

## PET565 PART B: EXERCISE SET 1

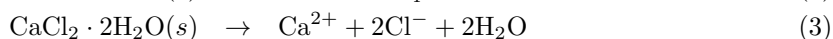
### IMPORTANT NOTES

- In all *reaction* calculations concentrations should enter with numerical magnitude of the unit *molality* M:  $M = \text{mol} / \text{kg w}$ .
- For simplicity we will assume  $1\text{L} = 1\text{L brine} = 1\text{L water} = 1\text{kg water}$ .
- The units of activity, activity coefficients and ionic strength are dimensionless.

### 1. EXERCISES

**1.1.** 0.04 mol NaCl, 0.03 mol Na<sub>2</sub>SO<sub>4</sub> and 0.02 mol CaCl<sub>2</sub>·2H<sub>2</sub>O are mixed into 1 L water. Find the concentration  $C$  of the ions Na<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup>.

*Answer.* The species dissolve from solid state into aqueous species as:



The concentrations are then given by

$$C_{\text{Na}^+} = (1\# \text{mol NaCl} + 2\# \text{mol Na}_2\text{SO}_4) / (1\text{L w}) \quad (4)$$

$$= 0.04 + 2 \cdot 0.03 \text{mol/L} = 0.10 \text{mol/L} \quad (5)$$

$$C_{\text{Cl}^-} = 0.04 + 2 \cdot 0.02 \text{mol/L} = 0.08 \text{mol/L} \quad (6)$$

$$C_{\text{SO}_4^{2-}} = 0.03 \text{mol/L} \quad (7)$$

$$C_{\text{Ca}^{2+}} = 0.02 \text{mol/L} \quad (8)$$

**1.2.** Given the composition  $C$ , calculate the ionic strength  $I_0$  from eqn. (4.11) in the book (assume  $m_i = C_i$  and no complexes).

*Answer.*

$$I_0 = 1/2 \sum C_i Z_i^2 = 0.1 \cdot 1^2 + 0.08 \cdot (-1)^2 + 0.03 \cdot (-2)^2 + 0.02 \cdot 2^2 = 0.19 \quad (9)$$

**1.3.** Calculate the activity coefficients  $\gamma$ , for all 4 ions, using Davies formula (eqn. (4.14) in Appelo's book). This formula is applicable for  $I_0 < 0.5$ . Is this fulfilled?

Assume the temperature coefficient  $A = 0.51$  as given by a temperature of 25°C.

Calculate the activity coefficient of Ca<sup>2+</sup> and Na<sup>+</sup> using Truesdell-Jones' formula (4.13) together with Table 4.3. Use that  $B = 0.33e10/m$

Compare your answers with Figure 4.2.

*Answer.* Davies:

$$\log \gamma_{\text{Na}^+} = \log \gamma_{\text{Cl}^-} = -0.51 \cdot 1^2 \left( \frac{\sqrt{0.19}}{1 + \sqrt{0.19}} - 0.3 \cdot 0.19 \right) = \log(0.749) \quad (10)$$

$$\log \gamma_{\text{SO}_4^{2-}} = \log \gamma_{\text{Ca}^{2+}} = -0.51 \cdot 2^2 \left( \frac{\sqrt{0.19}}{1 + \sqrt{0.19}} - 0.3 \cdot 0.19 \right) = \log(0.315) \quad (11)$$

TJ:

Ion specific parameters:

$$\text{Ca} : a = 5.0e - 10m, b = 0.165 \quad \text{SO}_4 : a = 5.0e - 10m, b = -0.04 \quad (12)$$

Activity coefficients:

$$\log \gamma_i = -\frac{0.51(\pm 2)^2 \sqrt{0.19}}{1 + 0.3 \cdot 5.0 \sqrt{0.19}} + b_i \cdot 0.19 = -0.538 + 0.19b_i \quad (13)$$

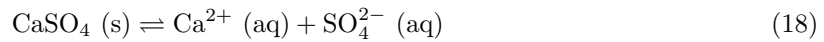
$$= -.507(Ca) \quad (14)$$

$$= -0.546(SO4) \quad (15)$$

$$\gamma_{ca} = 0.311 \quad (16)$$

$$\gamma_{so4} = 0.285 \quad (17)$$

1.4. Anhydrite  $\text{CaSO}_4$  is a mineral which is formed by the reaction:



The solubility constant at  $25^\circ\text{C}$  is  $10^{-4.35}$ .

Based on the composition of the fluid (still assuming no complexes), calculate the ion activity product  $IAP$ , the saturation state  $\Omega$  and saturation index  $SI$  for anhydrite.

PS: Remember to use *activity*  $a$  in the calculations, where  $a = \gamma C$  (apply results from Davies eq). Is the solution stable, i.e. will anhydrite mineral form?

*Answer.*

$$IAP = a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}} \quad (19)$$

$$= \gamma_{\text{Ca}^{2+}} C_{\text{Ca}^{2+}} \gamma_{\text{SO}_4^{2-}} C_{\text{SO}_4^{2-}} \quad (20)$$

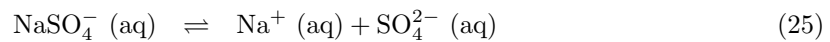
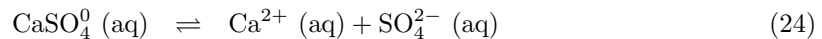
$$= 0.315 \cdot 0.02 \cdot 0.315 \cdot 0.03 = 0.0000595 = 10^{-4.23} \quad (21)$$

$$\Omega = IAP / K_{\text{CaSO}_4} = \frac{10^{-4.23}}{10^{-4.35}} = 10^{0.12} = 1.32 \quad (22)$$

$$SI = \log_{10} \Omega = 0.12 \quad (23)$$

Since  $\Omega > 1$  or equivalently  $SI > 0$  the solution is oversaturated on anhydrite and should precipitate this mineral. Note however that we have not considered the effect of aqueous complexes.

1.5. Now assume that two aqueous complexes,  $\text{Na}_2\text{SO}_4$  and  $\text{CaSO}_4$ , can form by the reactions



where  $K_{\text{CaSO}_4^0} = 10^{-2.3}$  and  $K_{\text{NaSO}_4^-} = 10^{-0.7}$ .

- Write 3 mass balance equations (for  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{SO}_4^{2-}$ ) to express the relation between the total concentrations  $C$ , the concentration of free ions  $m_i$ , where  $i = \text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  and the concentration of complexes  $n_i$  where  $i = \text{CaSO}_4^0$  and  $\text{NaSO}_4^-$ .
- Express 2 equilibrium equations for the reactions (23)-(24).

The 5 above equations should be solved to determine the composition of the brine in terms of the 5 concentrations  $m_i(3)$ ,  $n_i(2)$ . This will be done using some simplifications and iterative procedures.

- In the equations involving  $\text{Na}^+$ : Assume the concentration of Na complexes is very small compared to the amount of Na by replacing  $m_{\text{Na}^+}$  with  $C_{\text{Na}^+}$ , thus eliminating the unknown  $m_{\text{Na}^+}$ . Update the involved equations.
- Solve the system for the 5 unknowns  $m_i(3)$  and  $n_i(2)$  using the 5 mentioned equations and simplification (that eliminates  $m_{na}$ ). Tip: Reduce the system to 1 equation and solve with Excel or another method.
- Given the complex concentrations, find an improved estimate of  $m_{na}$  using the original mass balance for Na.
- Calculate the fraction of free ions for Na, Ca and SO4:  $m_i/C_i$ .

Answer.

a) Mass balance equations:

$$C_{\text{SO}_4^{2-}} = m_{\text{SO}_4^{2-}} + n_{\text{CaSO}_4^0} + n_{\text{NaSO}_4^-} \quad (26)$$

$$C_{\text{Ca}^{2+}} = m_{\text{Ca}^{2+}} + n_{\text{CaSO}_4^0} \quad (27)$$

$$C_{\text{Na}^+} = m_{\text{Na}^+} + n_{\text{NaSO}_4^-} \quad (28)$$

b) Equilibrium equations:

$$K_{\text{CaSO}_4^0} = \frac{\gamma_{\text{Ca}^{2+}} m_{\text{Ca}^{2+}} \gamma_{\text{SO}_4^{2-}} m_{\text{SO}_4^{2-}}}{\gamma_{\text{CaSO}_4^0} n_{\text{CaSO}_4^0}} \quad (29)$$

$$K_{\text{NaSO}_4^-} = \frac{\gamma_{\text{Na}^+} m_{\text{Na}^+} \gamma_{\text{SO}_4^{2-}} m_{\text{SO}_4^{2-}}}{\gamma_{\text{NaSO}_4^-} n_{\text{NaSO}_4^-}} \quad (30)$$

c) The approximation  $m_{\text{Na}^+} = C_{\text{Na}^+}$  replaces (27) and we have one less unknown. The equilibrium equation for  $\text{NaSO}_4^-$  becomes:

$$K_{\text{NaSO}_4^-} = \frac{\gamma_{\text{Na}^+} C_{\text{Na}^+} \gamma_{\text{SO}_4^{2-}} m_{\text{SO}_4^{2-}}}{\gamma_{\text{NaSO}_4^-} n_{\text{NaSO}_4^-}} \quad (31)$$

d) Reformulate the system such that

$$n_{\text{CaSO}_4^0} = m_{\text{Ca}^{2+}} m_{\text{SO}_4^{2-}} \frac{\gamma_{\text{Ca}^{2+}} \gamma_{\text{SO}_4^{2-}}}{\gamma_{\text{CaSO}_4^0} K_{\text{CaSO}_4^0}} = m_{\text{Ca}^{2+}} m_{\text{SO}_4^{2-}} K_1, \quad (32)$$

$$K_1 = \frac{\gamma_{\text{Ca}^{2+}} \gamma_{\text{SO}_4^{2-}}}{\gamma_{\text{CaSO}_4^0} K_{\text{CaSO}_4^0}} = \frac{0.315 \cdot 0.315}{1 \cdot 10^{-2.3}} = 19.80, \quad (33)$$

$$n_{\text{NaSO}_4^-} = m_{\text{Na}^+} m_{\text{SO}_4^{2-}} \frac{\gamma_{\text{Na}^+} \gamma_{\text{SO}_4^{2-}}}{\gamma_{\text{NaSO}_4^-} K_{\text{NaSO}_4^-}} = m_{\text{Na}^+} m_{\text{SO}_4^{2-}} K_2, \quad (34)$$

$$K_2 = \frac{\gamma_{\text{Na}^+} \gamma_{\text{SO}_4^{2-}}}{\gamma_{\text{NaSO}_4^-} K_{\text{NaSO}_4^-}} = \frac{0.749 \cdot 0.315}{1 \cdot 10^{-0.7}} = 1.18 \quad (35)$$

$K_1, K_2$  are defined above such to collect the constant parameters.

Substitute the complex concentrations  $n_i$  given by (31) and (33) into the mass balance equations.

$$C_{\text{SO}_4^{2-}} = m_{\text{SO}_4^{2-}} + m_{\text{Ca}^{2+}} m_{\text{SO}_4^{2-}} K_1 + m_{\text{Na}^+} m_{\text{SO}_4^{2-}} K_2 \quad (36)$$

$$= m_{\text{SO}_4^{2-}} (1 + m_{\text{Ca}^{2+}} K_1 + m_{\text{Na}^+} K_2) \quad (37)$$

Solve for  $m_{\text{SO}_4^{2-}}$ :

$$m_{\text{SO}_4^{2-}} (m_{\text{Ca}^{2+}}) = \frac{C_{\text{SO}_4^{2-}}}{(1 + m_{\text{Ca}^{2+}} K_1 + m_{\text{Na}^+} K_2)} \quad (38)$$

Do the same for the Ca equation:

$$C_{\text{Ca}^{2+}} = m_{\text{Ca}^{2+}} + m_{\text{Ca}^{2+}} m_{\text{SO}_4^{2-}} K_1 \quad (39)$$

Eliminate  $m_{\text{SO}_4^{2-}}$  from the above equation using the relation  $m_{\text{SO}_4^{2-}} = (m_{\text{Ca}^{2+}})^{-1}$ :

$$m_{\text{Ca}^{2+}} = C_{\text{Ca}^{2+}} - \frac{m_{\text{Ca}^{2+}} C_{\text{SO}_4^{2-}}}{(1 + m_{\text{Ca}^{2+}} K_1 + m_{\text{Na}^+} K_2)} K_1 \quad (40)$$

The above equation is of the form  $x = f(x)$ , where  $x = m_{\text{Ca}^{2+}}$  is the only unknown.

It can be solved by plotting the line  $y = x$  and the function  $y = f(x)$  to see where they cross.

Another option is to use that since  $x = f(x)$  the equation above should return a value that approximates the correct solution. A good starting point is assuming  $x = C_{\text{Ca}}$ .  $f(x)$  will return an estimate of  $m_{\text{Ca}}$  with better approximation for each iteration.

By the iteration procedure we get  $m_{\text{Ca}^{2+}} = 0.0140 \text{ mol/L}$ . Backsubstitution leads to

$$m_{\text{SO}_4^{2-}} = \frac{C_{\text{SO}_4^{2-}}}{(1+m_{\text{Ca}^{2+}}K_1+m_{\text{Na}^+}K_2)} = 0.0215 \text{ mol/L} \quad (41)$$

$$n_{\text{CaSO}_4^0} = C_{\text{Ca}^{2+}} - m_{\text{Ca}^{2+}} = 0.02 - 0.0140 = 0.00596 \text{ mol/L} \quad (42)$$

$$n_{\text{NaSO}_4^-} = m_{\text{Na}^+}m_{\text{SO}_4^{2-}}K_2 = 0.1 \cdot 0.0215 \cdot 1.18 = 0.00254 \text{ mol/L} \quad (43)$$

e) Updated values for Na:

$$m_{\text{Na}^+} = C_{\text{Na}^+} - n_{\text{NaSO}_4^-} = 0.1 - 0.00254 = 0.0975 \text{ mol/L} \quad (44)$$

Note that mass balance is ensured, while equilibrium is not. In practice we should update ionic strength, activity coefficients and iterate the equation system until all equations are fulfilled.

f)

$$\frac{m_{\text{so4}}}{C_{\text{so4}}} = \frac{0.0215}{0.03} = 0.717 \quad (45)$$

$$\frac{m_{\text{ca}}}{C_{\text{ca}}} = \frac{0.014}{0.02} = 0.70 \quad (46)$$

$$\frac{m_{\text{na}}}{C_{\text{na}}} = \frac{0.0975}{0.10} = 0.975 \quad (47)$$

Note that the assumption  $m_{\text{na}} \approx C_{\text{na}}$  is validated.

**1.6.**  $m_i$  represents the free ions of main species available to reactions. Assuming  $\gamma$  are the same (Davies), recalculate the *IAP* and saturation state  $\Omega$  for anhydrite. Is the solution stable with respect to anhydrite? Is the effect of complexes significant?

*Answer.*

$$IAP = \gamma_{\text{Ca}^{2+}}m_{\text{Ca}^{2+}}\gamma_{\text{SO}_4^{2-}}m_{\text{SO}_4^{2-}} \quad (48)$$

$$= 0.315 \cdot 0.014 \cdot 0.315 \cdot 0.0215 = 0.0000299 = 10^{-4.52} \quad (49)$$

$$\Omega = IAP/K_{\text{CaSO}_4} = \frac{10^{-4.52}}{10^{-4.35}} = 10^{-0.17} = 0.676 \quad (50)$$

The more accurate calculation shows that by taking complexes into consideration the solution is actually undersaturated with respect to anhydrite (since  $\Omega < 1$ ).