Modeling of geochemical processes

Equilibrium modeling

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Equilibrium modeling

A set of functions, *f*, are defined that must be solved simultaneously to determine equilibrium for a given set of conditions.

Many of these functions are derived from

- **mole-balance equations** for *each element* or *element valence state, exchange site,* and *surface site*

- **mass-action equations** for pure phases and solid solutions.

- **aqueous charge balance**

Additional functions are derived for

- **alkalinity**

- **activity of water**

- **gas-phase equilibria**

- **ionic strength**

- **surface-complexation equilibria**.

Each function is reduced to contain a minimum number of variables, such that **the number of functions equals the number of variables**.

The program uses a modified *Newton-Raphson method* to solve the simultaneous nonlinear equations.

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In the following equations, lack of a subscript or the subscript "(aq)" will refer to entities in the aqueous phase, "(e)" refers to exchangers, "(g)" refers to gases, "(s)" refers to surfaces, "(ss)" refers to solid solutions, and "(p)" refers to phases.

The unknowns for each aqueous species i are the activity, a_i, activity coefficient, γ_i, molality, m_i, and moles in solution, n_i.

The activity of water, a_{H2O}, the ionic strength, μ, and the mass of solvent water in an aqueous solution, W_{aq}.

The following relationships apply

$$a_i = \gamma_i m_i \qquad\qquad n_i = m_i W_{aq}$$

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Components of base:

- A_{aq} – water
- A_i – dissolved species, base components
- A_p – mineral phases in equilibrium
- A_g – gases of known fugacity

Another species:

- A_j – dissolved species (secondary)
- A_{pj} – secondary minerals, (they can be virtual)

Formation of mineral, Aj, from the base components $\mathbf{B} = (A_{aq}, A_i, A_p, A_g)$

$$\nu_p A_p + \nu_{aq} A_{aq} + \nu_g A_g + \nu_i A_i + \nu_j A_j = 0 \qquad\qquad \sum_u \nu_u A_u = 0$$

$$\nu_j A_j = \nu_p A_p + \nu_{aq} A_{aq} + \nu_g A_g + \nu_i A_i$$

$$A_j = \frac{\nu_p}{\nu_j} A_p + \frac{\nu_{aq}}{\nu_j} A_{aq} + \frac{\nu_g}{\nu_j} A_g + \frac{\nu_i}{\nu_j} A_i$$

$$A_j = \nu_{pj} A_p + \nu_{aq,j} A_{aq} + \nu_{gj} A_g + \nu_{ij} A_i$$

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Example

Let us have the base **B** = (H_2O, H^+, HCO_3^-),

Secondary species are $CO_{2(aq)}$ and CO_3^{2-}.

Build the secondary species from the base components:

$$CO_{2(aq)} = HCO_3^- + H^+ - H_2O$$

and $$CO_3^{2-} = HCO_3^- - H^+$$
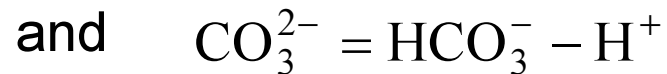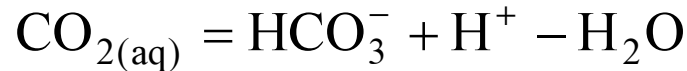
Reaction between the secondary species can be expressed by linear combination of both equations (e.g. by subtracting of second equation from the first one):

$$CO_{2(aq)} - CO_3^{2-} = HCO_3^- - HCO_3^- + H^+ + H^+ - H_2O$$

It gives: $$CO_{2(aq)} + H_2O = CO_3^{2-} + 2H^+$$
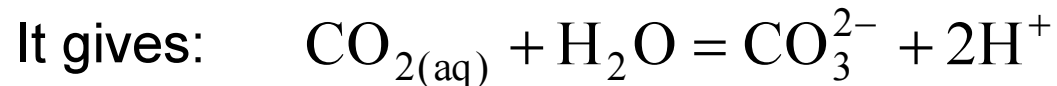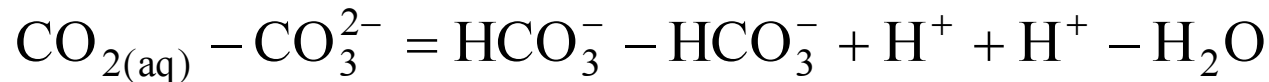
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Mass-action equations

In general, mass-action equations can be written as

$$K_i = a_i \prod_m^{M_{aq}} a_m^{\nu_{m,i}}$$

where K_i is a temperature-dependent equilibrium constant, $\nu_{m,i}$ is the stoichiometric coefficient of master species m in species i and M_{aq} is the total number of aqueous master species. The values of $\nu_{m,i}$ may be positive or negative.

The total moles of an aqueous species i can be derived from the mass-action expression:

$$n_i = m_i W_{aq} = K_i W_{aq} \frac{\prod_m^{M_{aq}} a_m^{-\nu_{m,i}}}{\gamma_i}$$

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Activity coefficients of aqueous species are defined with the Davies equation:

$$\log \gamma_i = -A\, z_i^2 \left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0{,}3\,\mu \right)$$

or the extended Debye-Hückel equation:

$$\log \gamma_i = -\frac{A\, z_i^2 \sqrt{\mu}}{1 + B\, a_i^o \sqrt{\mu}} + b_i\, \mu$$

where z_i is the ionic charge of aqueous species i, and A and B are constants dependent only on temperature. a_i^o and b_i are ion-specific parameters in the Debye-Hückel equation.

The ionic strength of the aqueous solution is

$$\mu = \frac{1}{2} \sum_i^{N_{aq}} z_i^2 \frac{n_i}{W_{aq}}$$

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Calcite dissolution

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2\,HCO_3^-$$

$$K_p = \frac{a_{Ca^{2+}}\,a^2_{HCO_3^-}}{a_{CaCO_3}\,a_{H_2O}\,a_{CO_2}} \qquad\qquad a_{Ca^{2+}} = \frac{K_p\,a_{CaCO_3}\,a_{H_2O}\,a_{CO_2}}{a^2_{HCO_3^-}}$$

$$m_{Ca^{2+}} = \frac{K_p\,m_{CaCO_3}\,\gamma_{CaCO_3}\,m_{H_2O}\,\gamma_{H_2O}\,m_{CO_2}\,\gamma_{CO_2}}{\gamma_{Ca^{2+}}\,m^2_{HCO_3^-}\,\gamma^2_{HCO_3^-}}$$

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Mole-balance equation

The total moles of an element in the system are the sum of the moles initially present in the

- *pure-phase*

- *solid-solution assemblages*,

- *aqueous phase*,

- *exchange assemblage*,

- *surface assemblage*,

- *gas phase*, and

- *diffuse layers* of the surfaces.

The following function is the general **mole-balance equation**:

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$$f_m = \left(T_m - \sum_p^{N_p} b_{m,p} n_p - \sum_{ss}^{SS} \sum_{p_{ss}}^{N_{ss}} b_{m,p_{ss}} n_{p_{ss}} \right) -$$

$$- \sum_i^{N_{aq}} b_{m,i} n_i - \sum_e^{E} \sum_{i_e}^{N_e} b_{m,i_e} n_{i_e} -$$

$$- \sum_s^{S} \sum_k^{K_s} \sum_{i_{(s_k)}}^{N_{s_k}} b_{m,i_{(s_k)}} n_{i_{(s_k)}} -$$

$$- \sum_g^{N_g} b_{m,g} n_g - \sum_s^{S} \sum_i^{N_{aq}} b_{m,i} n_{i,s}$$

f_m is zero when mole-balance is achieved
T_m is the total moles of the element
N_p is the number of phases
SS is the number of solid solutions
N_{ss} is the number of components in solid solution ss
N_{aq} is the number of aqueous species
E is the number of exchangers
N_e is the number of exchange species for exchange site e
S is the number of surfaces
K_s is the number of surface types for surface s
N_{sk} is the number of surface species for surface type s_k
N_g is the number of gas-phase components

The moles of each entity are represented by n_p for phases, n_{pss} for components in a solid solution, n_i for aqueous species, n_{ie} for the exchange species of exchange site e, $n_{i(sk)}$ for surface species for surface site type n_{sk}, n_g for the gas components, and $n_{i,s}$ for aqueous species in the diffuse layer of surface s.
The moles of element m per mole of each entity are represented by b_m, with an additional subscript to define the relevant entity
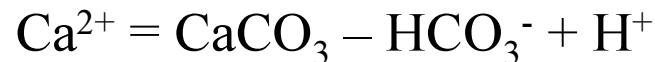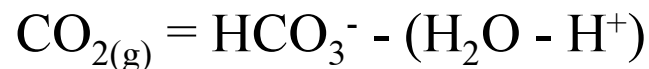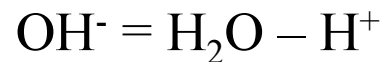
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Example

- Distribution of carbonate species in closed carbonate system

Components of base, $\mathbf{B} = [CaCO_3, H^+, H_2O, HCO_3^-]$

Secondary species, $Ca^{2+}, OH^-, CO_3^{2-}, H_2CO_3, CO_{2(g)}\ldots$

$OH^- = H_2O - H^+$

$CO_3^{2-} = HCO_3^- - H^+$

$H_2CO_3 = HCO_3^- + H^+$

$CO_{2(g)} = HCO_3^- - (H_2O - H^+)$

$Ca^{2+} = CaCO_3 - HCO_3^- + H^+$

Total mass of carbonate species, $m_{TOT} = 10^{-3}$ mol

$$f_m = 10^{-3} - m_{CaCO_3} - m_{HCO_3^-} - m_{CO_3^{2-}} - m_{H_2CO_3} - m_{CO_{2(g)}}$$

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Aqueous Charge Balance

$$f_z = T_z - \sum_i^{N_{aq}} z_i n_i - \left(\sum_s^{S} \sum_k^{K_s} \sum_{i_{(s_k)}}^{N_{s_k}} z_{i_{(s_k)}} n_{i_{(s_k)}} + \sum_s^{S} \sum_i^{N_{aq}} z_i n_{i,s} \right) - \sum_e^{E} \sum_{i_e}^{N_e} z_{i_e} n_{i_e}$$

where f_z is zero when charge balance has been achieved. If the diffuse-layer composition is explicitly calculated, a separate charge-balance equation is included for each surface and the sum of the terms in the parentheses will be zero when surface charge balance is achieved. If the diffuse-layer composition is not calculated, the second term inside the parentheses is zero.
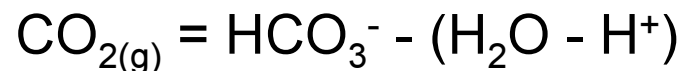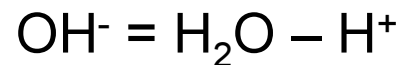
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Example

Charge balance of carbonate system

Components of base, $\mathbf{B} = [Ca^{2+}, H^+, H_2O, HCO_3^-]$

Secondary species $OH^-, CO_3^{2-}, H_2CO_3, CO_{2(g)}\ldots$

$OH^- = H_2O - H^+$

$CO_3^{2-} = HCO_3^- - H^+$

$H_2CO_3 = HCO_3^- + H^+$

$CO_{2(g)} = HCO_3^- - (H_2O - H^+)$

Charge balance

$$f_z = 2\,m_{Ca^{2+}} + m_{H^+} - m_{OH^-} - m_{HCO_3^-} - 2\,m_{CO_3^{2-}}$$