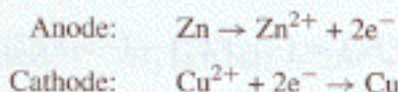


- 7.2 Calculate the emf of the Daniell cell at 298 K when the concentrations of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  are 0.50 M and 0.10 M, respectively. What would the emf be if activities were used instead of concentrations? (The  $\gamma_{\pm}$  values for  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  at their respective concentrations are 0.068 and 0.15, respectively.)

The half reactions for the Daniell cell are



Thus, for the cell,

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

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

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

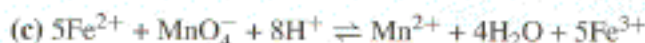
Using activities,

$$\begin{aligned} E &= E^{\circ} - \frac{0.0257 \text{ V}}{\nu} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \\ &= E^{\circ} - \frac{0.0257 \text{ V}}{\nu} \ln \frac{\gamma_{\pm, \text{ZnSO}_4} [\text{Zn}^{2+}]}{\gamma_{\pm, \text{CuSO}_4} [\text{Cu}^{2+}]} \\ &= 1.104 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{(0.15)(0.10)}{(0.068)(0.50)} \\ &= 1.115 \text{ V} \end{aligned}$$

- 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)  $E^{\circ}$ , (c)  $Q$ , (d)  $\ln Q$ , and (e)  $\nu$

(a) None.  $E$  is an intensive property, (b) none.  $E^\circ$  is an intensive property, (c) squared, (d) doubled, (e) doubled.

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



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

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

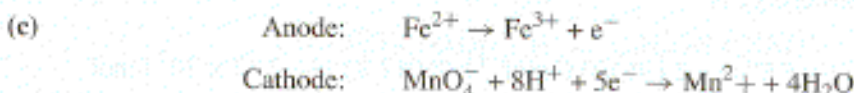
$$K = \exp \left( -\frac{\Delta_r G^\circ}{RT} \right) = \exp \left[ -\frac{(-1.762 \times 10^5 \text{ J mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298.2 \text{ K})} \right] = 7.34 \times 10^{30}$$



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

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

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



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

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

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

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

The reduction potentials for the half cells are



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

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

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

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

The standard Gibbs energy is

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