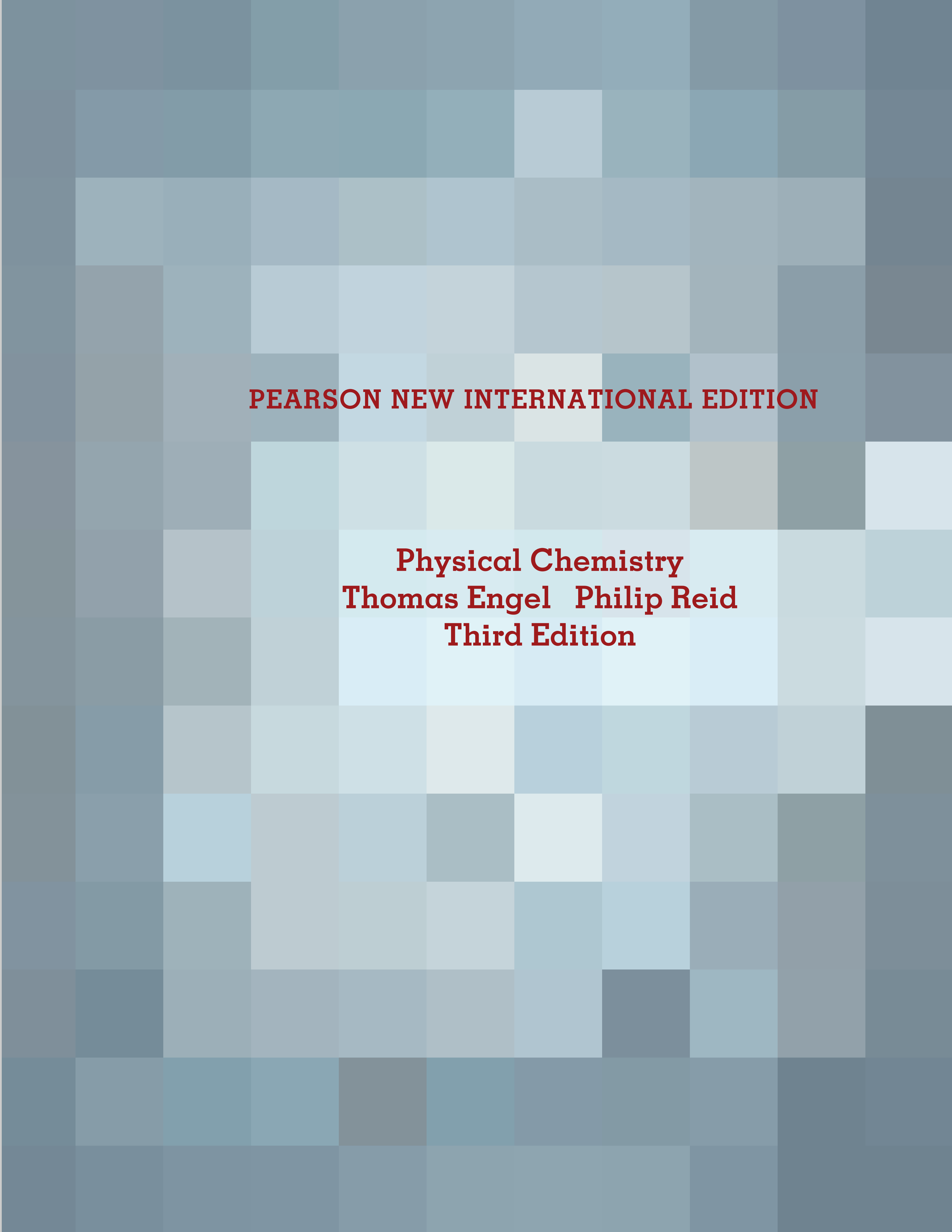

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As this result shows, the equilibrium corresponds to essentially complete conversion of reactants to products. Example Problem 5 shows the same calculation for the Daniell cell.

EXAMPLE PROBLEM 5

For the Daniell cell $E^\circ = 1.10$ V. Calculate K for the reaction at 298.15 K $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$.

Solution

$$\begin{aligned}\ln K &= \frac{nF}{RT}E^\circ = \frac{2 \times 96485\text{ C mol}^{-1} \times 1.10\text{ V}}{8.314\text{ J K}^{-1}\text{ mol}^{-1} \times 298.15\text{ K}} \\ &= 85.63 \\ K &= 1.55 \times 10^{37}\end{aligned}$$

Note that the equilibrium constant calculated in Example Problem 5 is so large that it could not have been measured by determining the activities of $a_{Zn^{2+}}$ and $a_{Cu^{2+}}$ by spectroscopic methods. This would require a measurement technique that is accurate over more than 30 orders of magnitude in the activity. By contrast, the equilibrium constant in an electrochemical cell can be determined with high accuracy using only a voltmeter.

A further example of the use of electrochemical measurements to determine equilibrium constants is the solubility constant for a weakly soluble salt. If the overall reaction corresponding to dissolution can be generated by combining half-cell potentials, then the solubility constant can be calculated from the potentials. For example, the following half-cell reactions can be combined to calculate the solubility product of AgBr.

$$\begin{array}{ll} AgBr(s) + e^- \rightarrow Ag(s) + Br^-(aq) & E^\circ = 0.07133\text{ V} \quad \text{and} \\ \underline{Ag(s) \rightarrow Ag^+(aq) + e^-} & \underline{E^\circ = -0.7996\text{ V}} \\ AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) & E^\circ = -0.7283\text{ V} \end{array}$$

$$\ln K_{sp} = \frac{nF}{RT}E^\circ = \frac{1 \times 96485\text{ C mol}^{-1} \times (-0.7283\text{ V})}{8.314\text{ J K}^{-1}\text{mol}^{-1} \times 298.15\text{ K}} = -28.35$$

The value of the solubility constant is $K_{sp} = 4.88 \times 10^{-13}$.

EXAMPLE PROBLEM 6

A concentration cell consists of two half-cells that are identical except for the activities of the redox components. Consider two half-cells based on the $Ag^+(aq) + e^- \rightarrow Ag(s)$ reaction. The left half-cell contains $AgNO_3$ at unit activity, and the right half-cell initially had the same concentration of $AgNO_3$, but just enough $NaCl(aq)$ has been added to precipitate the $Ag^+(aq)$ as AgCl. Write an equation for the overall cell reaction. If the emf of this cell is 0.29 V, what is K_{sp} for AgCl?

Solution

The overall reaction is $Ag^+(aq, a = 1) \rightleftharpoons Ag^+(aq, a)$ with a concurrent transport of Cl^- in the opposite direction through the salt bridge between the half-cells. In the right half-cell we have the equilibrium $AgCl(s) \rightleftharpoons Ag^+(aq, a_\pm) + Cl^-(aq, a_\pm)$, so that $a_{Ag^+}a_{Cl^-} = a_\pm^2 = K_{sp}$.

Because the half-cell reactions are the same, $E^\circ = 0$ and

$$\begin{aligned}E &= -\frac{0.05916\text{ V}}{n}\log_{10}\frac{a_\pm}{1} = -\frac{0.05916}{1}\log_{10}\sqrt{K_{sp}} \\ &= -\frac{0.05916\text{ V}}{2}\log_{10} K_{sp} \\ \log_{10} K_{sp} &= -\frac{2E}{0.05916} = -\frac{2 \times (0.29\text{ V})}{0.05916\text{ V}} = -9.804 \\ K_{sp} &= 1.57 \times 10^{-10}\end{aligned}$$

8 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

$$E = E^\circ_{Ag^+/Ag} + \frac{RT}{F}\ln a_{Ag^+} = E^\circ_{Ag^+/Ag} + \frac{RT}{F}\ln(m/m^\circ) + \frac{RT}{F}\ln\gamma_\pm \qquad \textbf{(41)}$$

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. Using this relation, Equation (41) can be rewritten in the form

$$\begin{aligned} E - 0.05916\,\log_{10}(m/m^\circ) &= E^\circ_{Ag^+/Ag} - 0.05916 \times 0.5090\sqrt{(m/m^\circ)} \\ &= E^\circ_{Ag^+/Ag} - 0.03011\sqrt{(m/m^\circ)} \qquad \textbf{(42)} \end{aligned}$$

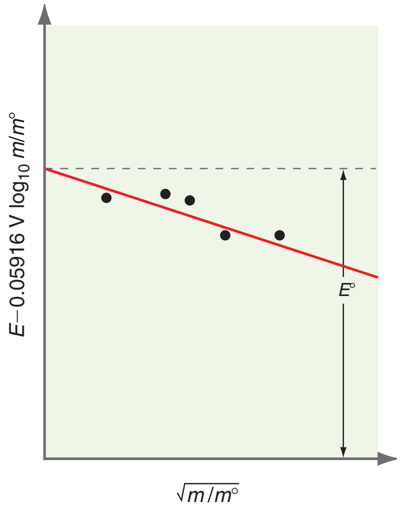


FIGURE 7

The value of E° and the activity coefficient can be measured by plotting the left-hand side of Equation (42) against the square root of the molality.

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 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 (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.

9 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.

For example, the abbreviated notation for the Daniell cell containing a salt bridge is

$$\mathrm{Zn}(s)|\mathrm{ZnSO_4}(aq)\|\mathrm{CuSO_4}(aq)|\mathrm{Cu}(s) \tag{43}$$

and a cell made up of the $\mathrm{Zn/Zn^{2+}}$ half-cell and the standard hydrogen electrode is described by

$$\mathrm{Zn}(s)|\mathrm{ZnSO_4}(aq)||\mathrm{H^+}(aq)|\mathrm{H_2}(g)|\mathrm{Pt}(s) \tag{44}$$

The overall reaction in this cell is $\mathrm{Zn}(s) + 2\,\mathrm{H^+}(aq) \rightleftharpoons \mathrm{Zn^{2+}}(aq) + \mathrm{H_2}(g)$. In general, in such a cell the solutions are physically separated by a porous membrane to prevent mixing of the solutions. In this case, the junction potential has not been eliminated.

The half-cell and overall reactions can be determined from the abbreviated notation in the following way. An electron is transferred from the electrode at the far left of the abbreviated notation to the electrode on the far right through the external circuit. The number of electrons is then adjusted to fit the half-cell reaction. This procedure is illustrated in Example Problem 7.

EXAMPLE PROBLEM 7

Determine the half-cell reactions and the overall reaction for the cell designated

$$\mathrm{Ag}(s)|\mathrm{AgCl}(s)|\mathrm{Cl^-}(aq, a_\pm = 0.0010)\|\mathrm{Fe^{2+}}(aq, a_\pm = 0.50)$$
$$\mathrm{Fe^{3+}}(aq, a_\pm = 0.10)|\mathrm{Pt}(s)$$

Solution

The anode and cathode reactions are

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

The overall reaction is

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

Only after the cell potential is calculated is it clear whether the reaction or the reverse reaction is spontaneous.

We have already discussed several specific half-cells and next discuss different types of half-cells. The standard hydrogen electrode involves the equilibrium between a gas and a dissolved species. A second such electrode is the $\mathrm{Cl_2/Cl^-}$ electrode, for which the reduction reaction is

$$\mathrm{Cl_2}(g) + 2\mathrm{e^-} \rightarrow 2\,\mathrm{Cl^-}(aq) \quad E^\circ = +1.36\ \mathrm{V} \tag{45}$$

Another type of half-cell that is frequently encountered involves a metal and a metal ion in solution. Both half-cells in the Daniell cell fall into this category.

$$\mathrm{Zn^{2+}}(aq) + 2\mathrm{e^-} \rightarrow \mathrm{Zn}(s) \quad E^\circ = -0.76\ \mathrm{V} \tag{46}$$

A number of half-cells consist of a metal, an insoluble salt containing the metal, and an aqueous solution containing the anion of the salt. Two examples of this type of half-cell are the Ag–AgCl half-cell for which the reduction reaction is

$$\mathrm{AgCl}(s) + \mathrm{e^-} \rightarrow \mathrm{Ag}(s) + \mathrm{Cl^-}(aq) \quad E^\circ = +0.22\ \mathrm{V} \tag{47}$$

and the calomel (mercurous chloride) electrode, which is frequently used as a reference electrode in electrochemical cells:

$$\mathrm{Hg_2Cl_2}(s) + 2\mathrm{e^-} \rightarrow 2\,\mathrm{Hg}(l) + 2\,\mathrm{Cl^-}(aq) \quad E^\circ = +0.27\ \mathrm{V} \tag{48}$$

In a further type of half-cell, both species are present in solution, and the electrode is an inert conductor such as Pt, which allows an electrical connection to be made to the solution. For example, in the $\mathrm{Fe^{3+}/Fe^{2+}}$ half-cell, the reduction reaction is

$$\mathrm{Fe^{3+}}(aq) + \mathrm{e^-} \rightarrow \mathrm{Fe^{2+}}(aq) \quad E^\circ = 0.771\ \mathrm{V} \tag{49}$$

10 The Electrochemical Series

Tables 1 and Tables 2 (see at the end of the chapter) 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

$$E^\circ_{cell} = E_1^\circ - E_2^\circ \tag{50}$$

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 2. The **electrochemical series** shown in Table 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 3 refers to the reduction reaction

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

In a redox couple formed from two entries in the list shown in Table 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 $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ and not the reverse reaction.

TABLE 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.)

EXAMPLE PROBLEM 8

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

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

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

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

Which of these metals will be oxidized by the MnO_4^- ion?

Solution

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

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

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

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

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 MnO_4^- ion.

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.

It is useful to compare the relative amount of work that can be produced through an electrochemical reaction with the work that a heat engine could produce using the same overall reaction. The maximum electrical work is given by

$$w_{electrical} = -\Delta G = -\Delta H\left(1 - \frac{T\Delta S}{\Delta H}\right) \quad \textbf{(51)}$$

whereas the maximum work available through a reversible heat engine operating between T_h and T_c is

$$w_{thermal} = q_{hot}\,\varepsilon = -\Delta H\left(\frac{T_h - T_c}{T_h}\right) \quad \textbf{(52)}$$

where ε is the efficiency of a reversible heat engine (see Section 5.2). To compare the maximum thermal and electrical work, we use the overall reaction for the familiar lead-acid battery used in cars. For this reaction, $\Delta G_R^\circ = -376.97\,\text{kJ mol}^{-1}$, $\Delta H_R^\circ = -227.58\,\text{kJ mol}^{-1}$, and $\Delta S_R^\circ = 501.1\,\text{J K}^{-1}\,\text{mol}^{-1}$. Assuming $T_h = 600.\ \text{K}$ and $T_c = 300.\ \text{K}$ and that the battery operates at 300. K, then

$$\frac{w_{electrical}}{w_{thermal}} = 3.31 \quad \textbf{(53)}$$

This calculation shows that much more work can be produced in the electrochemical reaction than in the thermal reaction. This comparison does not even take into account that the lead-acid battery can be recharged, whereas the thermal reaction can only be run once.

12 The Electrochemistry of Commonly Used Batteries

The lead-acid battery was invented in 1859 and is still widely used in automobiles. Because the power required to start an automobile engine is on the order of a kilowatt, the current capacity of such a battery must be on the order of a hundred amperes. Additionally, such a battery must be capable of 500 to 1500 recharging cycles from a deep discharge. In recharging batteries, the reaction product in the form of a solid must be converted back to the reactant, also in the form of a solid. Because the solids in general have a different crystal structure and density, the conversion induces mechanical stress in the anode and cathode, which ultimately leads to a partial disintegration of these electrodes. This is the main factor that limits the number of charge–discharge cycles that a battery can tolerate.

The electrodes in the lead-acid battery consist of Pb powder and finely divided PbO and $PbSO_4$ supported on a Pb frame. The electrodes are supported in a container containing concentrated H_2SO_4. In use, a battery is discharged. Some batteries, including the lead-acid battery, can be recharged by applying an external voltage to convert products back to reactants. In that case, the role of anode and cathode are reversed. To avoid confusion, we write half cell and overall reactions for the discharge mode. In the lead-acid battery, the cell reactions at the cathode and anode are

$$PbO_2(s) + 4\,H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2\,H_2O(l) \qquad E^\circ = 1.685\ \text{V} \quad \textbf{(54)}$$

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^- \qquad E^\circ = -0.356\ \text{V} \quad \textbf{(55)}$$

respectively, and the overall reaction is

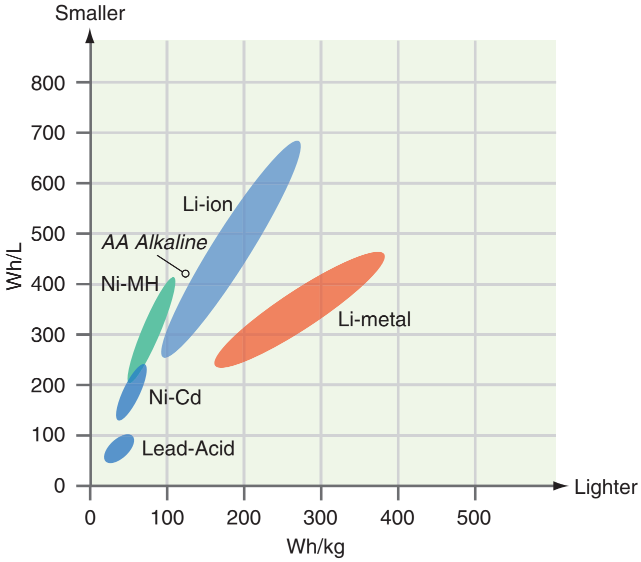
$$PbO_2(s) + Pb(s) + 2\,H_2SO_4(aq) \rightleftharpoons 2\,PbSO_4(s) + 2\,H_2O(l) \quad E^\circ = 2.04\ \text{V} \quad \textbf{(56)}$$

The arrows would point in the opposite direction and the sign of the emfs would be reversed for the charging mode.

Six such cells connected in series are required for a battery that provides a nominal potential of 12 V. The lead-acid battery is very efficient in that more than 90% of the electrical charge used to charge the battery is available in the discharge part of the cycle.

FIGURE 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 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 9. The anode in this cell is powdered zinc, and the cathode is in the form of a MnO_2 paste mixed with

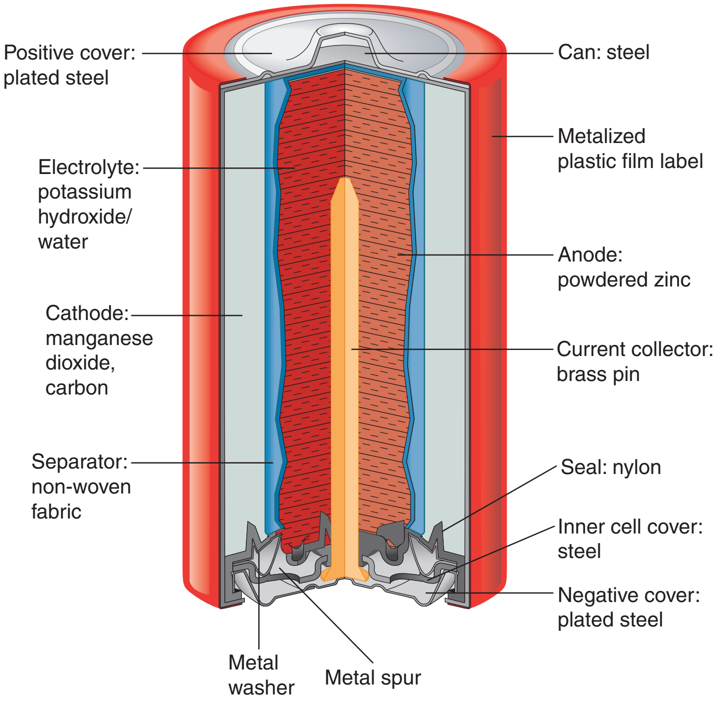


FIGURE 9

Schematic diagram of an alkaline cell.