Department of Earth and Planetary Sciences

EPSC-220

Principles of Geochemistry

Assignment # 4
Fall term, 2017
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Question 1

a) Derive an exact solution which would allow you to determine the HCO_3^- concentration in a solution from measurements of the pH and ΣCO_2.
b) Solutions A and B are saturated with respect to calcite. Calculate the saturation state of a 1:1 mixture of these two solutions with respect to calcite out of contact with the atmosphere.

Solution A: pH = 8.20, $A_c = 10^{-3}$ equiv. l^{-1}
Solution B: pH = 7.10, $A_c = 10^{-4}$ equiv. l^{-1}

c) Calculate the pH of the mixture if it is allowed to equilibrate with the atmosphere ($P_{CO_2} = 10^{-3.5}$atm).

$K^o_0 = 10^{-1.47}$, $K^o_1 = 10^{-6.35}$, $K^o_2 = 10^{-10.33}$, $K^o_C = 10^{-8.48}$ at 25°C

(assume ideal behaviour, i.e., $a_i = [i]$).

Question 2

Because there is compelling evidence of acute Pb poisoning of waterfowl, state legislation in the U.S. prohibits the use of Pb shot for hunting, requiring the use of steel or bismuth (Bi). Nevertheless, in concentrations greater than 10^{-5} molal, Bi^{3+} can also be toxic. Consider the reactions below and determine if natural waters at normal E_h and pH conditions (E_h = +600 mV and pH= 6.5) can contain dangerous concentrations of Bi^{3+}. Construct an E_h-pH diagram to answer this question.
(Hint: Use a concentration/activity of 10^{-5} for all aqueous species in your calculations and don't forget to add the water stability boundaries.

Reaction	**$\Delta_r G°$** (kJ/mol, 298 K, 1 bar)
$Bi^{3+}_{(aqueous)} + 3e^- \Leftrightarrow Bi_{(crystal)}$	-82.84
$Bi_2O_{3\,(crystal)} + 6\,H^+ \Leftrightarrow 2\,Bi^{3+}_{(aqueous)} + 3\,H_2O$	-52.14
$Bi_2O_{3\,(crystal)} + 6\,e^- + 6\,H^+ \Leftrightarrow 2\,Bi_{(crystal)} + 3\,H_2O$	-208.28
$O_{2(g)} + 4\,e^- + 4\,H^+ \Leftrightarrow 2\,H_2O_{(l)}$	-474.70
$2\,H^+ + 2\,e^- \Leftrightarrow H_{2(g)}$	0.00

Look for more entertainment on the back side of this sheet!

Question 3

Fluorite, CaF_2, is often used as a fluoridation agent in municipal water systems. Given that its solubility constant, K_{sp}, is 1.7×10^{-10}.

a) Calculate the concentration of fluoride in a pure water solution saturated with CaF_2.
b) Calculate the concentration of fluoride in a solution saturated with SiO_2 and CaF_2 at pH=7.
c) What would the concentration of fluoride be if CaF_2 was being added to a solution containing $[Ca^{2+}] = 0.07$ mol l^{-1} in the form of $CaCl_2$?
d) How many moles of CaF_2 would be dissolved if added to a solution containing 0.25 mol l^{-1} of fluoride in the form of NaF?

(Note that both $CaCl_2$ and NaF are strong electrolyte salts and dissociate completely)

After solving for ideal solutions, solve for the concentrations in the above problem for real solutions using either the Debye-Huckel (a,b,c) or Davies (d) equations.