CH302H – Principles of Chemistry II: Honors
Spring 2014, Unique 51880

Quiz 5
17 April 2014

I know we all enjoyed our discussions last Thursday. Let's apply our new found knowledge:

Consider making a solution with the following initial composition:

2.2×10^{-4} F $Hg_2(NO_3)_2$ and 1.2×10^{-4} F $Fe(NO_3)_2$ in a pH=3.00 buffered solution.

The question is whether Hg_2^{2+} will oxidize Fe^{2+} to Fe^{3+} … and to what extent?

The reactions of interest are:

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E^o = +0.77$ V

$Hg_2^{2+} + 2e^- \rightarrow 2Hg_{(l)}$ $E^o = +0.90$ V

My request is quite simple: After this is mixed and the system comes to equilibrium, I stick a Hg electrode in the solution along with an SCE (saturated calomel reference electrode, $E^o = +0.24$ V) into the solution and measure the potential of the Hg electrode relative to the SCE (which is used as the anode). What E_{cell} voltage do I read? (Note: A hanging Hg drop is a typical electrode in electrochemistry. From the perspective of the iron system, it looks like an inert (e.g., Pt) electrode. Be concerned only with redox reactions in this problem.)

(Hint: To begin, will Hg_2^{2+} oxidize Fe^{2+} to Fe^{3+} … and to what extent?)

$$Hg_2^{2+} + 2Fe^{2+} \rightarrow 2Fe^{3+} + 2Hg_{(l)}$$

$$F_{Hg_2^{2+}} = [Hg_2^{2+}]_0 = \underbrace{2.2\times10^{-4}}_{\alpha} \underline{M} \; ; \; F_{Fe} = [Fe^{2+}]_0 = \underbrace{1.2\times10^{-4}}_{\beta} \cdot \underline{M}.$$

(A) Find K for reaction.

$$\log K = \frac{+n \cdot E^\circ}{0.059} \quad \text{or} \quad K = 10^{nE^\circ/0.059}$$

$$E^\circ = 0.90 - 0.77 \qquad n = 2.$$

$$\underline{K = 2.6\times10^{4}.}$$

(B) Find equilib conc.

$$K = \frac{[Fe^{3+}]^2}{[Hg_2^{2+}][Fe^{2+}]^2}.$$

$$[Fe^{3+}] = x$$
$$[Fe^{2+}] = \beta - x$$
$$[Hg_2^{2+}] = \alpha - \frac{x}{2}$$

$$K = \frac{x^2}{(\alpha - \frac{x}{2})(\beta - x)^2}$$

Assume $x \ll \alpha$; $x \ll \beta$

$$K = \frac{x^2}{\alpha\beta^2}$$ BAD!

$$x = 2.8\times10^{-4}$$

($x \gg \alpha$ or β NO GOOD).

CUBIC EQ.!

IF SOLVED...

soln: $x = 8.2\times10^{-5} = [Fe^{3+}]$

$[Fe^{2+}] = 3.8\times10^{-5}$

$[Hg_2^{2+}] = 1.8\times10^{-4}$

(C) use Fe conc → $E_{cell} = E^\circ_{Fe} - 0.059 \log \frac{[Fe^{2+}]}{[Fe^{3+}]} - 0.24 = \underline{\underline{0.55}}$ V ✓

OR

use Hg_2^{2+} conc $\quad E_{cell} = E^\circ_{Hg} - \frac{0.059}{2} \log \frac{1}{[Hg_2^{2+}]} - 0.241 = \underline{\underline{0.55}}$ V ✓