PET565 PART B: EXERCISE SET 3

Goals

- Calculate surface activities of species and compositions.
- Be familiar with some adsorption isotherms and their application.

Important notes

- Assume the activity of surface species is given by equivalent fraction, β_i (Gaines-Thomas convention).

1. Exercises

1.1. Assume a surface storing cations is in equilibrium with a brine containing $m_{\mathrm{Na}^{2+}} = 2, m_{\mathrm{K}^+} = 0.5, m_{\mathrm{Ca}^{2+}} = 0.2$mmol/L. Assume the activity coefficients are 1.

- Write the relevant equilibrium and mass balance equations for this system. Table parameters can be found in the book.
- Calculate the composition of the surface represented by equivalent fractions $\beta_{\mathrm{Na}^{2+}}, \beta_{\mathrm{K}^+}, \beta_{\mathrm{Ca}^{2+}}$. The Gaines-Thomas convention should be applied.
- Derive mathematically, the relation between equivalent fraction composition and the composition in terms of molar fractions.
- From the previous answers, calculate the surface composition in terms of molar fractions $\beta^M_{\mathrm{Na}^{2+}}, \beta^M_{\mathrm{K}^+}, \beta^M_{\mathrm{Ca}^{2+}}$.

Answer.

- The relevant reactions for exchange and equilibria equations are given as:

$$\mathrm{Na}^+ + \mathrm{KX} \rightarrow \mathrm{NaX} + \mathrm{K}^+(aq) \tag{1}$$

$$K_{Na/K} = \frac{\beta_{Na}[K]}{\beta_K[Na]} = 0.2 \tag{2}$$

$$\mathrm{Na}^+ + 1/2\mathrm{CaX}_2 \rightarrow \mathrm{NaX} + 1/2\mathrm{Ca}^{2+}(aq) \tag{3}$$

$$K_{Na/Ca} = \frac{\beta_{Na}[Ca]^{1/2}}{\beta_{Ca}^{1/2}[Na]} = 0.4 \tag{4}$$

We use these equations to express β_K, β_{Ca} in terms of β_{Na}:

$$\beta_K = \frac{\beta_{Na}[K]}{K_{Na/K}[Na]} \tag{5}$$

$$\beta_{Ca} = \frac{\beta_{Na}^2[Ca]}{K_{Na/Ca}^2[Na]^2} \tag{6}$$

Finally the activities must satisfy mass balance:

$$\beta_K + \beta_{Ca} + \beta_{Na} = 1 \tag{7}$$

- We insert the above expressions

$$\frac{\beta_{Na}[K]}{K_{Na/K}[Na]} + \frac{\beta_{Na}^2[Ca]}{K_{Na/Ca}^2[Na]^2} + \beta_{Na} = 1 \quad (8)$$

$$\beta_{Na}^2\frac{[Ca]}{K_{Na/Ca}^2[Na]^2} + \beta_{Na}(\frac{[K]}{K_{Na/K}[Na]} + 1) - 1 = 0 \quad (9)$$

$$\beta_{Na}^2\frac{0.2\cdot 10^{-3}}{0.4^2(2\cdot 10^{-3})^2} + \beta_{Na}(\frac{0.5\cdot 10^{-3}}{0.2\cdot 2\cdot 10^{-3}} + 1) - 1 = 0 \quad (10)$$

$$\beta_{Na}^2\cdot 312.5 + \beta_{Na}\cdot 2.25 - 1 = 0 \quad (11)$$

$$\beta_{Na} = 0.0531 \quad (12)$$

$$\beta_K = \frac{\beta_{Na}[K]}{K_{Na/K}[Na]} = \frac{0.0531\cdot 0.5\cdot 10^{-3}}{0.2\cdot 2\cdot 10^{-3}} = 0.0664 \quad (13)$$

$$\beta_{Ca} = \frac{\beta_{Na}^2[Ca]}{K_{Na/Ca}^2[Na]^2} = \frac{0.0531^2\cdot 0.2\cdot 10^{-3}}{0.4^2(2\cdot 10^{-3})^2} = 0.881 \quad (14)$$

Check:

$$\beta_{Na} + \beta_K + \beta_{Ca} = 0.0531 + 0.0664 + 0.881 = 1.00 \quad (15)$$

- To convert the equivalent fractions β to molar fractions β^M we note that

$$\beta_i^M = \frac{n_i}{\sum_i n_i} = \frac{n_i Z_i \frac{1}{Z_i}}{\sum_i(n_i Z_i \frac{1}{Z_i})} = \frac{\frac{n_i Z_i}{\sum n_i Z_i}\frac{1}{Z_i}}{\sum_i(\frac{n_i Z_i}{\sum n_i Z_i}\frac{1}{Z_i})} = \frac{\beta_i \frac{1}{Z_i}}{\sum_i \beta_i \frac{1}{Z_i}} \quad (16)$$

where n_i and Z_i denote the number of moles on the surface and the valence of that species.

- We then get:

$$\beta_{Na}^M = \frac{0.0531\cdot\frac{1}{1}}{0.0531\cdot\frac{1}{1} + 0.0664\cdot\frac{1}{1} + 0.881\cdot\frac{1}{2}} = 0.0948 \quad (17)$$

$$\beta_K^M = \frac{0.0664\cdot\frac{1}{1}}{0.0531\cdot\frac{1}{1} + 0.0664\cdot\frac{1}{1} + 0.881\cdot\frac{1}{2}} = 0.116 \quad (18)$$

$$\beta_{Ca}^M = \frac{0.881\cdot\frac{1}{2}}{0.0531\cdot\frac{1}{1} + 0.0664\cdot\frac{1}{1} + 0.881\cdot\frac{1}{2}} = 0.787 \quad (19)$$

Again we have:

$$\beta_{Na}^M + \beta_K^M + \beta_{Ca}^M = 0.0948 + 0.116 + 0.787 = 1.00 \quad (20)$$

1.2. The Langmuir isotherm for adsorption of the species I can be written in the form

$$s_I(c) = s_{\max}\frac{rc_I}{1 + rc_I} \quad (21)$$

where s_I is adsorbed amount in mol/L and c_I is the brine concentration in mol/L.

- Show that the isotherm function is linear for small concentrations.
- Calculate the distribution coefficient as function of brine concentration.
- Show that the isotherm function does not exceed $s_{\max}$.
- We want to ensure that less than 3 mol / L adsorbs. Assume that $s_{\max}$=10mol/L and $r = 1.5[L/mol]$. What is the maximum concentration we can inject?

Answer.

- Let c be a small value, then $1 + rc_I \approx 1$ and

$$s_I(c) = s_{\max}\frac{rc_I}{1 + rc_I} \approx s_{\max}rc_I \quad (22)$$

which means the adsorbed amount increases linearly with concentration in this range.

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$$K_d' = s_I(c_I)/c_I = s_{\max}\frac{r}{1 + rc_I} \quad (23)$$

- First of all

$$s_I(0) = s_{\max}\frac{r\cdot 0}{1+r\cdot 0} = 0 \tag{24}$$

The function is increasing for all c_I:

$$\begin{aligned} s_I'(c_I) &= s_{\max}\left(\frac{r}{1/c_I+r}\right)' = -s_{\max}\left(\frac{r}{(1/c_I+r)^2}\right)(-1/c_I^2) && (25)\\ &= s_{\max}\frac{r}{(1/c_I+r)^2c_I^2} = s_{\max}\frac{r}{(1+rc_I)^2} \geq 0 && (26)\end{aligned}$$

As $c_I \to \infty$ the adsorbed amount approaches s_{max}:

$$s_I(c) = s_{\max}\frac{rc_I}{1+rc_I} = s_{\max}\frac{r}{1/c_I+r} \to s_{\max}\frac{r}{0+r} = s_{\max} \tag{27}$$

- We can calculate the concentration corresponding to the given adsorption. Any higher concentration will result in higher adsorption.

$$\begin{aligned} s_I &= s_{\max}\frac{rc_I}{1+rc_I} && (28)\\ s_I + rs_Ic_I &= s_{\max}rc_I && (29)\\ s_{\max}rc_I - rs_Ic_I &= s_I && (30)\\ c_I &= \frac{s_I}{r(s_{\max}-s_I)} && (31)\end{aligned}$$

We then obtain

$$c_I = \frac{s_I}{r(s_{\max}-s_I)} = \frac{3}{1.5(10-3)} = 0.286\text{mol / L} \tag{32}$$

1.3. A species adsorbs according to a Langmuir isotherm with parameters $s_{\max}$=6mol/L pore and $r = 1.5$ [L/mol].

The species is injected at a concentration of 10 mol/L and a speed of 1 m/min through a porous medium. The initial concentration is 2 mol/L. Consider the state after 1 min injection.

- Calculate the position of the water front, x_w.
- For the concentrations $c = 2, 6, 10$ calculate the retardation factor R and the distance travelled by each concentration. What type of front is observed?
- Plot brine concentration $c(x)$ from $x = 0$ until the water front position.
- Plot adsorbed concentration $q(x)$ from $x = 0$ until the water front position.
- Consider the point $x = 0.5$. Plot the brine concentration at this point as function of time from $t = 0$ to 1 min.
- Repeat the calculations if the initial concentration is $c_0 = 10$mol/L and the injected concentration is 2mol/L.

Answer.

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$$x_w = v_wt = 1m \tag{33}$$

- First we note that

$$\begin{aligned} q(c) &= s_{\max}\frac{rc}{1+rc} && (34)\\ \frac{dq}{dc} &= s_{\max}\frac{r}{(1+rc_I)^2} = 6\frac{1.5}{(1+1.5c_I)^2} = \frac{9}{(1+1.5c_I)^2} && (35)\end{aligned}$$

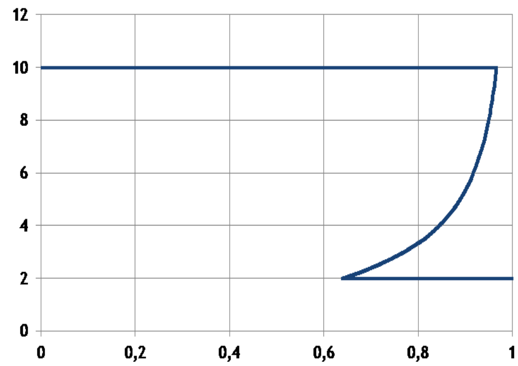

FIGURE 1. Plot of concentration c against position x after $t = 1$ min. Initial concentration is 2mol/L and injected concentration is 10mol/L. Since high concentrations travel faster this solution form is unphysical and must be represented by a front, see next figure.

For the different concentrations we get:

$$c = 2: \qquad \frac{dq}{dc} = \frac{9}{(1+1.5\cdot 2)^2} = 0.56 \qquad R = 1.56 \qquad x_{c=2} = 0.64 \tag{36}$$

$$c = 6: \qquad \frac{dq}{dc} = \frac{9}{(1+1.5\cdot 6)^2} = 0.09 \qquad R = 1.09 \qquad x_{c=6} = 0.92 \tag{37}$$

$$c = 10: \qquad \frac{dq}{dc} = \frac{9}{(1+1.5\cdot 10)^2} = 0.035 \qquad R = 1.035 \qquad x_{c=10} = 0.97 \tag{38}$$

where we use that $R = 1 + dq/dc$ and $x_c = x_w/R_c = 1/R_c$ [m].

The high injected concentrations travel faster than the low initial ones, i.e. sharpening front. The front position is given such that:

$$R_f = 1 + \frac{\Delta q}{\Delta c} = 1 + \frac{q(10)-q(2)}{10-2} = 1 + \frac{5.625-4.5}{10-2} = 1.14 \tag{39}$$

$$x_f = x_w/R_f = 1m/R_f = 1/1.14 = 0.88 \tag{40}$$

- $c(x)$ is given in Figure 2.
- $$q(x) = q(c_{inj}) = 6\frac{1.5\cdot 10}{1+1.5\cdot 10} = 5.6 \qquad (x < x_f) \tag{41}$$
  $$q(x) = q(c_{init}) = 6\frac{1.5\cdot 2}{1+1.5\cdot 2} = 4.5 \qquad (x > x_f) \tag{42}$$
- $$t_w = x/v_w = 0.5/1 = 0.5min \tag{43}$$
  The concentrations arrive at this position after the time $t_c = t_w R_c$ or $t_c = t_w R_f$ if it is a sharp front. See Figure 4.
- For the broadening front case:
  $$q(x) = q(c(x)) \tag{44}$$
  Calculate $c(x)$ and then evaluate $q(c)$ in each point.

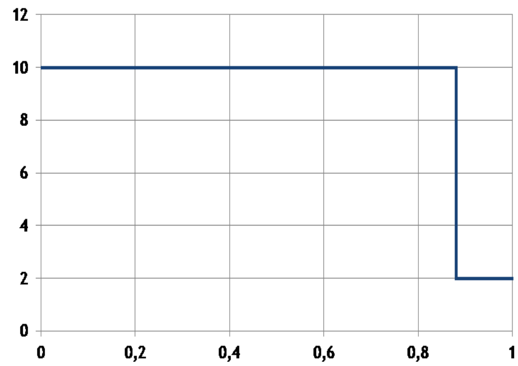

FIGURE 2. Plot of concentration c against position x after $t = 1$ min. Initial concentration is 2mol/L and injected concentration is 10mol/L. The physically correct solution is constructed with position determined such that mass is preserved. This illustrates a sharpening front.

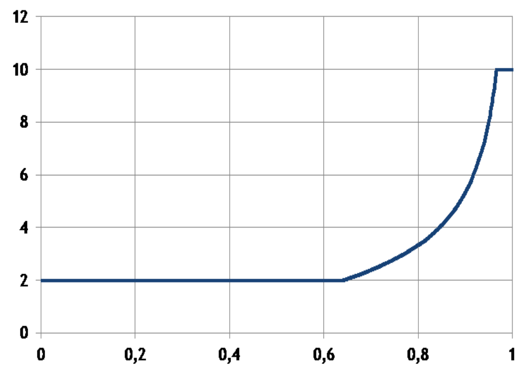

FIGURE 3. Plot of concentration c against position x after $t = 1$ min. Initial concentration is 10mol/L and injected concentration is 2mol/L.
This illustrates a broadening front.

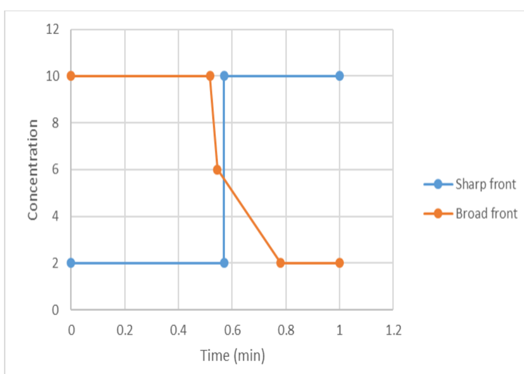

FIGURE 4. Plot of concentration c against time t at $x = 0.5$ m. Orange graph: Initial concentration is 2 mol/L and injected concentration is 10 mol/L. Broadening front. Blue graph: Initial concentration is 10 mol/L and injected concentration is 2 mol/L. Sharpening front.