PET565 PART B: EXERCISE SET 1

Important notes

- In all *reaction* calculations concentrations should enter with numerical magnitude of the unit *molality* M: M = mol / kg w.
- For simplicity we will assume 1L = 1L brine = 1L water = 1kg 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 $CaCl_2 \cdot 2H_2O$ 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:

$$CaSO_4 \text{ (s)} \rightleftharpoons Ca^{2+} \text{ (aq)} + SO_4^{2-} \text{ (aq)} \quad (1)$$

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

$$CaSO_4^0 \text{ (aq)} \rightleftharpoons Ca^{2+} \text{ (aq)} + SO_4^{2-} \text{ (aq)} \quad (2)$$

$$NaSO_4^- \text{ (aq)} \rightleftharpoons Na^+ \text{ (aq)} + SO_4^{2-} \text{ (aq)} \quad (3)$$

where $K_{CaSO_4^0} = 10^{-2.3}$ and $K_{NaSO_4^-} = 10^{-0.7}$.

a) 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 $i = Ca^{2+}$, Na^+ and SO_4^{2-} and the concentration of complexes n_i where $i = CaSO_4^0$ and $NaSO_4^-$.
b) 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.

c) 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.
d) 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.
e) 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?