

**PRINCIPLES OF GEOCHEMISTRY**  
**GEOL 423**  
**FALL 2009**  
**PROBLEM SET #7**

Note that this problem set counts as two problem sets.

Problem 1:

a) Using the following data, construct an Eh-pH diagram for the system Cu-O-H at 25°C and 1 bar. Assume  $\Sigma\text{Cu} = 10^{-6} \text{ mol L}^{-1}$ . Also draw the water breakdown lines for  $p_{\text{H}_2} = p_{\text{O}_2} = 1 \text{ bar}$ . Plot all slopes quantitatively! Hint: there are seven stable boundaries that appear in addition to the water breakdown lines.

Species	$\Delta G_f(\text{kcal/mole})$	Species	$\Delta G_f(\text{kcal/mole})$
$\text{Cu}^{2+}$	15.65	$\text{CuO(s)}$	-31.00
$\text{Cu}_2\text{O(s)}$	-34.98	$\text{CuO}_2^{2-}(\text{aq})$	-43.88

Don't forget to include native copper (Cu) on the diagram. Additional information you may need:  $\mathfrak{F} = 23.06 \text{ kcal/volt}$ ;  $\Delta G_f^\circ$  (kcal/mole) for  $\text{H}_2\text{O(l)} = -56.69 \text{ kcal/mole}$ ;  $R = 1.987 \text{ cal/K-mole}$ .

b) It is generally considered that more than  $10^{-4} \text{ mol L}^{-1}$  copper must be transported in solution to form a Cu ore deposit. Based on the Eh-pH diagram constructed in part a), under what types of conditions should it be possible to transport this amount of copper?

c) The  $\text{Cu}^{2+}$  ion can form an aqueous complex with  $\text{Cl}^-$  with the formula:  $\text{CuCl}_2^0$ . Using the following free energy values together with the appropriate values from the table above, plot the positions of the boundaries between  $\text{CuCl}_2^0$ , and  $\text{Cu(s)}$ ,  $\text{Cu}_2\text{O(s)}$  and  $\text{CuO(s)}$  on your previous Eh-pH diagram.  $\Delta G_f^\circ = -57.4 \text{ kcal/mole}$  for  $\text{CuCl}_2^0$  and  $\Delta G_f^\circ = -31.3 \text{ kcal/mole}$  for  $\text{Cl}^-$ . Assume  $\Sigma\text{Cu} = 10^{-6} \text{ mol L}^{-1}$  and  $[\text{Cl}^-] = 1 \text{ mol L}^{-1}$ . Does the presence of dissolved chloride enhance, depress or have no effect on the ability of an aqueous solution to transport copper?

Problem 2:

a) Draw an Eh-pH diagram for the U-O-H system at 25 °C and 1 bar given the following data and  $\Sigma U = 10^{-6} \text{ mol L}^{-1}$ .

Phase or species	$\Delta G_{f,298K}^{\circ}$ (kcal/mole)
$\text{UO}_2^{2+}$	-227.66
$\text{UO}_2(\text{s})$	-246.62
$\text{U}_3\text{O}_8(\text{s})$	-805.35
$\text{U}(\text{OH})_5^{-}$	-389.77

Hint: there are five stable boundaries, in addition to the water break-down lines, that appear on the correctly drawn diagram. Don't forget to add the water breakdown lines to your diagram. Native uranium is metastable and does not plot on the diagram. Plot all slopes quantitatively!

$\mathfrak{F} = 23.06 \text{ kcal/volt-mole}$ ;  $\Delta G_f(\text{kcal/mole})$  for  $\text{H}_2\text{O}(\text{l}) = -56.69 \text{ kcal/mole}$ ;  $R = 1.987 \text{ cal/K-mole}$ .

b) Uranium is a major constituent of nuclear waste. According to your Eh-pH diagram, under what conditions would you expect U to be mobile if groundwater interacted with buried, U-bearing nuclear waste.