PET565 PART B: EXERCISE SET 2

Goals

- Use thermodynamics theory to predict equilibrium constants.
- Become familiar with carbon chemistry and relevant reactions.
- Be familiar with the concept of ion exchange and basic definitions.
- Perform simple calculations on equilibrium compositions

Important notes

- The activity of a gas species is given by its partial pressure. At atmospheric conditions the partial pressure in magnitude of atmospheres (as if the unit was atmospheres) corresponds to the activity. Typically CO_2 has partial pressure of $10^{-3.5}$atm.
- In an open system (between a brine and atmosphere) the brine is in equilibrium with the atmosphere (given sufficient time).
- In a closed system (only involving a brine) the total inorganic carbon, TIC, is constant.
- pH is defined as $pH = -\log([H^+])$

1. Exercises

1.1. Show by integration that van't Hoffs equation (4.28) results in equation (4.29). Which assumptions are made?

1.2. Villiaumite, NaF (s) is a mineral that dissolves according to

$$\mathrm{NaF}(s) \quad \rightarrow \quad \mathrm{Na}^+(aq) + \mathrm{F}^-(aq) \tag{1}$$

The following table values (measured at 25 C) are given:

$$\Delta G^0_{f,NaF} = -543.5, \quad \Delta G^0_{f,Na^+} = -261.9, \quad \Delta G^0_{f,F^-} = -278.8 \quad \text{(kJ/mol)}, \tag{2}$$

$$\Delta H^0_{f,NaF} = -573.6, \quad \Delta H^0_{f,Na^+} = -240.1, \quad \Delta H^0_{f,F^-} = -332.6 \quad \text{(kJ/mol)}, \tag{3}$$

and $R = 8.314 \cdot 10^{-3}$kJ/mol/deg.

- Calculate ΔG^0_r and ΔH^0_r for the reaction above.
- Calculate the solubility constant of villiaumite at 25C using equation (4.26).
- Use Van't Hoffs equation (4.29) to calculate the solubility constant at 10C.

1.3. We here consider the role of carbon species on pH in a brine.
The following reactions represent the interaction between water and carbon in a system OPEN to the atmosphere:

$$\mathrm{CO_2}(g) + \mathrm{H_2O}(g) \quad \rightarrow \quad \mathrm{H_2CO_3}^*(aq) \tag{4}$$

$$\mathrm{H_2CO_3}^*(aq) \quad \rightarrow \quad \mathrm{H}^+(aq) + \mathrm{HCO_3^-}(aq) \tag{5}$$

$$\mathrm{HCO_3^-}(aq) \quad \rightarrow \quad \mathrm{H}^+(aq) + \mathrm{CO_3^{2-}}(aq) \tag{6}$$

$$\mathrm{H_2O}(aq) \quad \rightarrow \quad \mathrm{H}^+(aq) + \mathrm{OH}^-(aq) \tag{7}$$

where the equilibrium constants are respectively $K_H = 10^{-1.5}, K_1 = 10^{-6.3}, K_2 = 10^{-10.3}, K_w = 10^{-14}$.

- For reference, if carbon is not available, only the fourth reaction is relevant. Calculate the pH in this case.
- Now assume carbon can enter the brine from the atmosphere.
  Express equilibrium equations for the 4 above reactions. Assume a dilute brine (i.e. $\gamma = 1$).
- List the 6 independent variables of the system.

- Assume P_{co2} and pH are known parameters (determined by atmosphere composition and brine composition, respectively).

  Solve the system and determine the concentrations of aqueous carbon species: $m_{\mathrm{H_2CO_3}^*}$, $m_{\mathrm{HCO_3^-}}$ and $m_{\mathrm{CO_3^-}}$ as function of P_{co2} and pH.

  PS: Note that m_{oh} follows directly from pH and does not require calculation.
- Calculate the TIC as a function of $m_{\mathrm{H^+}}$ and P_{co2}.
  - What is the effect of P_{co2} on TIC?
  - What is the effect of pH (as given by $m_{\mathrm{H^+}}$) on TIC?
  - Which species become more dominating (has higher fraction of the TIC) at different pH?
- Assume now that the pH is unknown and only the listed species above are in the brine.
  - Formulate the charge balance equation for the brine species:

$$\sum_i m_i z_i = 0 \tag{8}$$

  - Simplify this equation by assuming an acidic solution. Then m_{co3} can be ignored. Insert the expressions of m_{hco3} and m_{oh} as function of m_h. Solve with respect to m_h
  - Use that $P_{co2} = 10^{-3.5}$ (typical atmospheric value) and calculate the pH. This is the pH due to carbon entering distilled water. Compare with the first task.

1.4.

- A sample of 100g (dry weight) quartz rock stores on its surface 0.5mmol Na^+, 1.0mmol Ca^{2+} and 0.5mmol Mg^{2+}. Calculate the cation exchange capacity, CEC in terms of mmeq/kg rock.
- The rock has grain density 2.65g/cc and porosity 0.3. Calculate the CEC in terms of mmeq/l pore volume.

1.5. Find the equilibrium constant K for ion exchange of Mg^{2+} and Ca^{2+} corresponding to the reaction of the form

$$\mathrm{CaX_2} + \mathrm{Mg^{2+}}(aq) \quad \rightarrow \quad \mathrm{MgX_2} + \mathrm{Ca^{2+}}(aq) \tag{9}$$

Use the theory from pages 254-255 and the reference reactions with Na^+ to derive the correct result.