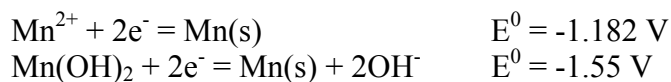


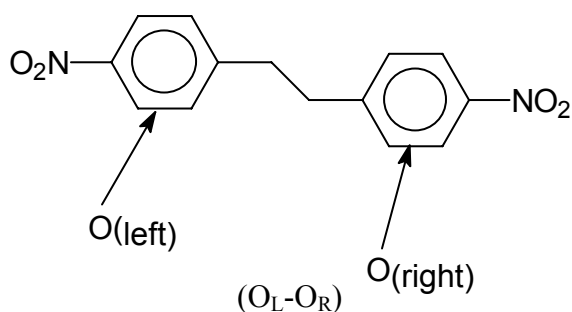
Chem 558 Homework Set 1

1] Given the following half reactions calculate the  $K_{sp}$  for  $Mn(OH)_2$ .

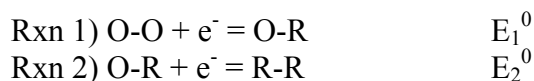


2] A Mind Bender

Consider the one electron reduction of covalently linked nitrobenzene molecules below.



The ethylene group insures the electronic isolation of the two nitrobenzenes ( $O_L-O_R$ ). Both groups undergo a one-electron reduction reaction below.



Intuition may indicate that the standard potentials of the attached groups should be equal with one another. However, a more rigorous derivation will show that the standard potentials of the attached species are not equal. The standard potentials are separated by

$$\Delta E^0 = E_1^0 - E_2^0 = 0.0592 \log(n)$$

Where  $n$  is an integer. **Solve for  $n$ .**

To do this you may want to consider the following.

$$\begin{array}{l} \text{Let } X_1 = [O-O]/[R-O] \\ X_2 = [R-O]/[R-R] \end{array}$$

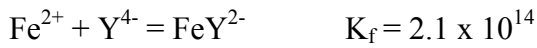
We would expect that equilibrium potential for Rxn 1 and 2 should equal each other, therefore:

$$E_1^0 + 0.0592 \log X_1 = E_2^0 + 0.0592 \log X_2$$

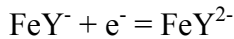
Now consider that  $X_1$  and  $X_2$  are comprised of smaller steps with the possibility of the reduction of the left-hand or right-hand nitrobenzenes.

$$\begin{aligned}x_1 &= [\text{O}_L\text{-O}_R]/[\text{R}_L\text{-O}_R] \\x_2 &= [\text{O}_L\text{-O}_R]/[\text{O}_L\text{-R}_R] \\x_3 &= [\text{R}_L\text{-O}_R]/[\text{R}_L\text{-R}_R] \\x_4 &= [\text{O}_L\text{-R}_R]/[\text{R}_L\text{-R}_R]\end{aligned}$$

3] Given the following ( $Y = \text{EDTA}$ ),



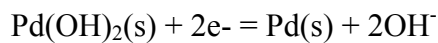
Calculate the standard potential for



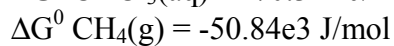
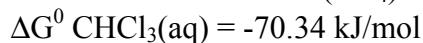
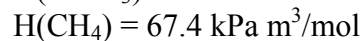
4] Given the following,



Calculate the standard potential for the following



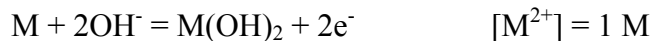
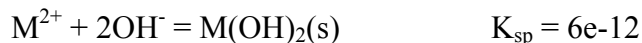
5] Calculate the standard potential for the reduction of chloroform to methane in aqueous solution given the following.



6] Draw a Pourbaix diagram for the reaction in Question 4. Label the regions that would have oxidize  $\text{CH}_4$  to  $\text{CHCl}_3$ .

7] What is  $E^0$  when  $\text{pH} = 7$  for this reaction?

8] Sketch a Pourbaix diagram for a metal, M from  $\text{pH} 0$  to  $14$  for the following processes.



9] Complete electrochemical cells can be abbreviated in the following form:

Anode:  $\text{Pb(s)}/\text{PbSO}_4(\text{s})/0.200\text{M SO}_4^{2-}(\text{aq})//0.150\text{M Sn}^{2+}(\text{aq}), 0.250\text{M Sn}^{4+}(\text{aq})/\text{Pt(s)}$  :Cathode

Where the symbol, /, represents a phase boundary, and // is a salt bridge. Calculate  $E_{\text{cell}}$  for the cell above. Is it spontaneous?

10] The potential of a  $\text{Pb(s)}/\text{Pb(OH)}_x(\text{aq})/\text{OH}^-, (\text{aq})//$  electrode was measured as a function of  $[\text{OH}^-]$ . The data is summarized below. Take  $E_{1/2}$  to be the measure potential of that electrode. What is the value of  $x$  in  $\text{Pb(OH)}_x$ ?

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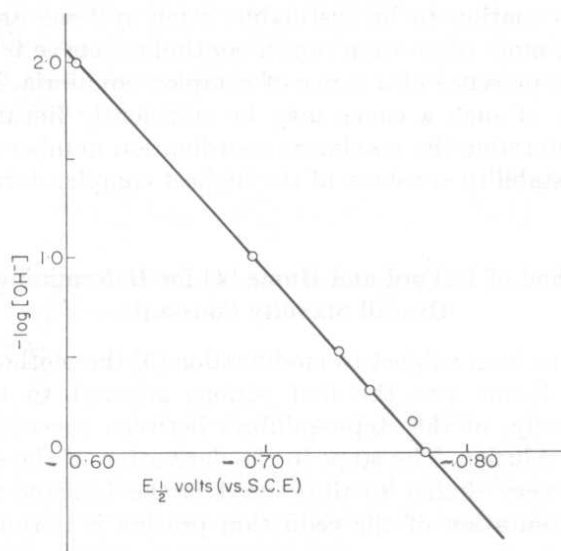


FIG. 4.3. Plot of  $(E_{1/2})_C$  for the  $\text{Pb}^{2+}-\text{OH}^-$  system as a function of  $-\log [\text{OH}^-]$  (at constant  $\mu = 1.0 \text{ M}$ ).