Solving transport equations

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We imagine a set of N species with aqueous concentrations c^α ($\alpha = 1, 2, \ldots N$) and M chemical reactions with rates $R_m(\boldsymbol{c})$ ($m = 1, 2, \ldots M$), where $\boldsymbol{c}$ indicates the vector containing all the aqueous concentrations. The rate of production or consumption of an aqueous species due to chemical reactions R^α is determined by the individual reaction rates:

$$R^\alpha(\boldsymbol{c}) = \sum_{m=1}^{M} \nu_m^\alpha R_m(\boldsymbol{c}), \tag{1}$$

where ν_m^α is the stoichiometry number of species α in reaction m. In general R_m are non linear functions of $\boldsymbol{c}$ with first derivatives:

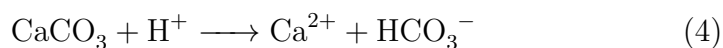$$R_m^\alpha(\boldsymbol{c}) = \left(\frac{\partial R_m}{\partial c^\alpha} \right)_{\boldsymbol{c}}. \tag{2}$$

The derivative of the overall reaction rate for a species is

$$R^{\alpha\alpha}(\boldsymbol{c}) = \sum_{m=1}^{M} \nu_m^\alpha R_m^\alpha(\boldsymbol{c}). \tag{3}$$
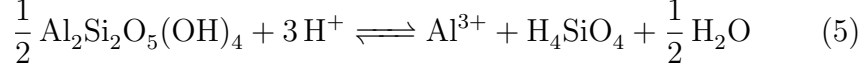
Note: only derivatives with respect to aqueous species (not mineral concentrations) are required

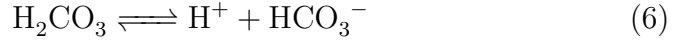As an example consider calcite replacement by kaolinite. A minimal set of reactions are:

- Reaction 1 – Calcite equilibrium.

$$\mathrm{CaCO_3 + H^+ \longrightarrow Ca^{2+} + HCO_3^-} \tag{4}$$

- Reaction 2 – Kaolinite equilibrium.

$$\frac{1}{2}\,\mathrm{Al_2Si_2O_5(OH)_4} + 3\,\mathrm{H^+} \rightleftharpoons \mathrm{Al^{3+}} + \mathrm{H_4SiO_4} + \frac{1}{2}\,\mathrm{H_2O} \qquad (5)$$

- Reaction 3 – Carbon equilibrium.

$$\mathrm{H_2CO_3} \rightleftharpoons \mathrm{H^+} + \mathrm{HCO_3^-} \qquad (6)$$

Reaction 1 has been taken as an irreversible dissolution reaction (a good approximation for calcite dissolution) with a simple rate law:

$$R_1 = k_1 c^{\mathrm{H^+}} H(\phi_1), \qquad R_1^{\mathrm{H^+}} = k_1 H(\phi_1). \qquad (7)$$

The Heaviside step function $H(\phi_1)$ ensures that there is no reaction in the absence of mineral (calcium carbonate). The reaction rate k_1 includes the reactive surface area and is in units of s^{-1}. Reaction 2 is reversible with typical kinetics:

$$R_2 = k_2 (c^{\mathrm{H^+}})^n \left(1 - I_2/K_2^{eq}\right) H(\phi_2), \qquad (8)$$
$$R_2^{\mathrm{H^+}} = k_2 (c^{\mathrm{H^+}})^{n-1} \left(n - (n-3)I_2/K_2^{eq}\right) H(\phi_2), \qquad (9)$$

where K_2^{eq} is the equilibrium constant for kaolinite dissolution and I_2 is the ion activity product

$$I_2 = \frac{c^{\mathrm{Al^{3+}}} c^{\mathrm{H_4SiO_4}}}{(c^{\mathrm{H^+}})^3}. \qquad (10)$$

Note that only one of the derivatives of R_2 has been written down explicitly; the others can be obtained in a similar fashion. Finally for reaction 3 we have:

$$R_3 = k_3 c^{\mathrm{H_2CO_3}} \left(1 - I_3/K_3^{eq}\right), \qquad R_3^{\mathrm{H_2CO_3}} = k_3, \qquad (11)$$

where $I_3 = c^{\mathrm{H^+}} c^{\mathrm{HCO_3^-}}/c^{\mathrm{H_2CO_3}}$; there are similar derivatives with respect to the remaining concentrations, as in Reaction 2. There is no mineral participating in this reaction.

Given the rates of the individual reactions we can calculate the rate of change of the aqueous ions from Eq. (1). For example:

$$R^{\mathrm{H^+}} = -R_1 - 3R_2 + R_3, \qquad (12)$$

taking into account the stoichiometry of each reaction. Similarly, to calculate the rates of gain or loss of minerals we have:

$$R^{calcite} = -R_1, \quad R^{kaolinite} = -\frac{1}{2}R_2. \tag{13}$$

The function to calculate reaction rates is based on a standard template which has a pointer to the data at a specific site $(\boldsymbol{\phi}, p, \boldsymbol{v}, \boldsymbol{c})$ for input and which creates a two-element vector $\boldsymbol{R}$ which contains the reaction rate R^α and its derivative $R^{\alpha\alpha}$. The function returns a pointer to this vector. The coding for this function is specific to the kinetics and should contain all the rate coefficients k_m, including any information needed to model the reactive surface area as a function of the mineral volume fractions.

For the aqueous ions we write a system of advection-dispersion-reaction equations for each species:

$$\mathcal{L}^\alpha c^\alpha = R^\alpha(\boldsymbol{c}), \tag{14}$$

where R^α follows from Eq. (1) and $\mathcal{L}^\alpha$ is the advection-dispersion operator

$$\mathcal{L}^\alpha = \boldsymbol{v} \cdot \boldsymbol{\nabla} - \boldsymbol{\nabla} \cdot \boldsymbol{D}^\alpha \cdot \boldsymbol{\nabla}. \tag{15}$$

Note that repeating subscripts are not summed implicitly here. We will solve this coupled non-linear system by a sequential solution of linearized transport equations.

Making a Taylor expansion of the rate of change of species α:

$$R^\alpha(\boldsymbol{c} + \delta\boldsymbol{c}) = R^\alpha(\boldsymbol{c}) + \sum_\beta R^{\alpha\beta}(\boldsymbol{c})\delta c^\beta, \tag{16}$$

where $R^{\alpha\beta}$ indicates a derivative of R^α with respect to c^β. Notes: we only need cases where α and β are the same species; R^α and $R^{\alpha\alpha}$ are sums over the individual reactions, weighted by the stoichiometry numbers for the species.

We construct an iteration procedure solving for each concentration at a time:

$$\mathcal{L}^\alpha c_{n+1}^\alpha = R^\alpha(\boldsymbol{c}_n) + R^{\alpha\alpha}(\boldsymbol{c}_n)\left(c_{n+1}^\alpha - c_n^\alpha\right). \tag{17}$$

If $A_n^\alpha = \mathcal{L}^\alpha - R^{\alpha\alpha}(\boldsymbol{c}_n)$ is the matrix representation of the linear operator and $b_n^\alpha = R^\alpha(\boldsymbol{c}_n) - R^{\alpha\alpha}(\boldsymbol{c}_n)c_n^\alpha$ contains the constant terms, then Eq. (17) is a linear system $A_n^\alpha c_{n+1}^\alpha = b_n^\alpha$ which can be solved for c_{n+1}^α.

The outer loop just requires sequential calculation of the matrices and right-hand side vectors for each component in turn, but these must be recalculated at each iteration of the outer loop. There is no need to store both $\boldsymbol{c}_n$ and $\boldsymbol{c}_{n+1}$; once c^α_{n+1} has been calculated it can be used to calculate A and b for the remaining components. This is the difference between Gauss-Seidel and Jacobi iteration. Replacement is easier, uses less space and converges faster.

The mineral volume fractions can be updated from the reaction rates by solving ordinary differential equations at each element:

$$\frac{d\phi^\alpha}{dt} = \frac{R^\alpha}{c^\alpha_{sol}}. \tag{18}$$

The rates should be normalized by c^α_{sol} within the rate function itself; the derivative $R^\alpha\alpha$ is not used.

Reaction rates should be scaled to prevent overdissolution ($\phi^\alpha < 0$) of any mineral or overprecipitation, when the porosity falls below some preset value ($\phi < \phi_{min}$); in addition we must ensure that the porosity remains below its upper limit (1). These conditions can be imposed on the transport equation for each species (17) as follows. For a given set of concentrations $\boldsymbol{c}_n$ we evaluate the rates $\boldsymbol{R}_m$ (1). First, if the current α corresponds to a mineral, we check that it is not overdissolved; if so we scale the rate of the dissolution reaction so that the mineral exactly vanishes at the end of the time step; we assume that a mineral species only appears in a single reaction. Next we calculate the change in porosity within the time step given the current rates. We check that the porosity remains within bounds, otherwise we scale all the reaction rates to have the porosity reach its bound (upper or lower) at the end of the time step. These prescriptions are then iterated to convergence as part of the outer loop.