

Exercise 1 (Geofluids – Part III)

Mass action and mass conservation equations and their use for chemical equilibrium calculations

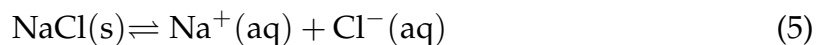
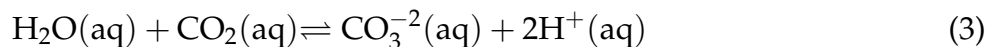
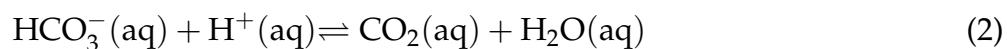
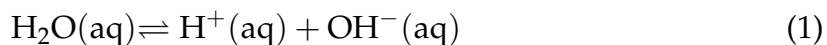
Lecturer: Dr. Svetlana Kyas

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Consider the following chemical species in three different phases, and the chemical elements that compose them:

Index	Species	Index	Element
1	$\text{CO}_2(\text{aq})$	1	C
2	$\text{CO}_3^{-2}(\text{aq})$	2	Cl
3	$\text{Cl}^{-}(\text{aq})$	3	H
4	$\text{H}^{+}(\text{aq})$	4	Na
5	$\text{H}_2\text{O}(\text{l})$	5	Ol
6	$\text{HCO}_3^{-}(\text{aq})$		
7	$\text{Na}^{+}(\text{aq})$		
8	$\text{OH}^{-}(\text{aq})$		
9	$\text{CO}_2(\text{g})$		
10	$\text{NaCl}(\text{s})$		

The following system of linearly independent reactions can be written for this chemical system:



Exercise

- Write the **system of mass action equations** for these reactions.
- Write the **system of mass conservation equations** for the elements.
- Discuss whether the combination of these systems of equations are enough to compute $n = (n_1, \dots, n_{10})$ and, if so, what kind of algorithm would you use for this.

Considerations:

- Use n_1, \dots, n_{10} to denote the amounts of the species (*unknown*);
- Use b_1, \dots, b_5 to denote the amounts of the elements (*known*);
- Use a_1, \dots, a_{10} to denote the activities of the species (*unknown, function of n*);
- Use K_1, \dots, K_5 to denote the equilibrium constants of the reactions (*known*).

Remarks:

- In the next classes, we will see how activities, a_i , are calculated for aqueous, gaseous and mineral species. For now, know that activities are non-linear functions that depend on the amounts of the species, $n = (n_1, \dots, n_{10})$, temperature T and pressure P . Thus, $a_i = a_i(n; T, P)$, where T and P are given and n is what we want to find.
- To write the mass conservation equations, determine the chemical formula coefficients A_{ji} below:

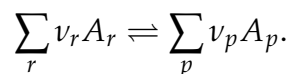
$$\sum_{i=1}^{10} A_{ji} n_i = b_j \quad (j = 1, \dots, 5).$$

For example, $A_{\text{O}, \text{HCO}_3^-} \equiv A_{2,6} = 3$.

- To write the mass action equations, use the general mass action equation:

$$K_m = \frac{\prod_p a_p^{\nu_p}}{\prod_r a_r^{\nu_r}} \quad (m = 1, \dots, 5),$$

for the reaction written in general form:



For example, for reaction (1), we have:

$$K_1 = \frac{a_2 a_3}{a_1}.$$