

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 $\text{Hg}_2(\text{NO}_3)_2$ and 1.2×10^{-4} F $\text{Fe}(\text{NO}_3)_2$ in a pH=3.00 buffered solution.

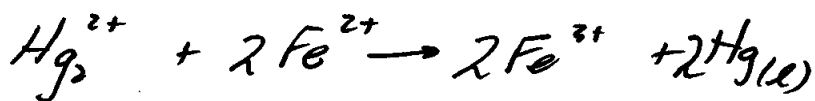
The question is whether Hg_2^{2+} will oxidize Fe^{2+} to Fe^{3+} ... and to what extent?

The reactions of interest are:



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, $E^\circ = +0.24 \text{ V}$) 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?)



$$F_{\text{Hg}_2^{2+}} = [\text{Hg}_2^{2+}]_0 = \underbrace{2.2 \times 10^{-4} \text{ M}}_{\alpha}; \quad F_{\text{Fe}} = [\text{Fe}^{2+}]_0 = \underbrace{1.2 \times 10^{-4} \text{ M}}_{\beta}$$

(A) Find K for reaction.

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

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

$$\underline{K = 2.6 \times 10^4}$$

(B) Find equilib. conc.

$$K = \frac{[\text{Fe}^{3+}]^2}{[\text{Hg}_2^{2+}][\text{Fe}^{2+}]^2}$$

$$[\text{Fe}^{3+}] = X$$

$$[\text{Fe}^{2+}] = \beta - X$$

$$[\text{Hg}_2^{2+}] = \alpha - \frac{X}{2}$$

$$K = \frac{X^2}{\left(\alpha - \frac{X}{2}\right)(\beta - X)^2}$$

CUBIC EQ.!

IF SOLVED... { soln: $X = 8.2 \times 10^{-5} = [\text{Fe}^{3+}]$
 $[\text{Fe}^{2+}] = 3.8 \times 10^{-5}$
 $[\text{Hg}_2^{2+}] = 1.8 \times 10^{-4}$

Assume $X \ll \alpha; X \ll \beta$

$$K = \frac{X^2}{\alpha \beta^2}$$

$$X = 2.8 \times 10^{-4}$$

↑ BAD!

($X \gg \alpha$ or β NO GOOD)

(C)

use Fe conc $\rightarrow E_{\text{cell}} = E_{\text{Fe}}^\circ - 0.059 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} - 0.24 = \underline{\underline{0.55V}}$

OR
 use Hg_2^{2+} conc $E_{\text{cell}} = E_{\text{Hg}}^\circ - \frac{0.059}{2} \log \frac{1}{[\text{Hg}_2^{2+}]} - 0.241 = \underline{\underline{0.55V}}$