

## 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

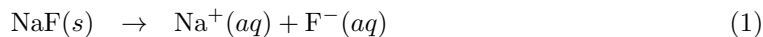
### IMPORTANT NOTES

- 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  $\text{CO}_2$  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



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

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

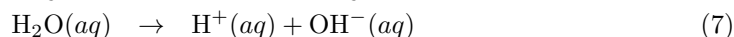
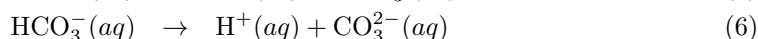
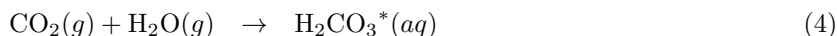
$$\Delta H_{f,NaF}^0 = -573.6, \quad \Delta H_{f,Na^+}^0 = -240.1, \quad \Delta H_{f,F^-}^0 = -332.6 \quad (\text{kJ/mol}), \quad (3)$$

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

- Calculate  $\Delta G_r^0$  and  $\Delta H_r^0$  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:



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:  $m_{H_2CO_3^*}$ ,  $m_{HCO_3^-}$  and  $m_{CO_3^{2-}}$  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  $m_{H^+}$  and  $P_{co2}$ .
  - What is the effect of  $P_{co2}$  on TIC?
  - What is the effect of pH (as given by  $m_{H^+}$ ) 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:

$$\sum_i m_i z_i = 0 \quad (8)$$

- 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



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