Exercise 1 (Geofluids – Part III)

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

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

Index	**Species**
1	$CO_2(aq)$
2	$CO_3^{-2}(aq)$
3	$Cl^-(aq)$
4	$H^+(aq)$
5	$H_2O(l)$
6	$HCO_3^-(aq)$
7	$Na^+(aq)$
8	$OH^-(aq)$
9	$CO_2(g)$
10	$NaCl(s)$

Index	**Element**
1	C
2	Cl
3	H
4	Na
5	Ol

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

$$H_2O(aq) \rightleftharpoons H^+(aq) + OH^-(aq) \tag{1}$$

$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons CO_2(aq) + H_2O(aq) \tag{2}$$

$$H_2O(aq) + CO_2(aq) \rightleftharpoons CO_3^{-2}(aq) + 2H^+(aq) \tag{3}$$

$$CO_2(g) \rightleftharpoons CO_2(aq) \tag{4}$$

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq) \tag{5}$$

Exercise

a) Write the **system of mass action equations** for these reactions.

b) Write the **system of mass conservation equations** for the elements.

c) Discuss whether the combination of these systems of equations are enough to compute $n = (n_1, \ldots, n_{10})$ and, if so, what kind of algorithm would you use for this.

Considerations:

- Use n_1, ..., n_{10} to denote the amounts of the species (*unknown*);
- Use b_1, ..., b_5 to denote the amounts of the elements (*known*);
- Use a_1, ..., a_{10} to denote the activities of the species (*unknown, function of* n);
- Use K_1, ..., 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, $n = (n_1, \ldots, n_{10})$, 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:

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

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

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

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

  for the reaction written in general form:

$$\sum_r \nu_r A_r \rightleftharpoons \sum_p \nu_p A_p.$$

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

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