

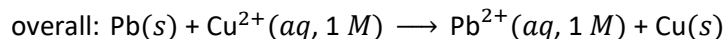
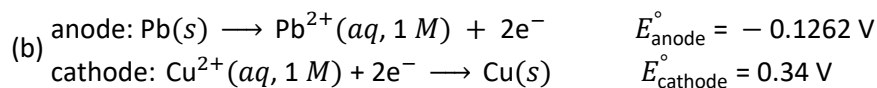
Electrochemistry

Section 108 – Batteries and Fuel Cells

- 108-1 Consider a battery made from one half-cell that consists of a copper electrode in 1 M CuSO₄ solution and another half-cell that consists of a lead electrode in 1 M Pb(NO₃)₂ solution.
- What is the standard cell potential for the battery?
 - What are the reactions at the anode, cathode, and the overall reaction?
 - Most devices designed to use dry-cell batteries can operate between 1.0 and 1.5 V. Could this cell be used to make a battery that could replace a dry-cell battery? Why or why not.
 - Suppose sulfuric acid is added to the half-cell with the lead electrode and some PbSO₄(s) forms. Would the cell potential increase, decrease, or remain the same?

Solution

(a) $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.34 \text{ V} - (-0.1262 \text{ V}) = 0.47 \text{ V}$



(c) Yes, if three cells were connected in series, the potential at standard conditions would be $E_{\text{battery}}^{\circ} = 3 \times E_{\text{cell}}^{\circ} = 1.41 \text{ V}$, which falls within the range of 1.0–1.5 V.

(d) If lead(II) sulfate forms, the concentration of lead(II) ion drops. Since lead(II) ions appear as products, Q becomes <1 (remember that at standard conditions, all concentrations are 1 M). From the Nernst equation

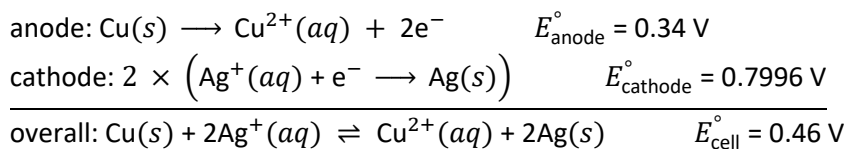
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q = E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Pb}^{2+}]}{[\text{Cu}^{2+}]}$$

The natural logarithm of a number <1 is negative; flipping the sign makes the contribution to the cell potential positive, so the cell potential would increase.

- 108-2 Consider a battery with the overall reaction: $\text{Cu}(s) + 2\text{Ag}^{+}(aq) \rightarrow 2\text{Ag}(s) + \text{Cu}^{2+}(aq)$.
- What is the reaction at the anode and cathode?
 - A battery is “dead” when its cell potential is zero. What is the value of Q when this battery is dead?
 - If a particular dead battery was found to have $[\text{Cu}^{2+}] = 0.11 \text{ M}$, what was the concentration of silver ion?

Solution

(a)



(b) Using the Nernst equation with $n = 2$:

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

$$0 = 0.46 \text{ V} - \frac{0.0592 \text{ V}}{2} \log Q \quad \text{or} \quad Q = 10^{2 \times 0.46 \text{ V} / 0.0592 \text{ V}} = 10^{15.54} = 3.5 \times 10^{15}; \text{ (c)}$$

Using the value of Q just calculated:

$$Q = 3.5 \times 10^{15} = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^2} \quad \text{or} \quad [\text{Ag}^{+}] = \sqrt{\frac{[\text{Cu}^{2+}]}{3.5 \times 10^{15}}} = 5.6 \times 10^{-9} \text{ M}.$$

108-3 Why do batteries go dead but fuel cells do not?

Solution

Batteries are self-contained and have a limited supply of reagents to expend before going dead. Alternatively, battery reaction byproducts accumulate and interfere with the reaction. Because a fuel cell is constantly resupplied with reactants and products are expelled, it can continue to function as long as reagents are supplied.

108-4 Use the Nernst equation to explain the drop in voltage observed for some batteries as they discharge.

Solution

As the reaction progresses, the value of Q will approach K . If we combine the equations for K and Q

$$\begin{aligned} -nFE_{\text{cell}} &= -nFE_{\text{cell}}^{\circ} + RT \ln Q & \text{or} & \quad E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q \\ -nFE_{\text{cell}}^{\circ} &= -RT \ln K & \text{or} & \quad E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln K \quad E_{\text{cell}} = \frac{RT}{nF} (\ln K - \\ & \ln Q) & \text{or} & \quad E_{\text{cell}} = \frac{RT}{nF} \left(\ln \frac{K}{Q} \right), \end{aligned}$$

we see the value in parentheses will approach zero, leading the cell potential to approach zero as well: a dead battery.

108-5 Automobile batteries are often rated with regard to “cold-cranking amps,” a measure of the ability of the battery to perform in low-temperature weather. Suggest a reason to explain why a battery’s ability to deliver current is diminished at low temperatures. (Hint: Consider the kinetics of chemical reactions.)

Solution

According to kinetic theory, chemical reactions occur more slowly at lower temperatures due to the decreased rate of collisions between reactant molecules. The rates of the redox reactions taking place within batteries decrease with temperature, resulting in a decreased production of electrical current.