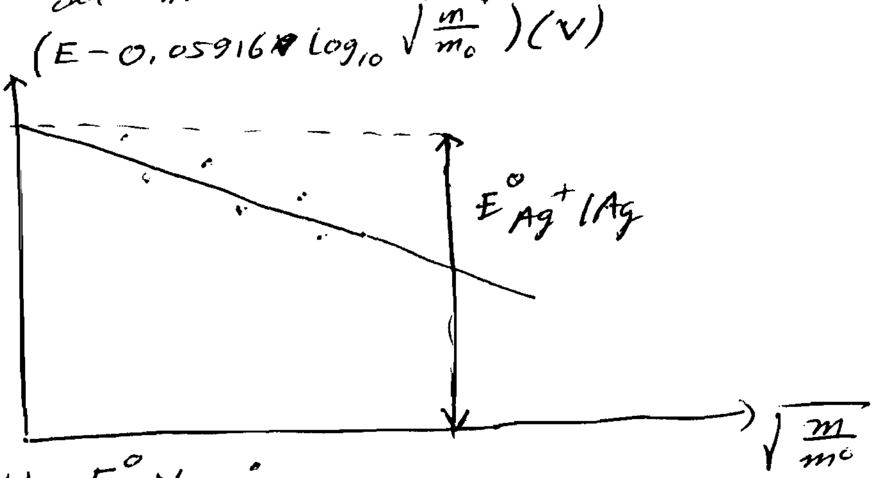
$$= E^\circ_{Ag^+/Ag} - 0.0516 \cdot 0.5092\,V \sqrt{\frac{m}{m^\circ}} \quad ⑭-31$$

$$\underbrace{E - 0.05916\,V \log_{10}\left(\frac{m}{m^\circ}\right)}_{\text{from measurements}} = E^\circ_{Ag^+/Ag} - 0.03011\,V\sqrt{\frac{m}{m^\circ}}$$

plot $\left(E - 0.05916\,V \log_{10}\left(\frac{m}{m_0}\right)\right)$ vs $\sqrt{\frac{m}{m^\circ}}$

→ straight line with $E^\circ_{Ag^+/Ag}$ as intercept

at $m = 0$



with $E^\circ_{Ag^+/Ag}$:

$$\frac{RT}{F} \ln \gamma_\pm = E - E^\circ_{Ag^+/Ag} - \frac{RT}{F} \ln \frac{m}{m_0}$$

to get $\gamma_\pm = f\left(\frac{m}{m^\circ}\right)$

DHLL was used to get $E^\circ_{Ag^+/Ag}$, but was <u>not</u> used to get $\gamma_\pm$

⇒ DHLL not needed to get $\gamma_\pm$

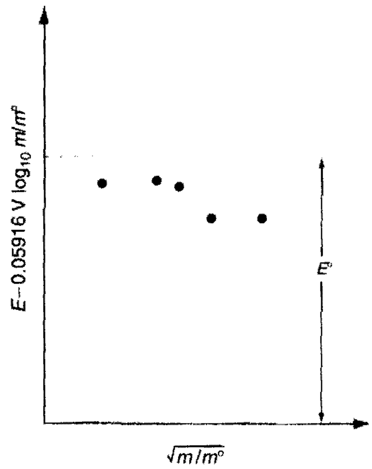


FIGURE 11.7

The value of $E°$ and the activity coefficient can be measured by plotting the left-hand side of Equation (11.42) against the square root of the molality.

Determination of $E°$ and Activity Coefficients Using an Electrochemical Cell

The main problem in determining standard potentials lies in knowing the value of the activity coefficient $\gamma_\pm$ for a given solute concentration. The best strategy is to carry out measurements of the cell potential at low concentrations, where $\gamma_\pm \rightarrow 1$, rather than near unit activity, where $\gamma_\pm$ differs appreciably from 1. Consider an electrochemical cell consisting of the Ag^+/Ag and standard hydrogen electrode half-cells at 298 K. The cell reaction is $Ag^+(aq) + 1/2\, H_2(g) \rightleftharpoons Ag(s) + H^+(aq)$ and $Q = (a_{Ag^+})^{-1}$. Because the activities of $H_2(g)$ and $H^+(aq)$ are 1, they do not appear in Q. Assume that the Ag^+ arises from the dissociation of $AgNO_3$. Recall that the activity of an individual ion cannot be measured directly. It must be calculated from the measured activity $a_\pm$ and the definition $a_\pm^\nu = a_+^{\nu+} a_-^{\nu-}$. In this case, $a_\pm^2 = a_{Ag^+} a_{NO_3^-}$ and $a_\pm = a_{Ag^+} = a_{NO_3^-}$. Similarly $\gamma_\pm = \gamma_{Ag^+} = \gamma_{NO_3^-}$ and $m_{Ag^+} = m_{NO_3^-} = m_\pm = m$, and E is given by

$$E = E^\circ_{Ag^+/Ag} + \frac{RT}{F} \ln a_{Ag^+} = E^\circ_{Ag^+/Ag} + \frac{RT}{F} \ln(m/m^\circ) + \frac{RT}{F} \ln \gamma_\pm \qquad \textbf{(11.41)}$$

At low enough concentrations, the Debye–Hückel limiting law is valid and $\log \gamma_\pm = -0.5092\sqrt{m_\pm/m^\circ}$ at 298 K as discussed in Section 10.4. Using this relation, Equation (11.41) can be rewritten in the form

$$\begin{aligned} E - 0.05916 \log_{10}(m/m^\circ) &= E^\circ_{Ag^+/Ag} - 0.05916 \times 0.5090\sqrt{(m/m^\circ)} \\ &= E^\circ_{Ag^+/Ag} - 0.03011\sqrt{(m/m^\circ)} \end{aligned} \qquad \textbf{(11.42)}$$

The left-hand side of this equation can be calculated from measurements and plotted as a function of $\sqrt{(m/m^\circ)}$. The results will resemble the graph shown in Figure 11.7. An extrapolation of the line that best fits the data to $m = 0$ gives $E°$ as the intercept with the vertical axis. Once $E°$ has been determined, Equation (11.41) can be used to calculate $\gamma_\pm$.

Electrochemical cells provide a powerful method of determining activity coefficients because cell potentials can be measured more accurately and more easily than colligative properties such as freezing point depression or boiling point elevation. Note that although the Debye–Hückel limiting law was used to determine $E°$, it is not necessary to use the limiting law to calculate activity coefficients once $E°$ is known.

Cell Nomenclature and Types of Electrochemical Cells

It is useful to use an abbreviated notation to describe an electrochemical cell. This notation includes all species involved in the cell reaction and phase boundaries within the cell, which are represented by a vertical line. As will be seen later in this section, the metal electrodes appear at the ends of this notation, the half-cell in which oxidation occurs is written on the left, and the electrode is called the anode. The half-cell in which reduction occurs is written on the right, and the electrode is called the cathode.

We briefly discuss an additional small contribution to the cell potential that arises from the differing diffusion rates of large and small ions in an electrical field. As an electrochemical reaction proceeds, ions that diffuse rapidly across a liquid–liquid junction, such as H^+, will travel farther than ions that diffuse slowly, such as Cl^-, in a given time. At steady state, a dipole layer is built up across this junction, and the rates of ion transfer through this dipole layer become equal. This kinetic effect will give rise to a small **junction potential** between two liquids of different composition or concentration. Such a junction potential is largely eliminated by a salt bridge. An interface for which the junction potential has been eliminated is indicated by a pair of vertical lines.The separation of different phases that are in contact and allow electron transfer is shown by a solid vertical line. A single dashed line is used to indicate a liquid–liquid interface across which charge transfer can occur.

cell symbol:

metal electrodes on left and right end of the symbol

| correspond to phase boundaries

|| corresponds to a salt bridge

left: half-cell where oxidation happens
= anode

right: half-cell where reduction happens
= cathode

example: $Zn(s) \mid ZnSO_4(aq, c) \parallel CuSO_4(aq, c) \mid Cu(s)$

$Zn \mid Zn^{2+}$ + SHE:

$Zn(s) \mid ZnSO_4(aq, c) \parallel H^+(aq) \mid H_2(g) \mid Pt(s)$

cell example:

$Ag(s) \mid AgCl(s) \mid Cl^-(aq,\ a_\pm = 0.0010 \parallel Fe^{2+}(aq,\ a_\pm = 0.50)$

$Fe^{3+}(aq,\ a_\pm = 0.10) \mid Pt(s)$

half-cell reactions, overall cell reaction?

anode (ox.): $Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e^-$

cathode (red.): $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$

overall (add equations simply, since n = 1 in both):

$\cancel{Ag^+}\ Ag(s) + Cl^-(aq) + Fe^{3+}(aq) \rightarrow AgCl(s) + Fe^{2+}(aq)$

SHE: $H_2 \mid H^+$

other one similar: $Cl_2 \mid Cl^-$: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$
$E^\circ = 1.36\ V$

metal in metal solution:

e.g.: $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $E^\circ = -0.76\ V$

Ag/AgCl half-cell

$AgCl(s) + e^- \rightarrow Ag^+(\overset{s}{\cancel{aq}}) + Cl^-(aq)$, $E^\circ = \overset{0.22}{\cancel{0.27}}\ V$

calomel (mercurous chloride) electrode: ⑭-33

$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$

calomel $E^0 = 0.27\ V$

<u>common</u> ox and red both in cell solution with Pt electrode,

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $E^0 = 0.771\ V$

cell from two half-cells:

$$E^0_{cell} = E^0_1 - E^0_2 = E^0_{right} - E^0_{left}$$

~~left~~ ~~right~~

$E^0_{cell} > 0$ and thus $\Delta G < 0$ if reduction potential for 1 is more positive than that for 2

<u>electrochemical series</u> oxidation of neutral metals to their most common oxidation state

for example

$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$ $E^0 = 1.498\ V$

Au^{3+} most common for Au, not Au^+

the chemical higher in the series will be reduced, the one lower will be oxidized in the spontaneous cell reaction

reduction of MnO_4^- to Mn^{2+} in acidic solution:

$E^0 = 1.51\ V$

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $E^0 = -0.7618\ V$

$Ag^+(aq) + e^- \rightarrow Ag(s)$ $E^0 = 0.7996\ V$

$Au^+(aq) + e^- \rightarrow Au(s)$ $E^0 = 1.692\ V$

TABLE 11.3
The Electrochemical Series

Most Strongly Reducing
(The metal is least easily oxidized.)

Gold
(most positive reduction potential)
Platinum
Palladium
Silver
Rhodium
Copper
Mercury
(Hydrogen; zero reduction potential by convention)
Lead
Tin
Nickel
Iron
Zinc
Chromium
Vanadium
Manganese
Magnesium
Sodium
Calcium
Potassium
Rubidium
Cesium
Lithium
(most negative reduction potential)

Least Strongly Reducing
(The metal is most easily oxidized.)

11.10 The Electrochemical Series

Tables 11.1 and 11.2 (see Appendix B, Data Tables) list the reduction potentials of commonly encountered half-cells. The emf of a cell constructed from two of these half-cells with standard reduction potentials E°_1 and E°_2 is given by

$$E^\circ_{cell} = E^\circ_1 - E^\circ_2 \qquad \textbf{(11.50)}$$

The potential E°_{cell} will be positive and, therefore, $\Delta G < 0$, if the reduction potential for reaction 1 is more positive than that of reaction 2. Therefore, the relative strength of a species as an oxidizing agent follows the order of the numerical value of its reduction potential in Table 11.2. The **electrochemical series** shown in Table 11.3 is obtained if the oxidation of neutral metals to their most common oxidation state is considered. For example, the entry for gold in Table 11.3 refers to the reduction reaction

$$\mathrm{Au^{3+}}(aq) + 3\mathrm{e^-} \rightarrow \mathrm{Au}(s) \quad E^\circ = 1.498\ \mathrm{V}$$

In a redox couple formed from two entries in the list shown in Table 11.3, the species lying higher in the list will be reduced, and the species lying lower in the list will be oxidized in the spontaneous reaction. For example, the table predicts that the spontaneous reaction in the copper–zinc couple is $\mathrm{Zn}(s) + \mathrm{Cu^{2+}}(aq) \rightarrow \mathrm{Zn^{2+}}(aq) + \mathrm{Cu}(s)$ and not the reverse reaction.

EXAMPLE PROBLEM 11.8

For the reduction of the permanganate ion $\mathrm{MnO_4^-}$ to $\mathrm{Mn^{2+}}$ in an acidic solution, $E^\circ = +1.51\ \mathrm{V}$. The reduction reactions and standard potentials for $\mathrm{Zn^{2+}}$, $\mathrm{Ag^+}$, and $\mathrm{Au^+}$ are given here:

$$\mathrm{Zn^{2+}}(aq) + 2\mathrm{e^-} \rightarrow \mathrm{Zn}(s) \qquad E^\circ = -0.7618\ \mathrm{V}$$

$$\mathrm{Ag^{+}}(aq) + \mathrm{e^-} \rightarrow \mathrm{Ag}(s) \qquad E^\circ = 0.7996\ \mathrm{V}$$

$$\mathrm{Au^{+}}(aq) + \mathrm{e^-} \rightarrow \mathrm{Au}(s) \qquad E^\circ = 1.692\ \mathrm{V}$$

Which of these metals will be oxidized by the $\mathrm{MnO_4^-}$ ion?

Solution

The cell potentials assuming the reduction of the permanganate ion and oxidation of the metal are

$$\mathrm{Zn}:\ 1.51\ \mathrm{V} + 0.761\ \mathrm{V} = 2.27\ \mathrm{V} > 0$$

$$\mathrm{Ag}:\ 1.51\ \mathrm{V} - 0.7996\ \mathrm{V} = 0.710\ \mathrm{V} > 0$$

$$\mathrm{Au}:\ 1.51\ \mathrm{V} - 1.692\ \mathrm{V} = -0.18\ \mathrm{V} < 0$$

If $E^\circ > 0$, $\Delta G < 0$. On the basis of the sign of the cell potential, we conclude that only Zn and Ag will be oxidized by the $\mathrm{MnO_4^-}$ ion.

11.11 Thermodynamics of Batteries and Fuel Cells

Batteries and fuel cells are electrochemical cells that are designed to maximize the ratio of output power to the cell weight or volume. **Batteries** contain the reactants needed to support the overall electrochemical reaction, whereas **fuel cells** are designed to accept a continuous flow of reactants from the surroundings. Batteries that cannot be recharged are called primary batteries, whereas rechargeable batteries are called secondary batteries.

which one is oxidized by MnO_4^- in the acidic?

Zn oxidation: $1.51 V + 0.762 V = 2.27 V > 0$

Zn will be oxidized, MnO_4^- reduced ⑭-34

Ag oxidation: $1.51 V - 0.7996 V = 0.710 V > 0$

Ag will be oxidized, ~~by~~ MnO_4^- reduced

Au oxidation to Au^+:

$1.51 V - 1.692 V = -0.18 V < 0$

→ ~~Ag~~ n Au will not be oxidized to Au^+,
MnO_4^- ~~reduced~~ oxidized

Au oxidation to Au^{3+}:

$1.51 V - 1.498 V > 0$

⇒ Au will be oxidized to Au^{3+}
but not to Au^+ MnO_4^- reduced

batteries contain the chemicals needed for the cell-reaction in them, in fuel cells the needed chemicals are continoauly flown in from the surroundings

not ~~rechargeble~~ rechargeably batteries:
primary batteries

rechargeable batteries:
secondary batteries

maximum electrical work:

$$W_{el} = -\Delta G = -\Delta H\left(1 - \frac{T\Delta S}{\Delta H}\right)$$

maximum work of a heat engine between colder T_c and hotter T_h:

$$W_{thermal} = q_h \varepsilon = -\Delta H \frac{T_h - T_c}{T_h}$$

E: efficiency of a heat engine

lead acid battery in cars (below):

$\Delta G_R^o = -376.97 \ kJ/mol$ ⑭-35

$\Delta H_R^o = -227.58 \ kJ/mol$

$\Delta S_R^o = 501.11 \ \frac{J}{K mol}$

with $T_h = 600K$ and $T_c = 300K$ at 300K this given

$\uparrow$ for the battery

$$\frac{W_{el}}{W_{thermal}} = 3,31$$

⇒ electrochemical cells can produce far more work than a heat engine

Further: car battery can be recharged
thermal engine not

Lead-acid battery invented 1859 and is still in use in cars

For car starting ≈ 100 A needed

to be useful for a car
500-1500 rechargeing cycles must be possible

in recharging: product which is a solid must be converted to reactant, also a solid

both have different structures and densities

→ recharging puts strain on the battery and destroys it partially

this limits life-time

electrodes: Pb powder and

$PbO + PbSO_4$ on a Pb frame

both in container with conc. H_2SO_4

recharging possibly with external voltage that converts products to reactants

discharge mode.

⑭-36

reduction (cathode):

$$\overset{+4}{Pb}O_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^-$$

$$\rightarrow PbSO_4(s) + 2H_2O(l) \quad E^\circ = 1.685\,V$$

oxidation (anode):

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^- \quad E^\circ = -0.356\,V$$

overall:

$$PbO_2(s) + Pb(s) + 2H_2SO_4(aq) \rightleftharpoons 2PbSO_4(s) + 2H_2O(l) \quad E^\circ = 2.04\,V$$

⇒ six cells in series give 12V

more than 90% of charge used in charging is obtained back in discharge.

⇒ side reaction like H_2O electrolysis play no big role in charging

But anly 50% of the lead is converted between PbO_2 and $PbSO_4$

Pb heavy ⇒ decrease of power/mass

also side reaction which yied self-discharge without current

capacity decreased by ≈ 0.5% per day by self-discharge

Fig. 11.8 on p. 274 in the book:
different battery types in a plot of Wh/L vs Wh/kg

alkaline cells

Fig. 11.9 on p. 274 in book
anode: powdered Zn
cathode: MnO_2 paste mixed with carbon powder
electrolyte: KOH

anode:
$Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$
$E^0 = 1.1\ V$

cathode:
$2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$
$E^0 = -0.76\ V$

Nichel-metal-hydride

used in hybrid cars in connection with a gasoline engine
28 modules of 6 cells each with 1.2 V
and a total of 201.6 V
capacity: 1100 Wh

anode: $MH(s) + OH^-(aq) \longrightarrow M + H_2O(l) + e^-$ $E^0 = 0.83\ V$
cathode: $NiOOH(s) + H_2O(l) + 2e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$
$E^0 = 0.52\ V$
electrolyte: KOH(aq)
overall:
$MH(s) + NiOOH(s) \rightleftharpoons M^{(s)} + Ni(OH)_2(s)$ $E^0 = 1.35\ V$

M: alloy containing: V, Ti, Zr, Ni, Cr, Co, Fe

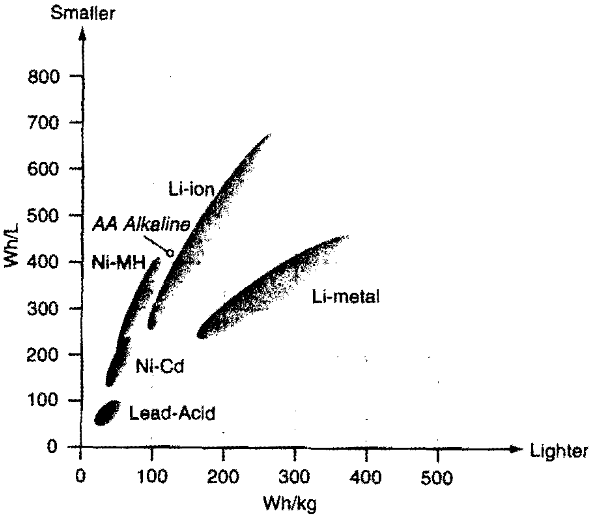


FIGURE 11.8
A number of different batteries are classified with their specific energy density per unit volume and per unit mass.

This means that side reactions such as the electrolysis of water play a minimal role in charging the battery. However, only about 50% of the lead in the battery is converted between PbO_2 and $PbSO_4$. Because Pb has a large atomic mass, this limited convertibility decreases the power per unit mass figure of merit for the battery. Parasitic side reactions also lead to a self-discharge of the cell without current flowing in the external circuit. For the lead-acid battery, the capacity is diminished by approximately 0.5% per day through self-discharge.

As batteries have become more common in portable devices such as cell phones and laptop computers, energy density is a major criterion in choosing the most suitable battery chemistry for a specific application. Figure 11.8 shows a comparison of different battery types. The lead-acid battery has the lowest specific energy either in terms of volume or mass. Next we discuss the chemistry of three commonly used rechargeable batteries: the alkaline, nickel metal hydride, and lithium ion batteries.

The individual elements of the alkaline cell are shown in Figure 11.9. The anode in this cell is powdered zinc, and the cathode is in the form of a MnO_2 paste mixed with

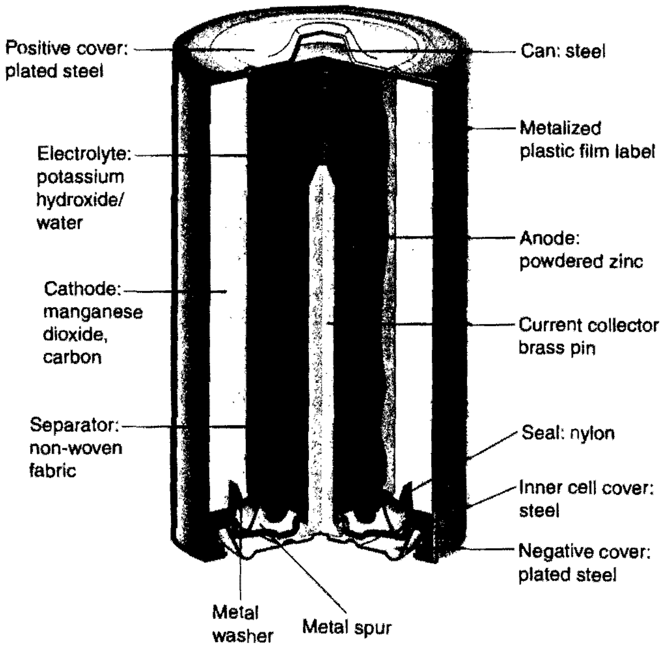


FIGURE 11.9
Schematic diagram of an alkaline cell.

~~Ett~~ Lithium ion batteries

Fig. 11.10, p. 275 in book

good, when high energy density per Volume and Mass
electrodes contain Li^+ ions
cell voltage from different binding
strength of Li^+ in the materials of electrodes

electrolyte ~~sep~~ saturated polymer membrane
separates the electrodes and the Li^+ ions
must move through it

electrolyte e.g. 1M $LiPF_6$ in mixture of
ethylene carbonate and
diethyl carbonate

water would limit the voltage to 1.2V.
at higher potentials H_2O ~~wolt~~ would
be reduced or oxidized

Fig. 11.11, page 276 in book shows cell potential
of Li ion batteries versus energy density
per mass for different electrode
materials

materials outside the band gap of the
electrolyte cannot be used, because they
would start oxidation or reduction of
the solvent

carbon is outside but a thin solid/electrolyte
interface layer stabilizes carbon against
solvent reactions

powdered carbon to impart conductivity. KOH is used as the electrolyte. The anode and cathode reactions are

$$\text{Anode: } Zn(s) + 2\,OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^- \quad E^\circ = 1.1\text{ V} \qquad \textbf{(11.57)}$$

$$\text{Cathode: } 2\,MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2\,OH^-(aq) \; E^\circ = -0.76\text{ V} \qquad \textbf{(11.58)}$$

Nickel metal hydride batteries are currently used in hybrid vehicles that rely on dc motors to drive the vehicle in city traffic and use a gasoline engine for higher speed driving. The Toyota Prius uses 28 modules of 6 cells, each with a nominal voltage of 1.2 V and a total voltage of 201.6 V to power the vehicle. The capacity of the battery pack is ~1100 Wh. The anode and cathode reactions are

$$\text{Anode: } MH(s) + OH^-(aq) \rightarrow M + H_2O(l) + e^- \quad E^\circ = 0.83\text{ V} \qquad \textbf{(11.59)}$$

$$\text{Cathode: } NiOOH(s) + H_2O(l) + 2e^- \rightarrow Ni(OH)_2(s) + OH^-(aq) \quad E^\circ = 0.52\text{ V} \qquad \textbf{(11.60)}$$

The electrolyte is KOH(aq), and the overall reaction is

$$MH(s) + NiOOH(s) \rightleftharpoons M + Ni(OH)_2(s) \quad E^\circ = 1.35\text{ V} \qquad \textbf{(11.61)}$$

where M designates an alloy that can contain V, Ti, Zr, Ni, Cr, Co, and Fe.

Lithium ion batteries find applications as diverse as cell phones, where a high energy density per unit volume is required, and electric vehicles, where a high energy density per unit mass is required. The electrodes in lithium ion batteries contain Li^+ ions, and the cell voltage reflects the difference in the binding strength of Li^+ in the two materials. The structure of a cylindrical lithium ion battery is shown schematically in Figure 11.10. The two electrodes are separated by an electrolyte–saturated polymer membrane through which the Li^+ ions move in the internal circuit. The electrolyte is a lithium salt dissolved in an organic solvent, for example, 1M $LiPF_6$ in a mixture of ethylene carbonate and diethyl carbonate. Aqueous electrolytes would limit the cell voltage to 1.2 V because at larger potentials, water is reduced or oxidized. Figure 11.11 shows a number of materials that can be used as electrodes. Materials that fall outside of the band gap of the electrolyte are unsuitable because their use initiates reduction or oxidation of the solvent. It would appear that carbon is unsuitable, but the formation of a thin solid/electrolyte interface layer stabilizes carbon with respect to solvent reactions, and it is the

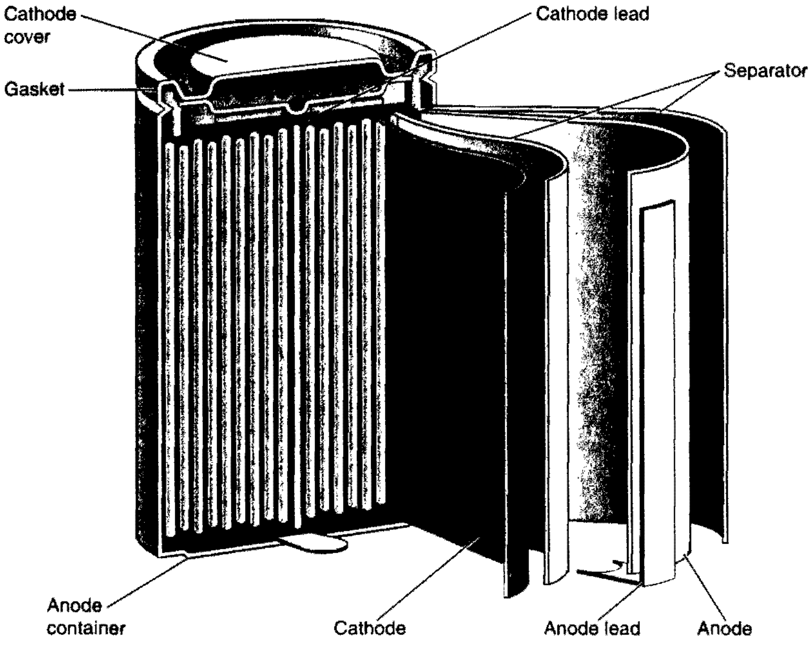


FIGURE 11.10
Schematic structure of a cylindrical lithium ion battery. The anode and cathode material are formed of thin sheets to optimize the transport kinetics of Li^+ ions.

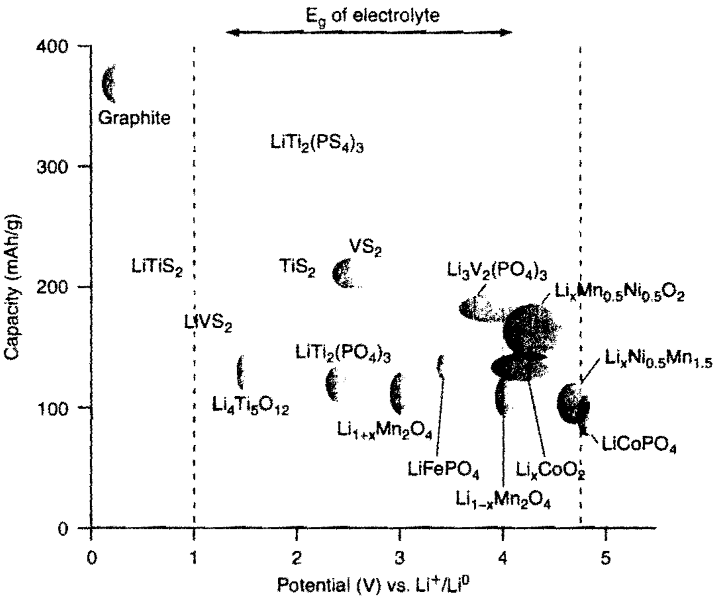


FIGURE 11.11
The cell potential of a lithium ion battery versus the energy density per unit mass for a number of electrode materials is shown. The dashed lines indicate the voltage range in which 1M LiPF$_6$ in a 1:1 mixture of ethylene carbonate and diethyl carbonate is stable with respect to reduction or oxidation.
Source: Goodenough J. B. and Kim Y. *Chemistry of Materials* 22 (2010), 587.

most widely used anode electrode. Using a carbon anode and LiCoO$_2$(s) as the cathode allows a cell potential of 3.7 V to be achieved. As Figure 11.11 shows, higher potentials are possible, but batteries with long life cycles using materials other than LiCoO$_2$(s) have not yet been developed.

Rechargeable lithium batteries have the following half-cell reactions while discharging the battery:

$$\text{positive electrode:}\quad \mathrm{Li}_{1-x}\mathrm{CoO}_2(s) + x\mathrm{Li}^+(solution) + xe^- \rightarrow \mathrm{LiCoO}_2(s) \qquad \textbf{(11.62)}$$

$$\text{negative electrode:}\quad \mathrm{CLi}_x \rightarrow \mathrm{C}(s) + x\mathrm{Li}^+(solution) + xe^- \qquad \textbf{(11.63)}$$

The right arrows indicate the discharge directions. In these equations, x is a small positive number. The overall cell reaction is

$$\mathrm{Li}_{1-x}\mathrm{CoO}_2(s) + \mathrm{CLi}_x \rightleftharpoons \mathrm{LiCoO}_2(s) + \mathrm{C}(graphite) \quad E^\circ \sim 3.7\ \mathrm{V} \qquad \textbf{(11.64)}$$

and the fully charged battery has a cell potential of ~3.7 V. The structures of LiCoO$_2$(s) and CLi$_x$ are shown schematically in Figure 11.12. CLi$_x$ designates Li atoms intercalated between sheets of graphite; it is not a stoichiometric compound. In a lithium-ion battery the lithium ions are transported to and from the cathode or anode, with the transition metal, cobalt (Co), in Li$_x$CoO$_2$ being oxidized from Co^{3+} to Co^{4+} during charging, and reduced from Co^{4+} to Co^{3+} during discharge.

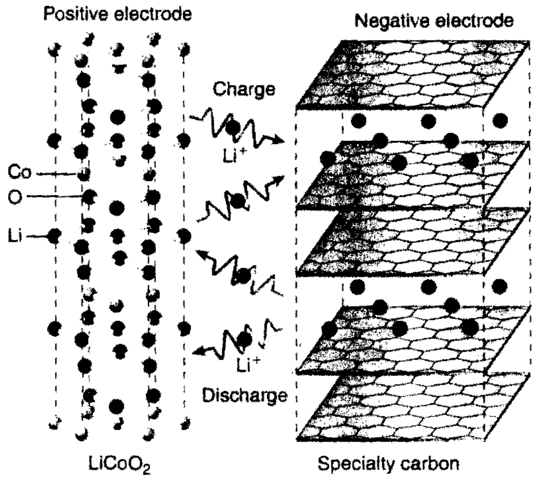


FIGURE 11.12
The cell voltage in a lithium battery is generated by moving the lithium between a lattice site in LiCoO$_2$ and an intercalation position between sheets of graphite.

carbon anodes + $LiCoO_2$ cathodes

allows 3,7 V

in discharge:

positive electrode
cathode (reduction) $Li_{1-x}CoO_2(s) + xLi^+(\text{solution}) + xe^- \rightarrow LiCoO_2$

negative electrode
anode (oxidation) $CLi_x \rightarrow C(s) + xLi^+(\text{solution}) + xe^-$

x: small positive number

overall:

$Li_{1-x}CoO_2(s) + CLi_x \rightleftharpoons LiCoO_2(s) + C(\text{grafite})$

$E^0 \approx 3,7$ V

Fig 11.12, p.276 in book:

structures of ~~$Li_{1-x}CoO_2$~~ $LiCoO_2(s)$ and CLi_x

CLi_x: non-stoichiometric compound

Li intercalated between grafite sheets

when Li^+ is transported,

Co in Li_xCoO_2 is oxidized from Co^{3+} to Co^{4+}

when charged and

reduced from Co^{4+} to Co^{3+} in discharge

Section 11.13 - 11.16 <u>not</u> in Exam