

## 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<sub>2</sub> has partial pressure of 10<sup>-3.5</sup>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?

*Answer.* Constant  $\Delta H_r$  with temperature.

$$\frac{d \ln K}{dT} = \frac{\Delta H_r}{RT^2} \quad (1)$$

$$\frac{d \ln K}{dT} = \frac{\Delta H_r}{R} \frac{dT}{T^2} \quad (2)$$

$$\int_{\ln K_1}^{\ln K_2} d \ln K = \frac{\Delta H_r}{R} \int_{T_1}^{T_2} T^{-2} dT \quad (3)$$

$$\ln K_2 - \ln K_1 = -\frac{\Delta H_r}{R} [T_2^{-1} - T_1^{-1}] \quad (4)$$

Note that

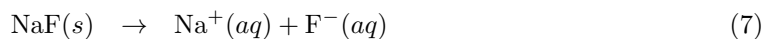
$$\ln a = \ln 10^{\log a} = \log a \ln 10 = \log(a) \cdot 2.303 \quad (5)$$

such that we get:

$$\log K_2 - \log K_1 = -\frac{\Delta H_r}{2.303R} [T_2^{-1} - T_1^{-1}] \quad (6)$$

which is equivalent to (4.29).

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



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

$$\Delta G_{f,NaF}^0 = -543.5, \quad \Delta G_{f,Na^+}^0 = -261.9, \quad \Delta G_{f,F^-}^0 = -278.8 \quad (\text{kJ/mol}), \quad (8)$$

$$\Delta H_{f,NaF}^0 = -573.6, \quad \Delta H_{f,Na^+}^0 = -240.1, \quad \Delta H_{f,F^-}^0 = -332.6 \quad (\text{kJ/mol}), \quad (9)$$

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.

Answer.

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$$\Delta G_r^0 = \Delta G_{f,Na^+}^0 + \Delta G_{f,F^-}^0 - \Delta G_{f,NaF}^0 = 2.8 \quad (\text{kJ/mol}) \quad (10)$$

$$\Delta H_r^0 = \Delta H_{f,Na^+}^0 + \Delta H_{f,F^-}^0 - \Delta H_{f,NaF}^0 = 0.9 \quad (\text{kJ/mol}) \quad (11)$$

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$$\Delta G_r^0 = -RT \ln K \quad (12)$$

$$K_{25} = \exp\left(-\frac{\Delta G_r^0}{RT}\right) = \exp\left(-\frac{2.8}{8.314 \cdot 10^{-3} \cdot (278 + 25)}\right) = 0.329 \quad (13)$$

$$\log K_{25} = -0.48 \quad (14)$$

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$$\log K_{10} - \log K_{25} = -\frac{\Delta H_r^0}{2.303R}(1/T_{10} - 1/T_{25}) \quad (15)$$

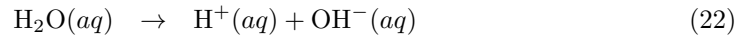
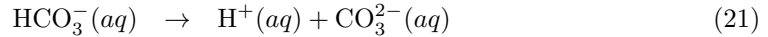
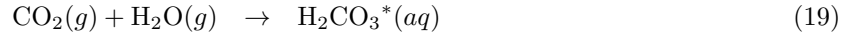
$$= \log K_{25} - \frac{0.9}{2.303 \cdot 8.314 \cdot 10^{-3}}(1/(278 + 10) - 1/(278 + 25)) \quad (16)$$

$$= -0.008 \quad (17)$$

$$\log K_{10} = 0.48 + 0.008 = 0.49 \quad (18)$$

**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:  $m_{\text{H}_2\text{CO}_3^*}$ ,  $m_{\text{HCO}_3^-}$  and  $m_{\text{CO}_3^{2-}}$  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  $m_{\text{H}^+}$  and  $P_{co2}$ .
  - What is the effect of  $P_{co2}$  on TIC?
  - What is the effect of pH (as given by  $m_{\text{H}^+}$ ) 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:

$$\sum_i m_i z_i = 0 \quad (23)$$

- 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.

Answer.

- H+ and OH- do not associate with any other ions. Therefore  $m_{oh} = m_h = m$  and

$$K_w = \gamma_m \gamma_{oh} m^2 \approx m^2 \quad (24)$$

$$\rightarrow m = \sqrt{K_w} = 10^{-7} \quad (25)$$

$$pH = -\log(\gamma_h m_h) \approx -\log(m_h) = 7 \quad (26)$$

- Since  $\gamma = 1$  we let concentrations represent activities for aqueous species.

EQ equations from LMA:

$$K_H = \frac{m_{H_2CO_3^*}}{P_{CO_2}} \quad (27)$$

$$K_1 = \frac{m_{H^+} m_{HCO_3^-}}{m_{H_2CO_3^*}} \quad (28)$$

$$K_2 = \frac{m_{H^+} m_{CO_3^{2-}}}{m_{HCO_3^-}} \quad (29)$$

$$K_w = m_h m_{oh} \quad (30)$$

- The 6 variables are:  $m_{H_2CO_3^*}, P_{CO_2}, m_{H^+}, m_{HCO_3^-}, m_{CO_3^{2-}}, m_{OH^-}$ .
- The carbon species concentrations as function of  $P_{co2}$  and  $m_h$ :

$$m_{H_2CO_3^*} = P_{CO_2} K_H \quad (31)$$

$$m_{HCO_3^-} = K_1 m_{H_2CO_3^*} \frac{1}{m_{H^+}} = K_1 K_H P_{CO_2} \frac{1}{m_{H^+}} \quad (32)$$

$$m_{CO_3^{2-}} = K_2 m_{HCO_3^-} \frac{1}{m_{H^+}} = K_2 K_1 K_H P_{CO_2} \frac{1}{(m_{H^+})^2} \quad (33)$$

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$$TIC = m_{H_2CO_3^*} + m_{HCO_3^-} + m_{CO_3^{2-}} \quad (34)$$

$$= P_{CO_2} K_H + K_1 K_H P_{CO_2} \frac{1}{m_{H^+}} + K_2 K_1 K_H P_{CO_2} \frac{1}{(m_{H^+})^2} \quad (35)$$

$$= P_{CO_2} K_H \left( 1 + K_1 \frac{1}{m_{H^+}} + K_2 K_1 \frac{1}{(m_{H^+})^2} \right) \quad (36)$$

- The carbon content of the brine increases proportionally with the partial pressure of CO<sub>2</sub> in the atmosphere, at a fixed pH.
- Increasing the pH (lower  $m_h$ ) increases the TIC. I.e., the brine has a greater capacity for adsorbing carbon at higher pH.
- At high pH (small  $m_{H^+}$ ) the concentrations of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> become large while that of H<sub>2</sub>CO<sub>3</sub><sup>\*</sup> remains constant.

Opposite, at low pH the TIC is dominated by H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>. Its concentration does not change with pH.  $m_{CO_3^{2-}}$  is negligible. See also Figure 5.6 in the book.

- Charge balance:

$$\sum_i m_i z_i = m_{hco3}(-1) + m_{h2co3} \cdot 0 + m_{co3}(-2) + m_h(+1) + m_{oh}(-1) \quad (37)$$

$$= -m_{hco3} - 2m_{co3} + m_h - m_{oh} \quad (38)$$

$$= 0 \quad (39)$$

- At low pH  $m_{co3}$  can be ignored.

$$-m_{hco3} + m_h - m_{oh} \quad (40)$$

$$= 0 \quad (41)$$

$$m_{HCO_3^-} = K_1 K_H P_{CO_2} \frac{1}{m_{H^+}} \quad (42)$$

$$m_{oh} = K_w / m_h \quad (43)$$

$$-K_1 K_H P_{CO_2} \frac{1}{m_{H^+}} + m_h - K_w / m_h \quad (44)$$

$$= 0 \quad (45)$$

$$-(K_1 K_H P_{co2} + K_w) \frac{1}{m_h} + m_h \quad (46)$$

$$= 0 \quad (47)$$

$$m_h^2 = (K_1 K_H P_{co2} + K_w) \quad (48)$$

$$m_h = \sqrt{K_1 K_H P_{co2} + K_w} \quad (49)$$

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$$m_h = \sqrt{10^{-6.3} 10^{-1.5} 10^{-3.5} + 10^{-14}} = \sqrt{10^{-11.3} + 10^{-14}} = \sqrt{10^{-11.3}} = 10^{-5.65} \quad (50)$$

The pH is then 5.65. This is a typical value of NaCl brine or distilled water measured at ambient conditions.

#### 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.

*Answer.*

- The CEC is given by the stored charge divided by the mass of rock it is stored on.

$$CEC = \left( \sum_i n_i Z_i \right) / \text{rock mass} = (0.5 \cdot 1 + 1.0 \cdot 2 + 0.5 \cdot 2) / 0.1 \text{ (meq / kg)} = 35.0 \text{ (meq / kg)} \quad (51)$$

- Note that

$$CEC[\text{meq/l pores}] = \frac{\text{meq}}{\text{mass rock}} \frac{\text{mass rock}}{\text{volume rock}} \frac{\text{volume rock}}{\text{volume pores}} \quad (52)$$

$$= CEC[\text{meq/kg rock}] \rho_{quartz} \frac{1 - \phi}{\phi} \quad (53)$$

$$= 35[\text{meq/kg rock}] \cdot 2.65[\text{kg rock / l rock}] \frac{1 - 0.3}{0.3} \quad (54)$$

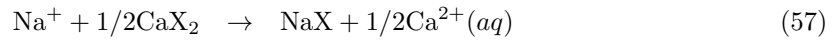
$$= 216[\text{meq / l pore}] \quad (55)$$

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

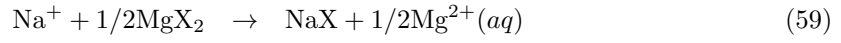


Use the theory from pages 254-255 and the reference reactions with  $Na^+$  to derive the correct result.

*Answer.* First consider the reference reactions involving  $\text{Na}^+$  exchanging with  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ :



$$K_{\text{Na}/\text{Ca}} = \frac{\beta_{\text{Na}}[\text{Ca}]^{1/2}}{\beta_{\text{Ca}}^{1/2}[\text{Na}]} = 0.4 \quad (58)$$



$$K_{\text{Na}/\text{Mg}} = \frac{\beta_{\text{Na}}[\text{Mg}]^{1/2}}{\beta_{\text{Mg}}^{1/2}[\text{Na}]} = 0.5 \quad (60)$$

We obtain the correct reaction by multiplying both reference reactions by 2 and subtracting the 2nd from the first. This corresponds to an equilibrium constant given by the square of the first constant divided by the other:

$$K = \frac{\beta_{\text{Mg}}[\text{Ca}]}{\beta_{\text{Ca}}[\text{Mg}]} = \left( \frac{\beta_{\text{Na}}[\text{Ca}]^{1/2}}{\beta_{\text{Ca}}^{1/2}[\text{Na}]} \frac{\beta_{\text{Mg}}^{1/2}[\text{Na}]}{\beta_{\text{Na}}[\text{Mg}]^{1/2}} \right)^2 \quad (61)$$

$$= \left( \frac{K_{\text{Na}/\text{Ca}}}{K_{\text{Na}/\text{Mg}}} \right)^2 = \left( \frac{0.4}{0.5} \right)^2 = 0.64 \quad (62)$$