Review Problems  –  Chapter 19
(Answers on next page)

(1) A large electrolytic cell that produces metallic aluminum from Al\textsubscript{2}O\textsubscript{3} ore is capable of making 250 kg of aluminum in 24 hours. Determine the current (in amps) that is required for this process. Include appropriate chemical reactions.

(2) An aqueous solution of NaCl was electrolyzed with a current of 2.50 amps for 15.0 minutes. What volume (in mL) of 0.500 M HCl would be required to neutralize the resulting solution? (Hint: H\textsubscript{2} is produced at the cathode and Cl\textsubscript{2} at the anode.)

(3) Under standard conditions, is the following a galvanic or an electrolytic cell? Support your conclusion with appropriate calculations and balanced chemical reactions.

\[ \text{Ag(s) | AgBr(s) | Br}^-\text{(aq) \parallel Au}^3+\text{(aq) | Au(s)} \]

(4) A silver wire coated with AgCl is sensitive to the chloride ion concentration because of the following half-cell reaction.

\[ \text{AgCl(s) + e}^- \rightarrow \text{Ag(s) + Cl}^-\text{(aq)} \quad E^\circ = 0.2223 \text{ v} \]

Calculate the molar concentration of Cl\textsuperscript{-} when the potential of this half-cell is measured to be 0.4900 volts relative to a standard hydrogen electrode.

(5) Consider the following electrochemical cell in which the volume of solution in each half-cell is 100 mL.

\[ \text{Zn(s) | Zn}^2+ \text{(1.00 M) \parallel Ag}^+ \text{(1.00 M) | Ag(s)} \]

(a) Write balanced chemical equations for the anode, cathode, and overall cell reactions.

(b) Determine \( E^\circ_{\text{cell}}, \Delta G^\circ, \) and the equilibrium constant (\( K_C \)) for the cell reaction.

(c) If current is drawn from this cell at a constant rate of 0.10 amp, what will the cell potential be after 24.0 hours?

(6) Given the following standard reduction potentials, calculate the solubility product constant (\( K_{sp} \)) for lead sulfate, PbSO\textsubscript{4}.

\[ \text{PbSO}_4(s) + 2 \text{ e}^- \rightarrow \text{Pb(s) + SO}_4^{2-}(aq) \quad E^\circ = -0.36 \text{ v} \]

\[ \text{Pb}^{2+} + 2 \text{ e}^- \rightarrow \text{Pb(s)} \quad E^\circ = -0.13 \text{ v} \]
(1) \(250,000 \text{ g} \) (1 mole Al / 26.95 g) (3 mole e\(^-\) / 1 mole Al) (96,500 coul / mole e\(^-\))
\[ = 2.686 \times 10^9 \text{ coul} = 2.686 \times 10^9 \text{ amp\cdotsec} \]
\[ (2.686 \times 10^9 \text{ amp\cdotsec}) / (24 \text{ hr}) (3600 \text{ sec/hr}) = 3.11 \times 10^4 \text{ amp} \]

(2) Cathode Rx: \(2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-\)
\[(2.50 \text{ amp}) (15 \text{ min}) (60 \text{ sec/min}) = 2250 \text{ amp\cdotsec} = 2250 \text{ coul}\]
\[ (2250 \text{ coul}) (1 \text{ mole e}^- / 96500 \text{ coul}) (2 \text{ mole OH}^- / 2 \text{ mole e}^-) \]
\[ = 0.02332 \text{ mole OH}^- = 0.02332 \text{ mole HCl} \]
\[ (0.02332 \text{ mole HCl}) (1000 \text{ mL} / 0.500 \text{ mole HCl}) = 46.6 \text{ mL HCl} \]

(3) Red: \(\text{Au}^{3+} + 3 \text{e}^- \rightarrow \text{Au} \quad E^{\circ}_{\text{red}} = 1.50 \text{ v} \)
Oxid: \(3 (\text{Ag} + \text{Br}^- \rightarrow \text{AgBr} + \text{e}^-) \quad E^{\circ}_{\text{oxid}} = 0.071 \text{ v} \)
Cell Rx: \(3 \text{Ag(s)} + \text{Au}^{3+} + 3 \text{Br}^-(\text{aq}) \rightarrow 3 \text{AgBr(s)} + \text{Au(s)} \)
\[ E^{\circ}_{\text{cell}} = 1.50 + (-0.071) = 1.43 \text{ v} \]
\[ \therefore \text{galvanic} \]

(4) Apply the Nernst equation to the given half-cell:
\[ E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0592 / n) \log Q \]
\[ 0.4900 \text{ v} = 0.2223 \text{ v} - (0.0592 / 1) \log Q \]
\[ Q = [\text{Cl}^-] = 3.0 \times 10^{-5} \text{ M} \]

(5) (a) Red: \(2(\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}) \quad E^{\circ}_{\text{red}} = 0.80 \text{ v} \)
Oxid: \(\text{Zn} \rightarrow \text{Zn}^{2+} + 2 \text{e}^- \quad E^{\circ}_{\text{oxid}} = -0.76 \text{ v} \)
Cell Rx: \(2 \text{Ag}^+ + \text{Zn} \rightarrow 2 \text{Ag} + \text{Zn}^{2+} \)
\[ E^{\circ}_{\text{cell}} = 0.80 + 0.76 = 1.56 \text{ v} \]
\[ \Delta G^{\circ} = -nF E^{\circ}_{\text{cell}} = - (2 \text{ moles}) (96,500 \text{ coul/mole}) (1.56 \text{ J/coul}) \]
\[ = -301,000 \text{ J} = -301 \text{ kJ} \]
\[ \log K_c = nE^{\circ}_{\text{cell}} / 0.0592 = (2)(1.56) / 0.0592 = 52.7 \]
\[ K_c = 5.0 \times 10^{52} \]
(c) \((0.10 \text{ amp}) (24 \text{ hr}) (3600 \text{ sec/hr}) = 8640 \text{ amp-sec} = 8640 \text{ coul}\)
\((8640 \text{ coul}) (1 \text{ mole e}^- / 96,500 \text{ coul}) = 0.0895 \text{ mole e}^- \text{ transferred}\)

\[\text{mole Ag}^+ \text{ consumed} = (0.0895 \text{ mole e}^-) (1 \text{ mole Ag}^+ / 1 \text{ mole e}^-)\]
\[= 0.0895 \text{ mole Ag}^+\]

\[\text{mole Ag}^+ \text{ remaining (after 24 hrs)} = 0.100 - 0.0895 = 0.0105 \text{ mole Ag}^+\]
\[[\text{Ag}^+] = 0.0105 \text{ mole} / 0.100 \text{ L} = 0.105 \text{ M}\]

\[\text{mole Zn}^{2+} \text{ produced} = (0.0895 \text{ mole e}^-) (1 \text{ mole Zn}^{2+} / 2 \text{ mole e}^-)\]
\[= 0.04475 \text{ mole}\]

\[\text{mole Zn}^{2+} \text{ after 24 hrs} = 0.100 + 0.04475 = 0.145 \text{ mole}\]
\[[\text{Zn}^{2+}] = 0.145 \text{ mole} / 0.100 \text{ L} = 1.45 \text{ M}\]

\[E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0592 / n) \log Q\]
\[Q = [\text{Zn}^{2+}] / [\text{Ag}^+]^2 = (1.45) / (0.105)^2 = 131.5\]

\[E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0592 / n) \log Q = 1.56 - (0.0592/2)\log(131.5)\]
\[E_{\text{cell}} = 1.56 - 0.063 = 1.50 \text{ v} \text{ (after ~ 90 \% completion)}\]

(6) \text{Red: PbSO}_4(s) + 2 \text{ e}^- \rightleftharpoons \text{Pb(s)} + \text{SO}_4^{2-}(aq) \quad E^{\circ}_{\text{red}} = -0.36 \text{ v}\]
\text{Oxid: Pb(s) \rightleftharpoons Pb}^{2+}(aq) + 2 \text{ e}^- \quad E^{\circ}_{\text{oxid}} = -0.13 \text{ v}\]
\text{Cell Rx: PbSO}_4(s) \rightleftharpoons Pb}^{2+}(aq) + \text{SO}_4^{2-}(aq) \quad E^{\circ}_{\text{cell}} = -0.36 + 0.23 \text{ v} = -0.23 \text{ v}\]

\[\log K_{\text{Sp}} = nE^{\circ}_{\text{cell}} / 0.0592 = 2 (-0.23) / (0.0592) = -7.77\]
\[K_{\text{Sp}} = 1.7 \times 10^{-8}\]