

Problem Set I
SHOW ALL YOUR WORK !!

- 1) Calculate E_{cell} and $\Delta_r G$ for the cell, computing activity coefficients as needed.



- 2) Calculate the pH in the right-hand electrode compartment, if $E_{\text{cell}} = +0.75$ Volts. Compute activity coefficients as needed. $\text{Fe}_{(s)} \mid \text{Fe}(\text{NO}_3)_3_{(aq)} (0.002 \text{ molal}) \parallel \text{KOH}_{(aq)}, \text{O}_2_{(g)} (0.21 \text{ bar}) \mid \text{Pt}_{(s)}$

- 3) Consider the cell: $\text{Z}_{(s)} \mid \text{ZCl}_{(aq)} \parallel \text{MSO}_4_{(aq)} \mid \text{M}_{(s)}$
At some arbitrary concentrations of ZCl and MSO_4 , E_{cell} is positive.

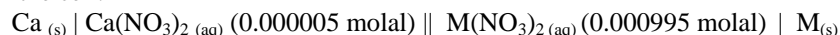
From the information given above, what, if anything, can you tell about:

- ...whether there will be more M^{2+} or more Z^+ at equilibrium?
- ...whether the reaction needs to shift to reactants (M^{2+}) or products (Z^+) to reach equilibrium?
- ...the sign of $\Delta_r G$? $\Delta_r G^\circ$? E°_{cell} ?
- ...whether Q is greater or smaller than K?

EXPLAIN YOUR ANSWERS (briefly) TO GET CREDIT !

- 4) Consider the data at http://www.hbcponline.com/articles/05_11_86.pdf (see link this problem set on course web page).
- Pick two compounds: one M^+X^- compound and one where at least one of the ions has a charge of two or more. Plot activity coefficient versus ionic strength for both compounds.
 - Compare activity coefficients for a range of compounds. What is the apparent range of validity of the Debye-Huckel limiting law for M^+X^- compounds? What is the apparent range of validity of the Debye-Huckel limiting law for MX_2 compounds?
 - Notice that for some compounds, the activity coefficient starts increasing at high molality. Identify at least one periodic trend in the tendency for this to occur.

- 5) Consider the cell:



where the solutions in both electrode compartments contains 1 kg of water. Take the standard reduction potential for M to be -2.89 Volts.

For this problem only, assume the activity coefficients of the ions are 1.00.

- a) Make a **quantitative** plot (using a spreadsheet program) of E_{cell} versus extent of reaction (=moles of Ca^{2+} present) for every 2.5×10^{-5} moles for the range 0 to 0.001

Graph $\Delta_r G$ over the same range. Turn in a printout of your spreadsheets and graphs!!

- Using one of your graphs**, determine the concentrations of both M^{2+} and Ca^{2+} present at equilibrium.
- Look at the graph on the next page. **Using a ruler and a calculator**, and drawing lines as needed on the graph, use the graph to calculate $\Delta_r G$ at each of the three following values of moles of Ca^{2+} present:

$$2 \times 10^{-5} \quad 8.0 \times 10^{-5} \quad 9.0 \times 10^{-4}$$

Turn in the graph with the lines drawn on them!

The results of (b) and (c) should agree with your spreadsheet to within the uncertainty of your measurements!

