7.2 Calculate the emf of the Daniell cell at 298 K when the concentrations of $CuSO_4$ and $ZnSO_4$ are 0.50 M and 0.10 M, respectively. What would the emf be if activities were used instead of concentrations? (The $\gamma_\pm$ values for $CuSO_4$ and $ZnSO_4$ at their respective concentrations are 0.068 and 0.15, respectively.)

The half reactions for the Daniell cell are

$$\text{Anode:} \quad Zn \rightarrow Zn^{2+} + 2e^-$$
$$\text{Cathode:} \quad Cu^{2+} + 2e^- \rightarrow Cu$$

Thus, for the cell,

$$E^\circ = 0.342\ \text{V} - (-0.762\ \text{V}) = 1.104\ \text{V}$$

The emf at the specified Cu^{2+} and Zn^{2+} concentrations is

$$E = E^\circ - \frac{0.0257\ \text{V}}{\nu} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]} = 1.104\ \text{V} - \frac{0.0257\ \text{V}}{2} \ln \frac{0.10}{0.50} = 1.125\ \text{V}$$

Using activities,

$$E = E^\circ - \frac{0.0257\ \text{V}}{\nu} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

$$= E^\circ - \frac{0.0257\ \text{V}}{\nu} \ln \frac{\gamma_{\pm,ZnSO_4}[Zn^{2+}]}{\gamma_{\pm,CuSO_4}[Cu^{2+}]}$$

$$= 1.104\ \text{V} - \frac{0.0257\ \text{V}}{2} \ln \frac{(0.15)(0.10)}{(0.068)(0.50)}$$

$$= 1.115\ \text{V}$$

7.4 Consider a Daniell cell operating under non-standard-state conditions. Suppose that the cell's reaction is multiplied by 2. What effect does this have on each of the following quantities in the Nernst equation? **(a)** E, **(b)** E°, **(c)** Q, **(d)** $\ln Q$, and **(e)** ν

(a) None. E is an intensive property, **(b)** none. E° is an intensive property, **(c)** squared, **(d)** doubled, **(e)** doubled.

7.8 Calculate the values of E°, $\Delta_r G^\circ$, and K for the following reactions at 25° C:

(a) $Zn + Sn^{4+} \rightleftharpoons Zn^{2+} + Sn^{2+}$

(b) $Cl_2 + 2I^- \rightleftharpoons 2Cl^- + I_2$

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

(a) Anode: $Zn \rightarrow Zn^{2+} + 2e^-$

Cathode: $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$

$$E^\circ = 0.151\ \mathrm{V} - (-0.762\ \mathrm{V}) = 0.913\ \mathrm{V}$$

$$\Delta_r G^\circ = -\nu F E^\circ = -2\left(96500\ \mathrm{C\ mol^{-1}}\right)(0.913\ \mathrm{V}) = -1.762 \times 10^5\ \mathrm{J\ mol^{-1}} = -1.76 \times 10^5\ \mathrm{J\ mol^{-1}}$$

$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left[-\frac{(-1.762 \times 10^5\ \mathrm{J\ mol^{-1}})}{(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\ (298.2\ \mathrm{K})}\right] = 7.34 \times 10^{30}$$

(b) Anode: $2I^- \rightarrow I_2 + 2e^-$

Cathode: $Cl_2 + 2e^- \rightarrow 2Cl^-$

$$E^{\circ} = 1.368\ \text{V} - 0.536\ \text{V} = 0.824\ \text{V}$$

$$\Delta_r G^{\circ} = -\nu F E^{\circ} = -2\left(96500\ \text{C mol}^{-1}\right)(0.824\ \text{V}) = -1.590 \times 10^{5}\ \text{J mol}^{-1} = -1.59 \times 10^{5}\ \text{J mol}^{-1}$$

$$K = \exp\left(-\frac{\Delta_r G^{\circ}}{RT}\right) = \exp\left[-\frac{(-1.590 \times 10^{5}\ \text{J mol}^{-1})}{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (298.2\ \text{K})}\right] = 7.12 \times 10^{27}$$

(c) Anode: $Fe^{2+} \rightarrow Fe^{3+} + e^-$

Cathode: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2}+ + 4H_2O$

$$E^{\circ} = 1.507\ \text{V} - 0.771\ \text{V} = 0.736\ \text{V}$$

$$\Delta_r G^{\circ} = -\nu F E^{\circ} = -5\left(96500\ \text{C mol}^{-1}\right)(0.739\ \text{V}) = -3.551 \times 10^{5}\ \text{J mol}^{-1} = -3.55 \times 10^{5}\ \text{J mol}^{-1}$$

$$K = \exp\left(-\frac{\Delta_r G^{\circ}}{RT}\right) = \exp\left[-\frac{(-3.551 \times 10^{5}\ \text{J mol}^{-1})}{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (298.2\ \text{K})}\right] = 1.60 \times 10^{62}$$

7.12 From the standard reduction potentials listed in Table 7.1 for Sn^{2+} | Sn and Pb^{2+} | Pb, calculate the ratio of $[Sn^{2+}]$ to $[Pb^{2+}]$ at equilibrium at 25° C and the $\Delta_r G^{\circ}$ value for the reaction.

The reduction potentials for the half cells are

$$Sn^{2+} + 2e^- \rightarrow Sn \qquad E^{\circ} = -0.138\ \text{V}$$

$$Pb^{2+} + 2e^- \rightarrow Pb \qquad E^{\circ} = -0.126\ \text{V}$$

The standard emf for the reaction $Sn + Pb^{2+} \rightarrow Sn^{2+} + Pb$ is

$$E^{\circ} = -0.126\ \text{V} - (-0.138\ \text{V}) = 0.012\ \text{V}$$

The ratio of $[Sn^{2+}]$ to $[Pb^{2+}]$ at equilibrium is directly related to the equilibrium constant, which can be calculated from E°.

$$K = \frac{[Sn^{2+}]}{[Pb^{2+}]} = \exp\left(\frac{\nu F E^{\circ}}{RT}\right) = \exp\left[\frac{2\ (96500\ \text{C mol}^{-1})\ (0.012\ \text{V})}{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (298.2\ \text{K})}\right] = 2.55$$

The standard Gibbs energy is

$$\Delta_r G^{\circ} = -\nu F E^{\circ} = -2\left(96500\ \text{C mol}^{-1}\right)(0.012\ \text{V}) = -2.32 \times 10^{3}\ \text{J mol}^{-1}$$