Ch 19.5: The Effect of Concentration on EMF

Homework #19-4: Problems pg. 833 #29, 31, 33, 34

29 **What is the potential of a cell made up of Zn/Zn^{2+} and Cu/Cu^{2+} half-cells at 25°C if [Zn^{2+}] = 0.25 *M* and [Cu^{2+}] = 0.15 *M*?**

If this were a standard cell, the concentrations would all be 1.00 *M*, and the voltage would just be the standard emf calculated from Table 19.1 of the text. Since cell emf's depend on the concentrations of the reactants and products, we must use the Nernst equation [Equation (19.8) of the text] to find the emf of a nonstandard cell.

Overall Reaction: Cu^{2+} (aq) + Zn (s) $\rightleftharpoons$ Cu (s) + Zn^{2+} (aq)

$$E^\circ = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn} = 0.34\text{ V} - (-0.76\text{ V}) = 1.10\text{ V}$$

$$E = E^\circ - \frac{0.0257\ V}{n}\ln Q = 1.10\ V - \frac{0.0257\ V}{2}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]} = 1.10\ V - \frac{0.0257\ V}{2}\ln\frac{0.25}{0.15}$$

$$\boldsymbol{E = 1.09\text{ V}}$$

31 **Calculate the standard potential of the cell consisting of the Zn/Zn^{2+} half-cell and the SHE. What will the emf of the cell be if [Zn^{2+}] = 0.45 *M*, P_{H_2} = 2.0 atm, and [H^+] = 1.8 *M*?**

The overall reaction is: $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

$$\boldsymbol{E^\circ_{cell}} = E^\circ_{cathode} - E^\circ_{anode} = 0.00\ V - (-0.76\ V) = \mathbf{0.76\ V}$$

$$\boldsymbol{E} = E^\circ - \frac{0.0257\ V}{n}\ln\frac{[Zn^{2+}]P_{H_2}}{[H^+]^2}$$

$$\boldsymbol{E} = 0.76\ V - \frac{0.0257\ V}{2}\ln\frac{(0.45)(2.0)}{(1.8)^2} = \mathbf{0.78\ V}$$

33 **Referring to the arrangement in Figure 19.1, calculate the [Cu^{2+}]/[Zn^{2+}] ratio at which the following reaction is spontaneous at 25°C:**

$Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$

As written, the reaction is not spontaneous under standard state conditions; the cell emf is negative:

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -0.76\ V - 0.34\ V = -1.10\ V$$

The reaction will become spontaneous when the concentrations of zinc(II) and copper(II) ions are such as to make the emf positive. The turning point is when the $E_{cell} = 0$. We solve the Nernst equation for the [Cu^{2+}]/[Zn^{2+}] ratio at this point.

$$E_{cell} = E^\circ - \frac{0.0257\ V}{n}\ln Q = 0 = -1.10\ V - \frac{0.0257\ V}{2}\ln\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$\ln\frac{[Cu^{2+}]}{[Zn^{2+}]} = -85.6\text{, so } \frac{\mathbf{[Cu^{2+}]}}{\mathbf{[Zn^{2+}]}} = e^{-85.6} = \mathbf{6.7 \times 10^{-38}}$$

In other words for the reaction to be spontaneous, the $[Cu^{2+}]/[Zn^{2+}]$ ratio must be less than 6.3×10^{-38}. Is the reduction of zinc(II) by copper metal a practical use of copper?

34 Calculate the emf of the following concentration cell:

Mg(s) | Mg^{2+} (0.24 *M*) || Mg^{2+} (0.53 *M*) | Mg(s)

All concentration cells have the same standard emf: *zero* volts.

$$Mg^{2+}(aq) + 2e^- \xrightarrow{\text{reduction (cathode)}} Mg(s) \qquad E^\circ_{cathode} = -2.37\ V$$

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

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -2.37\ V - (-2.37\ V) = 0.00\ V$$

We use the Nernst equation to compute the emf. There are two moles of electrons transferred from the reducing agent to the oxidizing agent in this reaction, so $n = 2$.

$$\boldsymbol{E} = E^\circ - \frac{0.0257\ V}{\boldsymbol{n}}\ln\boldsymbol{Q}$$

$$\boldsymbol{E} = E^\circ - \frac{0.0257\ V}{\boldsymbol{n}}\ln\frac{[Mg^{2+}]_{ox}}{[Mg^{2+}]_{red}} = E^\circ - \frac{0.0257\ V}{\boldsymbol{n}}\ln\frac{[Mg^{2+}]_{dil}}{[Mg^{2+}]_{con}}$$

$$\boldsymbol{E} = 0\ V - \frac{0.0257\ V}{2}\ln\frac{0.24}{0.53} = \mathbf{0.010\ V}$$

What is the direction of spontaneous change in all concentration cells?