Review Problems – Chapter 19

(Answers on next page)

(1) A large electrolytic cell that produces metallic aluminum from Al_2O_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_2 is produced at the cathode and Cl_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.

$$Ag_{(s)} \mid AgBr_{(s)} \mid Br^-_{(aq)} \parallel Au^{3+}_{(aq)} \mid Au_{(s)}$$

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

$$AgCl_{(s)} + e^- \longrightarrow Ag_{(s)} + Cl^-_{(aq)} \qquad E^o = 0.2223 \text{ v}$$

Calculate the molar concentration of Cl^- 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.

$$Zn_{(s)} \mid Zn^{2+}\ (1.00\ M) \parallel Ag^+\ (1.00\ M) \mid Ag_{(s)}$$

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

(b) Determine E^o_{cell}, ΔG°, 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, $PbSO_4$.

$$PbSO_{4(s)} + 2\,e^- \longrightarrow Pb_{(s)} + SO_4{}^{2-}{}_{(aq)} \qquad E^o = -0.36 \text{ v}$$

$$Pb^{2+} + 2\,e^- \longrightarrow Pb_{(s)} \qquad E^o = -0.13 \text{ v}$$

(1) (250,000 g) (1 mole Al / 26.95 g) (3 mole e^- / 1 mole Al) (96,500 coul / mole e^-)

= 2.686×10^9 coul = 2.686×10^9 amp·sec

(2.686×10^9 amp·sec) / (24 hr) (3600 sec/hr) = 3.11×10^4 amp

(2) Cathode Rx: $2\ H_2O + 2\ e^- \longrightarrow H_2 + 2\ OH^-$

(2.50 amp) (15 min) (60 sec/min) = 2250 amp·sec = 2250 coul

(2250 coul) (1 mole e^- / 96500 coul) (2 mole OH^- / 2 mole e^-)

= 0.02332 mole OH^- = 0.02332 mole HCl

(0.02332 mole HCl) (1000 mL / 0.500 mole HCl) = 46.6 mL HCl

(3) Red: $Au^{3+} + 3\ e^- \longrightarrow Au$ $\quad E°_{red} = 1.50$ v

Oxid: $3\ (Ag + Br^- \longrightarrow AgBr + e^-)$ $\quad E°_{oxid} = 0.071$ v

Cell Rx: $3\ Ag_{(s)} + Au^{3+} + 3\ Br^-_{(aq)} \longrightarrow 3\ AgBr_{(s)} + Au_{(s)}$

$E°_{cell} = 1.50 + (-\ 0.071) = 1.43$ v $\quad \therefore$ galvanic

(4) Apply the Nernst equation to the given half-cell:

$E_{cell} = E°_{cell} - (0.0592 / n) \log Q$

0.4900 v = 0.2223 v - (0.0592 / 1) log Q

$Q = [Cl^-] = 3.0 \times 10^{-5}$ M

(5) (a) Red: $2\ (Ag^+ + e^- \longrightarrow Ag)$ $\quad E°_{red} = 0.80$ v

Oxid: $Zn \longrightarrow Zn^{2+} + 2\ e^-$ $\quad E°_{oxid} = -\ 0.76$ v

Cell Rx: $2\ Ag^+ + Zn \longrightarrow 2\ Ag + Zn^{2+}$

(b) $E°_{cell} = 0.80 + 0.76 = 1.56$ v

$\Delta G° = -\ nFE°_{cell}$ = - (2 moles) (96,500 coul/mole) (1.56 J/coul)

= - 301,000 J = - 301 kJ

$\log K_c = nE°_{cell} / 0.0592 = (2)(1.56) / 0.0592 = 52.7$

$K_c = 5.0 \times 10^{52}$

(c) (0.10 amp) (24 hr) (3600 sec/hr) = 8640 amp·sec = 8640 coul

(8640 coul) (1 mole e^- / 96,500 coul) = 0.0895 mole e^- transferred

mole Ag^+ consumed = (0.0895 mole e^-) (1 mole Ag^+ / 1 mole e^-)
= 0.0895 mole Ag^+

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

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

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

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

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

(6) Red: $PbSO_{4(s)} + 2e^- \rightleftharpoons Pb_{(s)} + SO_4{}^{2-}{}_{(aq)}$ $E^\circ_{\text{red}} = -0.36$ v
Oxid: $Pb(s) \rightleftharpoons Pb^{2+}{}_{(aq)} + 2e^-$ $E^\circ_{\text{oxid}} = -0.13$ v
Cell Rx: $PbSO_{4(s)} \rightleftharpoons Pb^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$

$E^\circ_{\text{cell}} = -0.36 + 0.23$ v $= -0.23$ v

$\log K_{sp} = nE^\circ_{\text{cell}} / 0.0592 = 2(-0.23) / (0.0592) = -7.77$
$K_{sp} = 1.7 \times 10^{-8}$