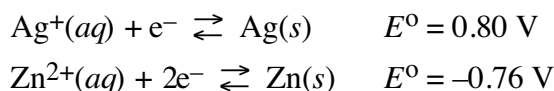


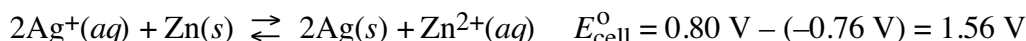
Problem Set 8 Solutions (For Wednesday, March 9)

as reactants in the second. Clearly, the net reaction water product has to have its hydrogens coming from the ammonium ion, and the oxygen in water has to come from somewhere! These half reactions, however, are more formalities than realities, in that the real reaction does not occur in two distinct half-reaction steps as we've imagined here.

3. We first turn to Table A5.5 and write down the two relevant standard reduction potentials:



These values tell us that the spontaneous reaction under standard conditions must be



because this is the combination that leads to a positive E_{cell}° . Reduction happens at the Ag electrode, and oxidation happens at the Zn electrode; the Ag electrode is positive. But we are not at standard conditions: the cell potential is 1.50 V, not 1.56 V, and $[\text{Ag}^+] = 0.05 \text{ M}$, not 1 M. Thus, we turn to the full Nernst equation, with $n = 2$:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591 \text{ V}}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \quad \text{or} \quad 1.50 \text{ V} = 1.56 \text{ V} - \frac{0.0591 \text{ V}}{2} \log \frac{[\text{Zn}^{2+}]}{(0.05)^2}$$

We solve this last expression for $[\text{Zn}^{2+}]$ and find $[\text{Zn}^{2+}] = 0.27 \text{ M}$. Now we add NaCl to the silver half cell. This doesn't alter $[\text{Zn}^{2+}]$, but it drops $[\text{Ag}^+]$ down to the *saturation concentration* for AgCl. We look up K_{sp} for AgCl in Table A5.4 and do a quick solubility calculation for a solution saturated with AgCl with no excess Ag^+ or Cl^- :

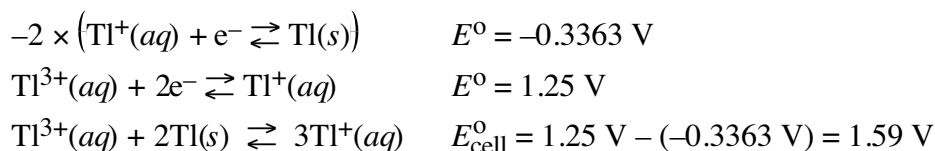
$$K_{\text{sp}} = 1.6 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-] = x^2 \quad \text{or} \quad x = [\text{Ag}^+] = 1.26 \times 10^{-5} \text{ M}$$

We substitute this concentration into the Nernst equation and find the new cell voltage:

$$E_{\text{cell}} = 1.56 \text{ V} - \frac{0.0591 \text{ V}}{2} \log \frac{0.27}{(1.26 \times 10^{-5})^2} = 1.29 \text{ V}$$

Note that it makes sense that the voltage should drop if $[\text{Ag}^+]$ is lowered: the reaction is spontaneous toward products, and E_{cell}° is large, meaning K for the net reaction is very large. (You might want to calculate it. You should find $K = 5.48 \times 10^{52}$.) This tells us that at equilibrium, $[\text{Ag}^+]$ should be very small indeed; at equilibrium, $E_{\text{cell}} = 0$.

4. We can combine the two half-reactions in the problem into a net reaction between $\text{Tl}(s)$ and $\text{Tl}^{3+}(aq)$, and find that reaction's E_{cell}° value:



Since E_{cell}° is positive, this reaction at standard conditions is spontaneous as written. Thus, we conclude that $\text{Tl}^{3+}(aq)$ is unstable in the presence of $\text{Tl}(s)$. Note, by the way, that we had to multiply the oxidation half reaction by 2 to combine it with the reduction half reaction to yield the net reaction, but we did *not* multiply the reduction potential by 2! No matter how the half reactions are manipulated to combine into a net reaction, $E_{\text{cell}}^\circ = E^\circ(\text{reduction half reaction}) - E^\circ(\text{oxidation half reaction})$. To find the equilibrium constant, we note that the net reaction involves a two-electron transfer, so that $n = 2$. We calculate a K considerably larger than 1:

$$K = e^{nFE_{\text{cell}}^\circ/RT} = e^{(2)(96485 \text{ C mol}^{-1})(1.59 \text{ V})/(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})} = 5.66 \times 10^{53}$$