

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_2SO_4 and 0.02 mol $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ are mixed into 1 L water. Find the concentration C of the ions Na^+ , Cl^- , SO_4^{2-} and Ca^{2+} .

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).

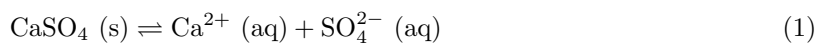
1.3. Calculate the activity coefficients γ , for all 4 ions, using Davies formula (eqn. (4.14) in Appelo's book). This formula is applicable for $I_0 < 0.5$. Is this fulfilled?

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

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

Compare your answers with Figure 4.2.

1.4. Anhydrite CaSO_4 is a mineral which is formed by the reaction:

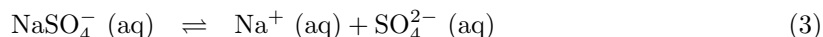
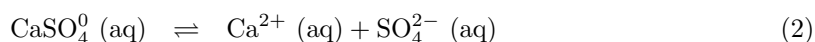


The solubility constant at 25°C is $10^{-4.35}$.

Based on the composition of the fluid (still assuming no complexes), calculate the ion activity product IAP , the saturation state Ω 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?

1.5. Now assume that two aqueous complexes, Na_2SO_4 and 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 Ca^{2+} , Na^+ and SO_4^{2-}) to express the relation between the total concentrations C , the concentration of free ions m_i , where $i = \text{Ca}^{2+}$, Na^+ and SO_4^{2-} and the concentration of complexes n_i where $i = \text{CaSO}_4^0$ and NaSO_4^- .
- Express 2 equilibrium equations for the reactions (2)-(3).

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 Na^+ : Assume the concentration of Na complexes is very small compared to the amount of Na by replacing m_{Na^+} with C_{Na^+} , thus eliminating the unknown m_{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.

f) Calculate the fraction of free ions for Na, Ca and SO₄: m_i/C_i .

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