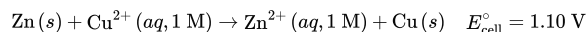
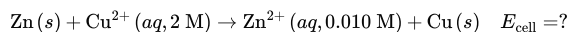


19.6: Cell Potential and Concentration

We have learned how to find E_{cell}° under standard conditions. For example, we know that when $[\text{Cu}^{2+}] = 1 \text{ M}$ and $[\text{Zn}^{2+}] = 1 \text{ M}$, the following reaction produces a potential of 1.10 V:



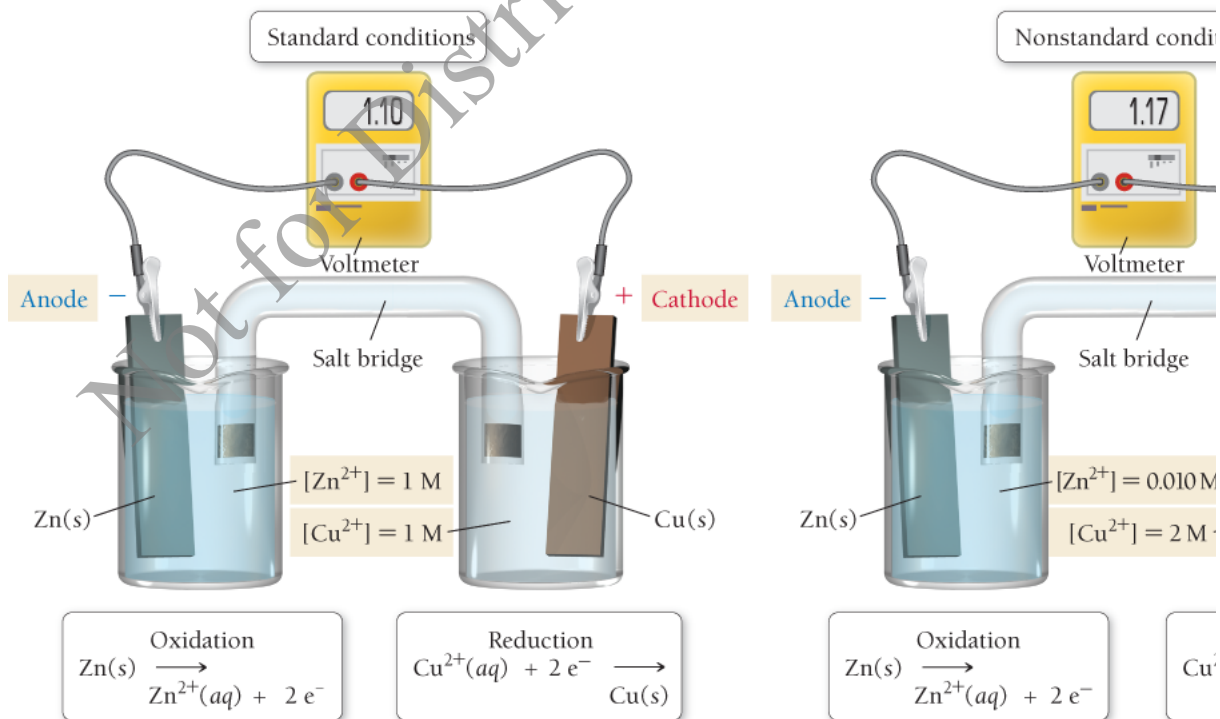
But what if $[\text{Cu}^{2+}] > 1 \text{ M}$ and $[\text{Zn}^{2+}] < 1 \text{ M}$? For example, how is the cell potential for the following conditions different from the potential under standard conditions?



Since the concentration of a reactant is greater than standard conditions, and since the concentration of product is less than standard conditions, we can use Le Châtelier's principle to predict that the reaction has an even stronger tendency to occur in the forward direction and that E_{cell} is therefore greater than +1.10 V (Figure 19.11).

Figure 19.11 Cell Potential and Concentration

This figure compares the Zn/Cu²⁺ electrochemical cell under standard and nonstandard conditions. In this case, the nonstandard conditions consist of a higher Cu²⁺ concentration ($[\text{Cu}^{2+}] > 1 \text{ M}$) at the cathode and a lower Zn²⁺ concentration at the anode ($[\text{Zn}^{2+}] < 1 \text{ M}$). According to Le Châtelier's principle, the forward reaction has a greater tendency to occur, resulting in a greater overall cell potential than the potential under standard conditions.



Cell Potential under Nonstandard Conditions: The Nernst Equation

We can derive an exact relationship between E_{cell} (under nonstandard conditions) and E_{cell}° by considering the relationship between the change in free energy (ΔG) and the *standard* change in free energy (ΔG°) from

Section 18.8:

[19.7]

$$\Delta G = \Delta G^{\circ} + RT \ln \mathcal{Q}$$

where R is the gas constant (8.314 J/mol · K), T is the temperature in kelvins, and \mathcal{Q} is the reaction quotient corresponding to the nonstandard conditions.

Because we know the relationship between ΔG and E_{cell} (Equation 19.3), we can substitute into Equation 19.7:

$$\begin{aligned}\Delta G &= \Delta G^{\circ} + RT \ln \mathcal{Q} \\ -nFE_{\text{cell}} &= -nFE_{\text{cell}}^{\circ} + RT \ln \mathcal{Q}\end{aligned}$$

We can then divide each side by $-nF$ to arrive at:

[19.8]

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \mathcal{Q}$$

As we have seen, R and F are constants; at $T = 25^{\circ}\text{C}$, $\frac{RT}{nF} \ln \mathcal{Q} = \frac{0.0592\text{ V}}{n} \log \mathcal{Q}$. Substituting into Equation 19.8, we arrive at the Nernst equation:

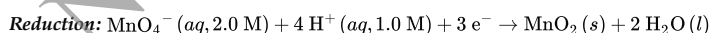
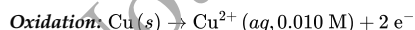
[19.9]

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592\text{ V}}{n} \log \mathcal{Q}$$

where E_{cell} is the cell potential in volts, E_{cell}° is the *standard* cell potential in volts, n is the number of moles of electrons transferred in the redox reaction, and \mathcal{Q} is the reaction quotient. Notice that, under standard conditions, $\mathcal{Q} = 1$, and (since $\log 1 = 0$) $E_{\text{cell}} = E_{\text{cell}}^{\circ}$, as expected. Example 19.8 demonstrates how to calculate the cell potential under nonstandard conditions.

Example 19.8 Calculating E_{cell} under Nonstandard Conditions

Determine the cell potential for an electrochemical cell based on the following two half-reactions:



SORT You are given the half-reactions for a redox reaction and the concentrations of the aqueous reactants and products. You are asked to find the cell potential.

GIVEN: $[\text{MnO}_4^{-}] = 2.0\text{ M}$; $[\text{H}^{+}] = 1.0\text{ M}$; $[\text{Cu}^{2+}] = 0.010\text{ M}$

FIND: E_{cell}

STRATEGIZE Use the tabulated values of electrode potentials to calculate E_{cell}° . Then use Equation 19.9 to calculate E_{cell} .

CONCEPTUAL PLAN

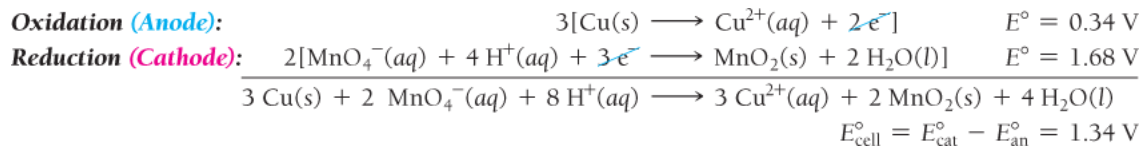


$$E_{\text{cell}}^{\circ}, [\text{MnO}_4^-], [\text{H}^+], [\text{Cu}^{2+}] \longrightarrow E_{\text{cell}}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q$$

SOLVE Write the oxidation and reduction half-reactions, multiplying by the appropriate coefficients to cancel the electrons. Find the standard electrode potentials for each. Find E_{cell}° .

SOLUTION

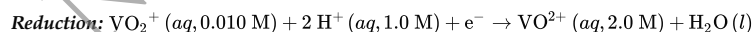


Calculate E_{cell} from E_{cell}° . The value of n (the number of moles of electrons) corresponds to the number of electrons (six in this case) canceled in the half-reactions. Determine Q based on the overall balanced equation and the given concentrations of the reactants and products. (Note that pure liquid water, solid MnO_2 , and solid copper are omitted from the expression for Q .)

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q \\ &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log \frac{[\text{Cu}^{2+}]^3}{[\text{MnO}_4^-]^2 [\text{H}^+]^8} \\ &= 1.34 \text{ V} - \frac{0.0592 \text{ V}}{6} \log \frac{(0.010)^3}{(2.0)^2 (1.0)^8} \\ &= 1.34 \text{ V} - (-0.065 \text{ V}) \\ &= 1.41 \text{ V} \end{aligned}$$

CHECK The answer has the correct units (V). The value of E_{cell} is larger than E_{cell}° , as expected, based on Le Châtelier's principle, because one of the aqueous reactants has a concentration greater than standard conditions and the one aqueous product has a concentration less than standard conditions. Therefore, the reaction has a greater tendency to proceed toward products and a greater cell potential.

FOR PRACTICE 19.8 Determine the cell potential of an electrochemical cell based on the following two half-reactions:



From Equation 19.9, we can conclude the following:

- When a redox reaction within a voltaic cell occurs under standard conditions $Q = 1$; therefore, $E_{\text{cell}} = E_{\text{cell}}^{\circ}$.

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q \\ &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log 1 \quad \log 1 = 0 \\ &= E_{\text{cell}}^{\circ} \end{aligned}$$

- When a redox reaction within a voltaic cell occurs under conditions in which $Q < 1$, the greater

concentration of reactants relative to products drives the reaction to the right, resulting in $E_{\text{cell}} > E_{\text{cell}}^{\circ}$.

- When a redox reaction within an electrochemical cell occurs under conditions in which $Q > 1$, the greater concentration of products relative to reactants drives the reaction to the left, resulting in $E_{\text{cell}} < E_{\text{cell}}^{\circ}$.
- When a redox reaction reaches equilibrium, $Q = K$. The redox reaction has no tendency to occur in either direction and $E_{\text{cell}} = 0$.
(see Equation 19.6)

$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q \\
 &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log K \\
 &= E_{\text{cell}}^{\circ} - E_{\text{cell}}^{\circ} \\
 &= 0
 \end{aligned}$$

This last point explains why batteries do not last forever—as the reactants are depleted, the reaction proceeds toward equilibrium and the potential tends toward zero.

Conceptual Connection 19.7 Relating Q , K , E_{cell} , and E_{cell}°

Concentration Cells

Since cell potential depends not only on the half-reactions occurring in the cell, but also on the *concentrations* of the reactants and products in those half-reactions, we can construct a voltaic cell in which both half-reactions are the same but in which *a difference in concentration drives the current flow*. For example, consider the electrochemical cell shown in Figure 19.12, in which copper is oxidized at the anode and copper(II) ions are reduced at the cathode. The second part of Figure 19.12 depicts this cell under nonstandard conditions, with $[\text{Cu}^{2+}] = 2.0 \text{ M}$ in one half-cell and $[\text{Cu}^{2+}] = 0.010 \text{ M}$ in the other:

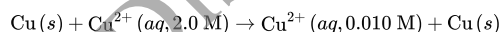
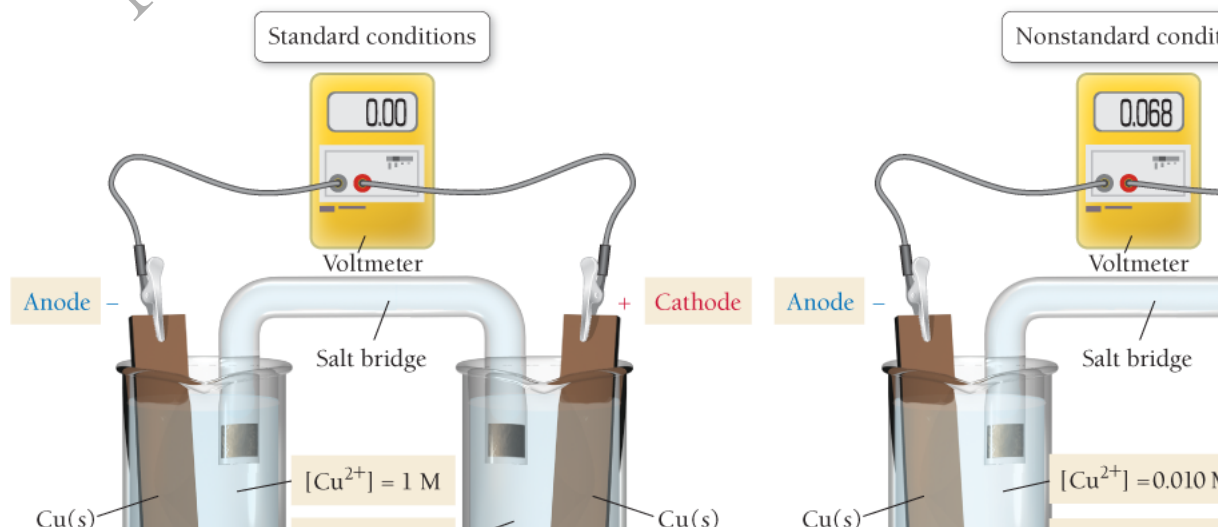


Figure 19.12 Cu/Cu²⁺ Concentration Cell

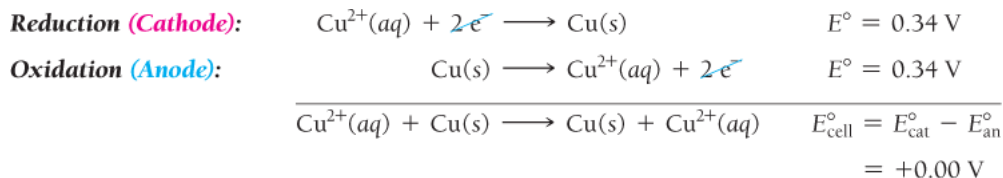
If two half-cells have the same Cu²⁺ concentration, the cell potential is zero. If one half-cell has a greater Cu²⁺ concentration than the other, a spontaneous reaction occurs. In the reaction, Cu²⁺ ions in the more concentrated cell are reduced (to solid copper), while Cu²⁺ ions in the more dilute cells are formed (from solid copper). The concentration of copper(II) ions in the two half-cells tends toward equality.

A Concentration Cell





The half-reactions are identical, so the *standard* cell potential is zero.



Because of the different concentrations in the two half-cells, we must calculate the cell potential using the Nernst equation.

$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{2} \log \frac{0.010}{2.0} \\
 &= 0.000 \text{ V} + 0.068 \text{ V} \\
 &= 0.068 \text{ V}
 \end{aligned}$$

The cell produces a potential of 0.068 V. *Electrons spontaneously flow from the half-cell with the lower copper ion concentration to the half-cell with the higher copper ion concentration.* We can imagine a concentration cell in the same way we think about any concentration gradient. If we mix a concentrated solution of Cu^{2+} with a dilute solution, the Cu^{2+} ions flow from the concentrated solution to the dilute one. Similarly, in a concentration cell, the transfer of electrons *from* the dilute half-cell results in the formation of Cu^{2+} ions in the dilute half-cell. The electrons flow to the concentrated cell, where they react with Cu^{2+} ions and reduce them to Cu(s) . Therefore, *the flow of electrons has the effect of increasing the concentration of Cu^{2+} in the dilute cell and decreasing the concentration of Cu^{2+} in the concentrated half-cell.*

Not for Distribution