**Pearson**

19.5: Cell Potential, Free Energy, and the Equilibrium Constant

Key Concept Video Cell Potential, Free Energy, and the Equilibrium Constant

We have seen that a positive standard cell potential $\left(E_{cell}^{\circ}\right)$ corresponds to a spontaneous oxidation–reduction reaction when the reactants and products are in their standard states (standard conditions). And we know (from Chapter 18⬚) that the spontaneity of a reaction under standard conditions is determined by the sign of ΔG°. Therefore, E_{cell}° and ΔG° must be related. We also know from Section 18.9⬚ that ΔG° for a reaction is related to the equilibrium constant (K) for the reaction. Since E_{cell}° and ΔG° are related, then E_{cell}° and K must also be related.
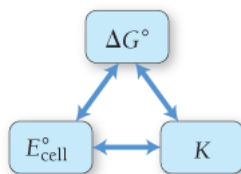
Remember that standard conditions (indicated by the symbol °) represent a very specific reaction mixture. For a reaction mixture under standard conditions, $Q = 1$.

Before we look at the nature of each of these relationships in detail, let's consider the following generalizations.

For a spontaneous redox reaction (one that will proceed in the forward direction when all reactants and products are in their standard states):

- ΔG° is negative (< 0)
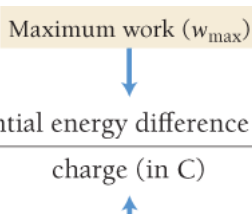- E_{cell}° is positive (> 0)
- $K > 1$

For a nonspontaneous reaction (one that will proceed in the reverse direction when all reactants and products are in their standard states):

- ΔG° is positive (> 0)
- E_{cell}° is negative (< 0)
- $K < 1$

The Relationship between ΔG° and E_{cell}°

We can derive a relationship between ΔG° and E_{cell}° by briefly returning to the definition of potential difference from Section 19.3⬚—a potential difference is a measure of the difference of potential energy per unit charge (q):

$$\text{Maximum work } (w_{max})$$
$$\downarrow$$
$$E = \frac{\text{potential energy difference (in J)}}{\text{charge (in C)}}$$
$$\uparrow$$

Charge (q)

Since the potential energy difference represents the maximum amount of work that can be done by the system on the surroundings, we can write:

[19.1]

$$w_{max} = -qE^{\circ}_{cell}$$

The negative sign follows the convention used throughout this book that work done by the system on the surroundings is negative.

We can quantify the charge (q) that flows in an electrochemical reaction by using **Faraday's constant (F)**, which represents the charge in coulombs of 1 mol of electrons:

$$F = \frac{96,485 \text{ C}}{\text{mol e}^-}$$

The total charge is $q = nF$, where n is the number of moles of electrons from the balanced chemical equation and F is Faraday's constant. Substituting $q = nF$ into Equation 19.1:

[19.2]

$$\begin{aligned} w_{max} &= -qE^{\circ}_{cell} \\ &= -nFE^{\circ}_{cell} \end{aligned}$$

Finally, recall from Chapter 18 that the standard change in free energy for a chemical reaction (ΔG°) represents the maximum amount of work that can be done by the reaction. Therefore, $w_{max} = \Delta G^{\circ}$. Making this substitution into Equation 19.2, we arrive at the following important result:

[19.3]

$$\Delta G^{\circ} = -nFE^{\circ}_{cell}$$

where ΔG° is the standard change in free energy for an electrochemical reaction, n is the number of moles of electrons transferred in the balanced equation, F is Faraday's constant, and E°_{cell} is the standard cell potential. Example 19.6 demonstrates how to apply this equation to calculate the standard free energy change for an electrochemical cell.

Example 19.6 Relating ΔG° and E°_{cell}

Use the tabulated electrode potentials to calculate ΔG° for the reaction.
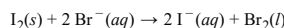
$$I_2(s) + 2 Br^-(aq) \rightarrow 2 I^-(aq) + Br_2(l)$$

Is the reaction spontaneous under standard conditions?

SORT   You are given a redox reaction and asked to find ΔG°.

GIVEN: $I_2(s) + 2 Br^-(aq) \rightarrow 2 I^-(aq) + Br_2(l)$

FIND: ΔG°

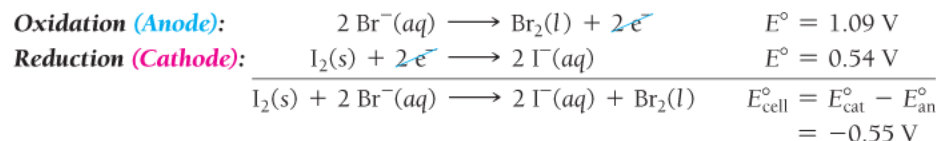**STRATEGIZE**   Refer to the values of electrode potentials in Table 19.1 to calculate E°_{cell}. Then use Equation 19.3 to calculate ΔG° from E°_{cell}.

CONCEPTUAL PLAN
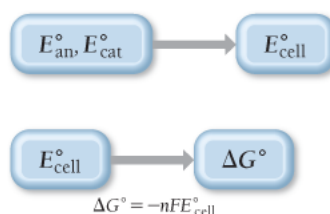
$$\Delta G^\circ = -nFE^\circ_{cell}$$

SOLVE   Separate the reaction into oxidation and reduction half-reactions and find the standard electrode potentials for each. Determine E°_{cell} by subtracting E°_{an} from E°_{cat}.

SOLUTION

|		
Oxidation (Anode):	$2\,Br^-(aq) \longrightarrow Br_2(l) + 2e^-$	$E^\circ = 1.09\ V$
Reduction (Cathode):	$I_2(s) + 2e^- \longrightarrow 2\,I^-(aq)$	$E^\circ = 0.54\ V$
	$I_2(s) + 2\,Br^-(aq) \longrightarrow 2\,I^-(aq) + Br_2(l)$	$E^\circ_{cell} = E^\circ_{cat} - E^\circ_{an}$
		$= -0.55\ V$

Calculate ΔG° from E°_{cell}. The value of n (the number of moles of electrons) corresponds to the number of electrons that are canceled in the half-reactions. Remember that $1\ V = 1\ J/C$.

$$\Delta G^\circ = -nFE^\circ_{cell}$$
$$= -2\ mol\ e^- \left(\frac{96{,}485\ C}{mol\ e^-}\right)\left(-0.55\frac{J}{C}\right)$$
$$= +1.1 \times 10^5\ J$$

Since ΔG° is positive, the reaction is not spontaneous under standard conditions.

CHECK   The answer is in the correct units (joules) and seems reasonable in magnitude ($\approx$ 110 kJ). You have seen (in Chapter 18⬚) that values of ΔG° typically range from plus or minus tens to hundreds of kilojoules. The sign is positive, as expected for a reaction in which E°_{cell} is negative.

FOR PRACTICE 19.6   Use tabulated electrode potentials to calculate ΔG° for the reaction.

$$2\,Na(s) + 2\,H_2O(l) \rightarrow H_2(g) + 2\,OH^-(aq) + 2\,Na^+(aq)$$
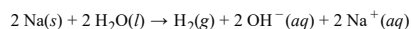
Is the reaction spontaneous under standard conditions?

Interactive Worked Example 19.6   Relating ΔG°, and E°_{cell}

Conceptual Connection 19.5   Periodic Trends and the Direction of Spontaneity for Redox Reactions

The Relationship between E°_{cell} and K

We can derive a relationship between the standard cell potential $\left(E^\circ_{cell}\right)$ and the equilibrium constant for the redox reaction occurring in the cell (K) by returning to the relationship between ΔG° and K that we learned in Chapter 18⬚. Recall from Section 18.9⬚ that:

[19.4]

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

By setting Equations 19.3 and 19.4 equal to each other, we get:

[19.5]

$$
\begin{aligned}
-nFE^\circ_{cell} &= -RT \ln K \\
E^\circ_{cell} &= \frac{RT}{nF} \ln K
\end{aligned}
$$

Equation 19.5 is usually simplified for use at 25 °C with the following substitutions:

$$R = 8.314 \frac{J}{mol \cdot K}; \; T = 298.15 \text{ K}; \; F = \left(\frac{96,485 \text{ C}}{mol \text{ e}^-} \right); \; \text{and } \ln K = 2.303 \log K$$

Substituting into Equation 19.5, we get the following important result:

[19.6]

$$E^\circ_{cell} = \frac{0.0592 \text{ V}}{n} \log K$$

where E°_{cell} is the standard cell potential, n is the number of moles of electrons transferred in the redox reaction, and K is the equilibrium constant for the balanced redox reaction at 25 °C. Example 19.7 demonstrates the use of Equation 19.6.

Example 19.7 Relating E°_{cell} and K

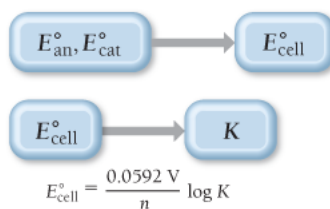Refer to tabulated electrode potentials to calculate K for the oxidation of copper by H^+ (at 25 °C).

$$Cu(s) + 2 H^+(aq) \rightarrow Cu^{2+}(aq) + H_2(g)$$

SORT   You are given a redox reaction and asked to find K.

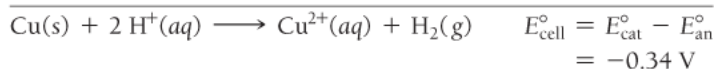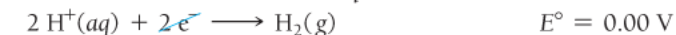**GIVEN:** $Cu(s) + 2 H^+(aq) \rightarrow Cu^{2+}(aq) + H_2(g)$

FIND: K

STRATEGIZE   Refer to the values of electrode potentials in Table 19.1 to calculate E°_{cell}. Use Equation 19.6 to calculate K from E°_{cell}.

CONCEPTUAL PLAN

$$E^\circ_{cell} = \frac{0.0592 \text{ V}}{n} \log K$$

SOLVE   Separate the reaction into oxidation and reduction half-reactions and find the standard electrode potentials for each. Find E°_{cell} by subtracting E°_{an} from E°_{cat}.

SOLUTION

Oxidation (Anode):	$Cu(s) \longrightarrow Cu^{+}(aq) + 2e^{-}$	$E^{\circ} = 0.34\ V$
Reduction (Cathode):	$2\ H^{+}(aq) + 2e^{-} \longrightarrow H_2(g)$	$E^{\circ} = 0.00\ V$

$$Cu(s) + 2\ H^{+}(aq) \longrightarrow Cu^{2+}(aq) + H_2(g) \qquad E^{\circ}_{cell} = E^{\circ}_{cat} - E^{\circ}_{an}$$
$$= -0.34\ V$$

Calculate K from E°_{cell}. The value of n (the number of moles of electrons) corresponds to the number of electrons that are canceled in the half-reactions.

$$E^{\circ}_{cell} = \frac{0.0592\ V}{n} \log K$$

$$\log K = E^{\circ}_{cell} \frac{n}{0.0592\ V}$$
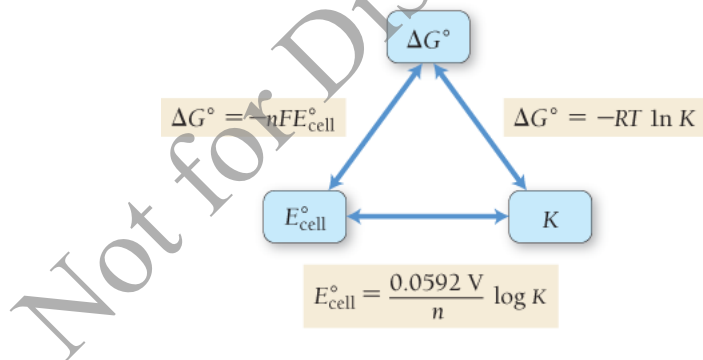
$$\log K = -0.34\ V \frac{2}{0.0592\ V} = -11.48$$

$$K = 10^{-11.48} = 3.3 \times 10^{-12}$$

CHECK The answer has no units, as expected for an equilibrium constant. The magnitude of the answer is small, indicating that the reaction lies far to the left at equilibrium, as expected for a reaction in which E°_{cell} is negative.

FOR PRACTICE 19.7 Use the tabulated electrode potentials to calculate K for the oxidation of iron by H^{+} (at 25 °C).

$$2\ Fe(s) + 6\ H^{+}(aq) \rightarrow 2\ Fe^{3+}(aq) + 3\ H_2(g)$$
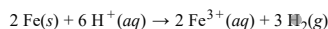
Notice that the fundamental quantity in the given relationships is the standard change in free energy for a chemical reaction $\left(\Delta G^{\circ}_{rxn}\right)$. From that quantity, we can calculate both E°_{cell} and K. The following diagram summarizes the relationships between these three quantities:

$$\Delta G^{\circ}$$

$$\Delta G^{\circ} = -nFE^{\circ}_{cell} \qquad \qquad \Delta G^{\circ} = -RT \ln K$$

$$E^{\circ}_{cell} \qquad \qquad K$$

$$E^{\circ}_{cell} = \frac{0.0592\ V}{n} \log K$$

Conceptual Connection 19.6   Relating K, ΔG°_{rxn}, and E°_{cell}

Interactive