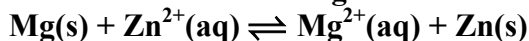


- 20 Compare the ease of measuring the equilibrium constant electrochemically with that by chemical means [see Equation (18.14)].

It is much easier to measure the equilibrium constant electrochemically because one simply has to measure the cell voltage to determine  $K = e^{\frac{nE_{cell}^{\circ}}{0.0257 V}}$ .

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



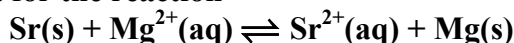
We find the standard reduction potentials in Table 19.1 of the text.

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

$$E_{cell}^{\circ} = \frac{0.0257 V}{n} \ln K, \text{ so } \ln K = \frac{nE_{cell}^{\circ}}{0.0257 V}$$

$$K = e^{\frac{nE_{cell}^{\circ}}{0.0257 V}} = e^{\frac{(2)(1.61 V)}{0.0257 V}} = 3 \times 10^{54}$$

- 22 The equilibrium constant for the reaction



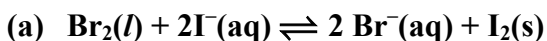
is  $2.6 \times 10^{12}$  at 25°C. Calculate  $E^{\circ}$  for a cell made up of Sr/Sr<sup>2+</sup> and Mg/Mg<sup>2+</sup> half cells.

$$E_{cell}^{\circ} = \frac{0.0257 V}{n} \ln K$$

We see in the reaction that Mg is oxidized to Mg<sup>2+</sup> and Zn<sup>2+</sup> is reduced to Zn, so two moles of electrons are transferred during the redox reaction ( $n = 2$ ).

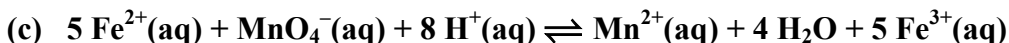
$$E^{\circ} = \frac{(0.0257 V) \ln K}{n} = \frac{(0.0257 V) \ln(2.69 \times 10^{12})}{2} = 0.368 V$$

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



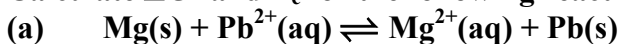
$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} = 1.07 V - 0.53 V = 0.54 V; n = 2 (\text{Br}_2 + 2\text{e}^{-} \rightarrow 2\text{Br}^{-}; 2\text{I}^{-} \rightarrow \text{I}_2 + 2\text{e}^{-})$$

$$\ln K = \frac{nE_{cell}^{\circ}}{0.0257 V}, \text{ so } K = e^{\frac{nE_{cell}^{\circ}}{0.0257 V}} = e^{\frac{(2)(0.54 V)}{0.0257 V}} = 2 \times 10^{18}$$

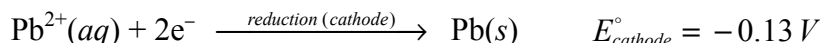
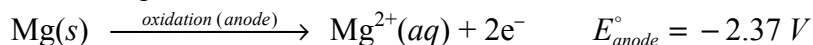


$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} = 1.51 V - 0.77 V = 0.74 V; n = 5 (\text{Mn}^{7+} + 5\text{e}^{-} \rightarrow \text{Mn}^{2+}; 5\text{Fe}^{2+} \rightarrow 5\text{Fe}^{3+} + 5\text{e}^{-})$$

$$K = e^{\frac{(5)(0.74 V)}{0.0257 V}} = 3 \times 10^{62}$$

24 Calculate  $\Delta G^\circ$  and  $K_c$  for the following reactions at  $25^\circ\text{C}$ :

We break the equation into two half-reactions:



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = -0.13 \text{ V} - (-2.37 \text{ V}) = 2.24 \text{ V}$$

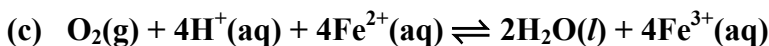
$$\Delta G^\circ = -nFE_{\text{cell}}^\circ = -(2)(96500 \text{ J/V} \cdot \text{mol})(2.24 \text{ V}) = -432 \text{ kJ/mol}$$

$$E_{\text{cell}}^\circ = \frac{0.0257 \text{ V}}{n} \ln K \quad \text{or} \quad \ln K = \frac{nE_{\text{cell}}^\circ}{0.0257 \text{ V}}; n = 2$$

so

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

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



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 1.23 \text{ V} - 0.77 \text{ V} = 0.46 \text{ V}$$

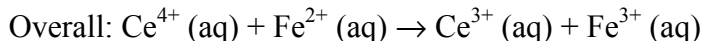
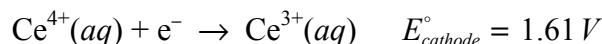
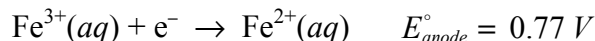
$$n = 4 (\text{O}_2 + 4e^- \rightarrow 2\text{O}^{2-}; 4\text{Fe}^{2+} \rightarrow 4\text{Fe}^{3+} + 4e^-)$$

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ = -(4)(96500 \text{ J/V} \cdot \text{mol})(0.46 \text{ V}) = -178 \text{ kJ/mol}$$

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

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

The half-reactions are:



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 1.61 \text{ V} - 0.77 \text{ V} = 0.84 \text{ V}$$

$$n = 1$$

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ = -(1)(96500 \text{ J/V} \cdot \text{mol})(0.84 \text{ V}) = -81 \text{ kJ/mol}$$

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