Ch. 19.4: Spontaneity of Redox Reactions
Homework #19-3: Problems pg. 833 #20, 21, 22, 23 (a&c), 24 (a&c), 25

20 Compare the ease of measuring the equilibrium constant electrochemically with that by chemical means [see Equation (18.14)].
It is much easier to measure the equilibrium constant electrochemically because one simply has to measure the cell voltage to determine $K = e^{\frac{nE^\circ_{cell}}{0.0257\ V}}$.

21 What is the equilibrium constant for the following reaction at 25°C?

$$\mathbf{Mg(s) + Zn^{2+}(aq) \rightleftharpoons Mg^{2+}(aq) + Zn(s)}$$

We find the standard reduction potentials in Table 19.1 of the text.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -0.76\ V - (-2.37\ V) = 1.61\ V$$

$$E^\circ_{cell} = \frac{0.0257\ V}{n}\ln K\text{, so }\ln K = \frac{nE^\circ_{cell}}{0.0257\ V}$$

$$\boldsymbol{K} = e^{\frac{nE^\circ_{cell}}{0.0257\ V}} = e^{\frac{(2)(1.61\ V)}{0.0257\ V}} = \mathbf{3 \times 10^{54}}$$

22 The equilibrium constant for the reaction

$$\mathbf{Sr(s) + Mg^{2+}(aq) \rightleftharpoons Sr^{2+}(aq) + Mg(s)}$$

is $\mathbf{2.6\times10^{12}}$ at 25°C. Calculate $\boldsymbol{E}$° for a cell made up of $\mathbf{Sr/Sr^{2+}}$ and $\mathbf{Mg/Mg^{2+}}$ half cells.

$$E^\circ_{cell} = \frac{0.0257\ \text{V}}{\boldsymbol{n}}\ln \boldsymbol{K}$$

We see in the reaction that Mg is oxidized to Mg^{2+} and Zn^{2+} is reduced to Zn, so two moles of electrons are transferred during the redox reaction (n = 2).

$$\boldsymbol{E}° = \frac{(0.0257\ V)\ln \boldsymbol{K}}{\boldsymbol{n}} = \frac{(0.0257\ V)\ln(2.69\times10^{12})}{2} = \mathbf{0.368\ V}$$

23 Use the standard reduction potentials to find the equilibrium constant for each of the following reactions at 25°C:

(a) $\mathbf{Br_2(\mathit{l}) + 2I^-(aq) \rightleftharpoons 2\ Br^-(aq) + I_2(s)}$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 1.07\ V - 0.53\ V = 0.54\ V$; n = 2 ($Br_2 + 2e^- \rightarrow 2\ Br^-$; $2I^- \rightarrow I_2 + 2\ e^-$)

$$\ln K = \frac{nE^\circ_{cell}}{0.0257\ V}\text{, so }\boldsymbol{K} = e^{\frac{nE^\circ_{cell}}{0.0257\ V}} = e^{\frac{(2)(0.54\ V)}{0.0257\ V}} = \mathbf{2\times10^{18}}$$

(c) $\mathbf{5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) \rightleftharpoons Mn^{2+}(aq) + 4\ H_2O + 5\ Fe^{3+}(aq)}$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 1.51\ V - 0.77\ V = 0.74\ V$; n = 5 ($Mn^{7+} + 5\ e^- \rightarrow Mn^{2+}$; $5\ Fe^{2+} \rightarrow 5\ Fe^{3+} + 5e^-$)

$$\boldsymbol{K} = e^{\frac{(5)(0.74\ V)}{0.0257\ V}} = \mathbf{3\times10^{62}}$$

24 Calculate $\Delta G°$ and K_c for the following reactions at 25°C:

(a) $Mg(s) + Pb^{2+}(aq) \rightleftharpoons Mg^{2+}(aq) + Pb(s)$

We break the equation into two half–reactions:

$$Mg(s) \xrightarrow{oxidation\,(anode)} Mg^{2+}(aq) + 2e^- \qquad E^\circ_{anode} = -2.37\ V$$

$$Pb^{2+}(aq) + 2e^- \xrightarrow{reduction\,(cathode)} Pb(s) \qquad E^\circ_{cathode} = -0.13\ V$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -0.13\ V - (-2.37\ V) = 2.24\ V$$

$$\boldsymbol{\Delta G°} = -nFE^\circ_{cell} = -(2)(96500\ \text{J/V}\cdot mol)(2.24\ V) = \mathbf{-432\ kJ/mol}$$

$$E^\circ_{cell} = \frac{0.0257\ \text{V}}{\boldsymbol{n}}\ln \boldsymbol{K} \ \text{ or } \ \ln \boldsymbol{K} = \frac{\boldsymbol{n}E^\circ_{cell}}{0.0257\ \text{V}}\ ;\ \text{n} = 2$$

so

$$\boldsymbol{K} = \boldsymbol{e}^{\frac{\boldsymbol{nE°}}{0.0257}} = \boldsymbol{e}^{\frac{(2)(2.24)}{0.0257}} = \mathbf{5 \times 10^{75}}$$

Tip: You could also calculate K_c from the standard free energy change, $\Delta G°$, using the equation: $\Delta G° = -RT\ln K_c$.

(c) $O_2(g) + 4H^+(aq) + 4Fe^{2+}(aq) \rightleftharpoons 2H_2O(l) + 4Fe^{3+}(aq)$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 1.23\ V - 0.77\ V = 0.46\ V$$

n = 4 ($O_2 + 4e^- \rightarrow 2O^{2-}$; $4Fe^{2+} \rightarrow 4Fe^{3+} + 4e^-$)

$$\Delta \boldsymbol{G}° = -nFE^\circ_{cell} = -(4)(96500\ \text{J/V·mol})(0.46\ \text{V}) = \mathbf{-178\ kJ/mol}$$

$$\boldsymbol{K} = \boldsymbol{e}^{\frac{\boldsymbol{nE°}}{0.0257}} = \boldsymbol{e}^{\frac{(4)(0.46)}{0.0257}} = \mathbf{1 \times 10^{31}}$$

25 Under standard-state conditions, what spontaneous reaction will occur in aqueous solution among the ions Ce^{4+}, Ce^{3+}, Fe^{3+}, and Fe^{2+}? Calculate $\Delta G°$ and K_c for the reaction.

The half-reactions are:

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad E^\circ_{anode} = 0.77\ V$$

$$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq) \qquad E^\circ_{cathode} = 1.61\ V$$

Overall: Ce^{4+} (aq) + Fe^{2+} (aq) $\rightarrow$ Ce^{3+} (aq) + Fe^{3+} (aq)

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 1.61\ V - 0.77\ V = 0.84\ V$$

n = 1

$$\boldsymbol{\Delta G°} = -nFE^\circ_{cell} = -(1)(96500\ \text{J/V}\cdot mol)(0.84\ V) = \mathbf{-81\ kJ/mol}$$

$$\ln K = \frac{nE^\circ_{cell}}{0.0257\ V},\ \text{so}\ \boldsymbol{K_c} = e^{\frac{nE^\circ_{cell}}{0.0257\ V}} = e^{\frac{(1)(0.84\ V)}{0.0257\ V}} = \mathbf{2 \times 10^{14}}$$