

## PET565 PART B: ASSIGNMENT 1

### INFORMATION

The assignments give you an indication about the main theory and exercises you should be in control of. The total number of points can be used to calculate your grade. 40% correct is required to pass an exam (grade E). 90% is required to get A. You can of course work together and ask for help, but to be given feedback the assignment must be handed in within the deadline 23 March 2018. The assignment is not mandatory to pass the course.

### 1. THEORY (40P)

- State the law of mass action. (5p)
- Define molality and molarity. Show how to calculate one from the other. (5p)
- Define the activity for aqueous, gaseous, surface and mineral species and water. (5p)
- What two classes of equations are used to determine the composition of a system? Which properties are assumed to be conserved? (5p)
- Using van't Hofs law: How does solubility change with temperature for an exotherm reaction? And for an endotherm reaction? (5p)
- Define Ficks laws mathematically. (5p)
- What is the difference between diffusion and dispersion? How are they related? (5p)
- Define the mechanisms and assumptions in the retardation model. (5p)

#### 1.1. Answer.

- At EQ the product activities divided by reactant activities are constant.
- Molality = mol/kg w. Molarity = mol / L brine.

$$V_{brine}[L] = \frac{(m_w + m_s)[kg]}{\rho_{brine}[kg/L]} \quad (1)$$

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$$\gamma_i m_i, \quad P_i, \quad \beta_i, \quad 1, \quad 1 \quad (2)$$

- EQ and conservation/balance eqs. Mass and charge.
- Solubility decreases with T for exotherm reactions and increases with T for endotherm reactions.

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$$Flux = -D\partial_x c \quad (3)$$

$$\partial_t c = D\partial_{xx} c \quad (4)$$

- Diff: random motion of molecules in system without bulk movement. Disp: enhanced distribution of molecules due to advection.
- Advection and adsorption by isotherm.

### 2. CALCULATIONS (55 P)

2.1. **Equilibrium calculations (35 p).** 0.3 mol CaCl<sub>2</sub> and 0.05 mol Na<sub>2</sub>SO<sub>4</sub> are mixed into 1 L water.

- Calculate the total concentration  $C_i$  of Ca, Cl, Na and SO<sub>4</sub>.  
Calculate the ionic strength of the brine.  
Calculate and the activity coefficients of the 4 ions (PS: which correlation should be applied?). (5p)

- Assume the complex  $\text{CaSO}_4^0$  can form with a dissociation constant  $K = 10^{-2.5}$ . Write the dissociation reaction and the corresponding EQ equation. Write mass balance equations for Ca and SO4. (5p)
- Find the composition of the brine in terms of  $m_i, n_i$ . (5p)

The brine is in equilibrium with a mineral surface that can exchange Ca and Na.

- Define the relevant exchange reaction, equilibrium equation and its constant (see Table 6.4). (5p)
- Assume the Gaines-Thomas convention is used. Calculate the surface composition in terms of  $\beta_i$ . (5p)
- Calculate the composition in terms of  $\beta_i^M$ . (5p)
- Calculate the equilibrium constant based on the brine/surface composition if the Vanselow convention is used (assumes  $[i] = \beta_i^M$  for surface species). (5p)

**Answer.** 0.3 mol CaCl2 and 0.05 mol Na2SO4 are mixed into 1 L water.

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$$C_{ca} = 0.3, \quad C_{cl} = 0.6, \quad C_{na} = 0.1, \quad C_{so} = 0.05, \quad (5)$$

$$I = 0.5(0.3 * 4 + 0.6 * 1 + 0.1 * 1 + 0.05 * 4) = 0.5(1.2 + 0.6 + 0.1 + 0.2) = 1.05 \quad (6)$$

Must use TJ formula. Can use figure or formula. Approximate:

$$\gamma_{ca} = 0.26, \quad \gamma_{cl} = 0.6, \quad \gamma_{na} = 0.7, \quad \gamma_{so} = 0.05 \quad (7)$$

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$$K_{caso} = \frac{a_{ca}a_{so}}{a_{caso}} = \frac{\gamma_{ca}m_{ca}\gamma_{so}m_{so}}{n_{caso}} = 10^{-2.5} \quad (9)$$

$$C_{ca} = m_{ca} + n_{caso} \quad (10)$$

$$C_{so} = m_{so} + n_{caso} \quad (11)$$

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$$n_{caso} = m_{ca}m_{so} \frac{\gamma_{ca}\gamma_{so}}{K_{caso}} = m_{ca}m_{so}K_1 \quad (12)$$

$$K_1 = \frac{0.26 * 0.05}{10^{-2.5}} = 4.11 \cdot 10^{-5} \quad (13)$$

$$C_{ca} = m_{ca}(1 + m_{so}K_1) \quad (14)$$

$$m_{ca} = \frac{C_{ca}}{(1 + m_{so}K_1)} \quad (15)$$

$$C_{so} = m_{so} + m_{ca}m_{so}K_1 = m_{so} + \frac{C_{ca}}{(1 + m_{so}K_1)}m_{so}K_1 \quad (16)$$

Solve:

$$C_{so} + m_{so}C_{so}K_1 = m_{so} + m_{so}^2K_1 + C_{ca}m_{so}K_1 \quad (17)$$

$$m_{so}^2K_1 + m_{so}(C_{ca}K_1 + 1 - C_{so}K_1) - C_{so} = 0 \quad (18)$$

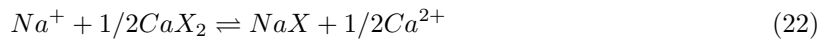
$$m_{so} = 0.0235 \quad (19)$$

$$n_{caso} = C_{so} - m_{so} = 0.0265 \quad (20)$$

$$m_{ca} = C_{ca} - n_{caso} = 0.274 \quad (21)$$

The brine is in equilibrium with a mineral surface that can exchange Ca and Na.

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$$K_{na/ca} = \frac{\beta_{na}(\gamma_{ca}m_{ca})^{1/2}}{(\gamma_{na}m_{na})\beta_{ca}^{1/2}} = 0.4 \quad (23)$$

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$$K_{na/ca} = \frac{\beta_{na}(\gamma_{ca}m_{ca})^{1/2}}{(\gamma_{na}m_{na})\beta_{ca}^{1/2}} = 0.4 \quad (24)$$

$$\beta_{ca} + \beta_{na} = 1 \quad (25)$$

$$\beta_{ca} = \beta_{na}^2 \frac{(\gamma_{ca}m_{ca})}{(\gamma_{na}m_{na})^2 K_{na/ca}^2} = \beta_{na}^2 K_1 \quad (26)$$

$$K_1 = \frac{(0.26 \cdot 0.3)}{(0.7 \cdot 0.1)^2 0.4^2} = 99.5 \quad (27)$$

$$\beta_{na}^2 K_1 + \beta_{na} - 1 = 0 \quad (28)$$

$$\beta_{na} = 0.095, \quad \beta_{ca} = 0.905 \quad (29)$$

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$$\beta_i^M = \frac{\beta_i/z_i}{\sum_j \beta_j/z_j} \quad (30)$$

$$\beta_{na}^M = \frac{0.095/1}{0.095/1 + 0.905/2} = 0.174 \quad \beta_{ca}^M = 0.826 \quad (31)$$

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$$K_{na/ca}^{van} = \frac{\beta_{na}^M (\gamma_{ca}m_{ca})^{1/2}}{(\gamma_{na}m_{na})(\beta_{ca}^M)^{1/2}} = \frac{0.174(0.26 \cdot 0.3)^{1/2}}{(0.7 \cdot 0.1)(0.826)^{1/2}} = 0.764 \quad (32)$$

**2.2. Retardation model (20 p).** Consider sorption of a species according to  $q = c^2$  where  $q$  and  $c$  have units mol/L. Water flows with velocity 10 cm/d and the system is 20 cm in length.

- The initial and injected concentrations are  $c_0 = 0, c_{inj} = 1$  mol/L. Calculate and plot:
  - the spatial concentration profile along the system after 1 day and 2 days. (5p)
  - the effluent concentration from 0 to 4 d. (5p)
- Now assume the initial and injected concentrations are  $c_0 = 1, c_{inj} = 0$  mol/L. Calculate and plot:
  - the spatial concentration profile along the system after 1 day and 2 days. (5p)
  - the effluent concentration from 0 to 4 d. (5p)

**Answer.**

- $c_0 = 0, c_{inj} = 1$  mol/L.
  - 1 day:

$$x_w = 10cm, \quad dq/dc = 2c, \quad R_c = 1 + 2c, \quad (33)$$

$$x(c=0) = 10/1 = 10cm, \quad x(c=0.5) = 10/2 = 5cm, \quad x(c=1) = 10/3 = 3.3cm, \quad (34)$$

The initial concentration is less delayed than the injected and the continuous solution is valid. After 2d:

$$x(c=0) = 20/1 = 20cm, \quad x(c=0.5) = 20/2 = 10cm, \quad x(c=1) = 20/3 = 6.7cm, \quad (35)$$

- The water requires 2d to reach the outlet.

$$t_w = L/v_w = 20/10 = 2d \quad (36)$$

The concentrations arrive at the outlet after the following times:

$$t(c=0) = R(c=0)t_w = 1 \cdot 2 = 2d \quad (37)$$

$$t(c=0.5) = 2 \cdot 2 = 4d \quad (38)$$

$$t(c=1) = 3.33 \cdot 2 = 6.7d \quad (39)$$

- $c_0 = 1, c_{inj} = 0$  mol/L.

- In this case the initial concentration travels slower than the injected and a front forms. Its position after 1d is given by:

$$R_f = 1 + \frac{1^2 - 0^2}{1 - 0} = 2, \quad (40)$$

$$x_f = 10/2 = 5 \quad (41)$$

Similarly, after 2d the front is at

$$x_f = 20/2 = 10\text{cm} \quad (42)$$

- The front arrives after

$$t_f = R_f t_w = 2 \cdot 2 = 4d \quad (43)$$

Before that time, only initial concentration is produced. After that, only injected concentration is produced.