About some numerical models for geochemistry

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1. Simple examples of geochemistry systems

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2. Chemistry model: reactions and variables

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5. Concluding remarks

One reaction with one salt

Chemical reactions

$$Na^{+} + Cl^{-} \rightleftharpoons Nacl$$

Electrical neutrality: $c_1 = c_2 = c$

Positivy of concentration: $c \geq 0$

Saturation threshold: $\gamma(c) = c^2$
Salt dissolved under saturation: $p = 0$ and $\gamma(c) \leq K$
Salt precipitated at saturation: $p > 0$ and $\gamma(c) = K$

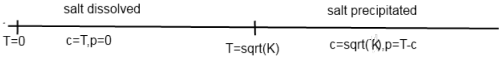
Mass conservation law: $T = c + p$

State diagram with one salt

Two cases

- salt dissolved $0 \leq T \leq \sqrt{K}, c = T, p = 0$
- salt precipitated $T \geq \sqrt{K}, c = \sqrt{K}, p = T - c$

State diagram



Two reactions with two salts

Chemical reactions

$$
\begin{aligned}
Na^+ + Cl^- &\rightleftharpoons Nacl \\
K^+ + Cl^- &\rightleftharpoons Kcl
\end{aligned}
$$

Electrical neutrality: $c_3 = c_1 + c_2$

Positivity of concentrations: $c_i \geq 0, i = 1, 2$

Saturation thresholds: $\gamma_i(c) = c_i(c_1 + c_2), i = 1, 2$
Salt dissolved under saturation: $p_i = 0$ and $\gamma_i(c) \leq K_i,\ i = 1, 2$
Salt precipitated at saturation: $p_i > 0$ and $\gamma_i(c) = K_i, i = 1, 2$

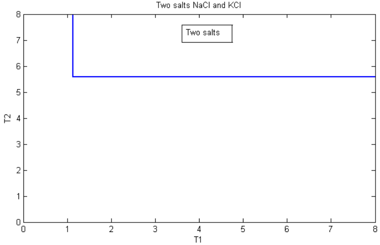
Mass conservation law: $T_i = c_i + p_i, i = 1, 2$

Case of two salts precipitated

$$p_i = T_i - c_i, i = 1, 2$$

$$\begin{cases} c_i(c_1 + c_2) = K_i, i = 1, 2, \\ 0 \leq c_i \leq T_i \end{cases}$$

$$\begin{cases} c_i = \frac{K_i}{\sqrt{K_1+K_2}}, i = 1, 2, \\ T_i \geq \frac{K_i}{\sqrt{K_1+K_2}}, i = 1, 2 \end{cases}$$

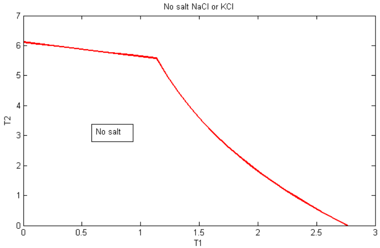


Two critical lines

Case of two salts dissolved

$$p_i = 0, i = 1, 2$$

$$\begin{cases} c_i = T_i, i = 1, 2, \\ T_i \geq 0, \\ T_i(T_1 + T_2) \leq K_i, i = 1, 2 \end{cases}$$



Two critical curves

Cases of one salt dissolved and one salt precipitated

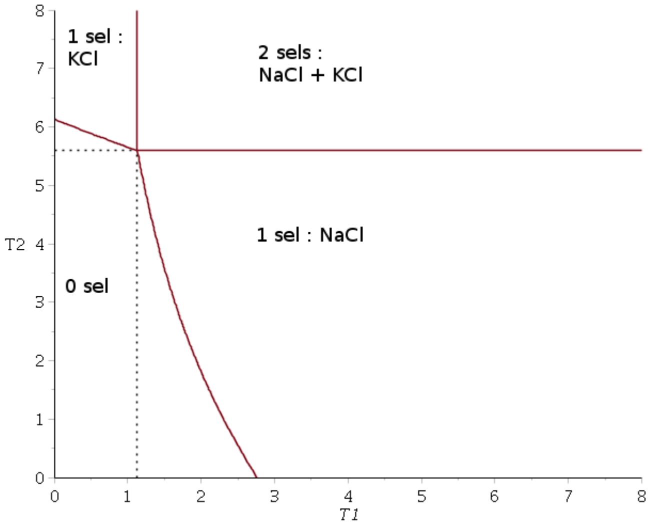
Case of NaCl dissolved:
$p_1 = 0$ and $p_2 = T_2 - c_2$

$$\begin{cases} c_1 = T_1, \\ c_2(T_1 + c_2) = K_2, \\ T_2(T_1 + T_2) \geq K_2, \\ 0 \leq T_1 \leq \frac{K_1}{\sqrt{K_1+K_2}} \end{cases}$$

Case of KCl dissolved:
$p_1 = T_1 - c_1$ and $p_2 = 0$

$$\begin{cases} c_2 = T_2, \\ c_1(c_1 + T_2) = K_1, \\ T_1(T_1 + T_2) \geq K_1, \\ 0 \leq T_2 \leq \frac{K_2}{\sqrt{K_1+K_2}} \end{cases}$$

State diagram with two salts



Présence de précipités. 2 sels : NaCl et KCl

Geochemistry system

Chemistry system at equilibrium
Aqueous reactions and precipitation-dissolution reactions

- Write the chemistry model
- Eliminate p from the equations
- Explore all the possible cases
- For each case, solve for c with $c \geq 0$
- Find the critical curves in the space of T
- Get the state diagram

Use of symbolic computations

Chemical reactions

Species involved

- N_c primary aqueous species
- N_α secondary aqueous species
- N_p minerals with $N_p \leq N_c$

Concentrations of species

- Assumption: all activities are equal to 1
- c: vector of concentrations of primary aqueous species
- α: vector of concentrations of secondary aqueous species
- p: vector of quantities of minerals
- Constraints: $c \geq 0$ and $p \geq 0$

Mass action laws and saturation thresholds

Stoichiometric matrices and constants of reactions

	Matrix	Constant
α	S	K_c
p	E	K_p

Assumptions: E of full rank

Mass action laws

$$\alpha_i(c) = K_{ci} \prod_{k=1}^{N_c} c_k^{S_{ik}}$$

Saturation thresholds

$$\gamma_i(c) = \prod_{k=1}^{N_c} c_k^{E_{ik}}$$

Precipitation-dissolution

Either mineral is dissolved: $\gamma_i(c) \leq K_{pi}$ and $p_i = 0$
Or mineral is precipitated: $\gamma_i(c) = K_{pi}$ and $p_i > 0$

Nonlinear complementarity problem

$$\left\{ \begin{array}{c} p.(K_p - \gamma(c)) = 0, \\ p \geq 0, \\ \gamma(c) \leq K_p \end{array} \right.$$

Conservations laws

Mass conservation law
T: vector of total analytical concentrations of primary species

$$T = c + S^T \alpha(c) + E^T p$$

In a closed system, T is given
In an open system, T is coupled with another model

Electrical neutrality
z: electrical charges of ions

$$z^T T = z^T c = 0$$

Can be used either as an invariant for validation or to remove one unknown

Chemistry model

System of $(N_c + N_p)$ unknowns (c, p)
with $(N_c + N_p)$ polynomial equations
and constraints

$$\begin{cases} T = c + S^T \alpha(c) + E^T p, \\ c \geq 0, \\ p.(K_p - \gamma(c)) = 0, \\ p \geq 0, \\ \gamma \leq K_p \end{cases}$$

with $\alpha_i(c) = K_{ci} \prod_{k=1}^{N_c} c_k^{S_{ik}}$ and $\gamma_i(c) = \prod_{k=1}^{N_c} c_k^{E_{ik}}$

Reduced model

QR factorization of E^T

$$\begin{cases} E^T = (Q_1 \; Q_2) \begin{pmatrix} R \\ 0 \end{pmatrix} = Q_1 R, \\ Q_1^T E^T = R, Q_2^T E^T = 0 \end{cases}$$

with Q orthogonal matrix and R triangular nonsingular matrix.
Elimination of p

$$p(c) = R^{-1} Q_1^T (T - c - S^T \alpha(c))$$

Conservative components decoupled from minerals

$$Q_2^T T = Q_2^T (c + S^T \alpha(c))$$

Reduced model with c unknowns

$$\begin{cases} Q_2^T (c + S^T \alpha(c)) = Q_2^T T, \\ p(c).(K_p - \gamma(c)) = 0, \\ c \geq 0, \\ p(c) \geq 0, \\ \gamma(c) \leq K_p \end{cases}$$

Minerals precipitated or dissolved

One case among 2^{N_p} different cases

Set of dissolved minerals $I = \{i, 1 \leq i \leq N_p, p_i(c) = 0\}$,
Set of precipitated minerals $J = \{j, 1 \leq j \leq N_p, \gamma_j(c) = K_{pj}\}$

System of N_c polynomial equations and $(N_c + N_p)$ constraints

$$\begin{cases} Q_2^T(c + S^T \alpha(c)) = Q_2^T T, \\ p_i(c) = 0, i \in I, \\ \gamma_j(c)) = K_{pj}, j \in J, \\ c \geq 0, \\ p_j(c) \geq 0, j \in J, \\ \gamma_i(c) \leq K_{pi}, i \in I \end{cases}$$

Algorithm for one case

Symbolic computations with a Computer Algebra System

- Solve system : solutions are algebraic numbers
- Find a solution $c(T)$ which satisfies $c(T) \geq 0$
- Write the N_p constraints for p and γ in function of T

Assumptions:

- The system has a unique solution $c(T)$ such that $c(T) \geq 0$
- The constraints for p and γ at equality give the equations of algebraic varieties
- There are $N_p 2^{N_p - 1}$ such algebraic varieties, which we call critical varieties
- The intersection of these varieties is a unique point, which we call critical point

The critical varieties form a stability diagram

Numerical application

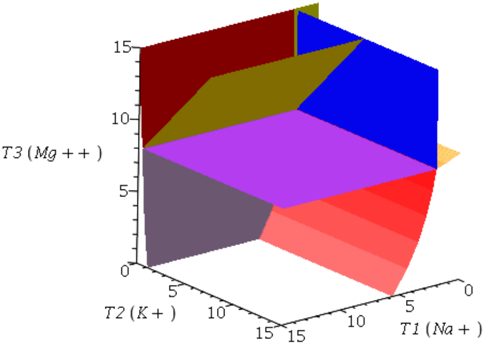
Assumption: equations of critical varieties are given with the variables T.
For given values of T, we can check all the equations and find the position of T in the state diagram.
This gives the set of minerals dissolved and the set of minerals precipitated.
Then it is easy to solve the system for c and p.

Example with three salts

Chemical reactions: $N_\alpha = 0$, $N_p = 3$ and, using the electrical neutrality, $N_c = 3$

$$Na^+ + Cl^- \rightleftharpoons NaCl$$
$$K^+ + Cl^- \rightleftharpoons KCl$$
$$Mg^{++} + K^+ + 3Cl^- \rightleftharpoons KMgCl3, 6H2o$$

Présence de sels : chimie avec 3 sels NaCl;Kcl;KMgCl3,6 H2o



Example with six minerals

Minerals and primary aqueous species

Table 2
Stoichiometric reactions and equilibrium constants K_k of all minerals in the DFN and EPM simulations (after Mayer et al., 2002; Molson et al., 2008).

Mineral	Reaction	Log K_k
Calcite	$CaCO_3 \Leftrightarrow Ca^{2+} + CO_3^{2-}$	−8.5
Siderite	$FeCO_3 \Leftrightarrow Fe^{2+} + CO_3^{2-}$	−10.5
Gibbsite	$Al(OH)_3 + 3H^+ \Leftrightarrow Al^{3+} + 3H_2O$	8.1
Gypsum	$CaSO_4{\cdot}2H_2O \Leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$	−4.6
Ferrihydrite	$Fe(OH)_3 + 3H^+ \Leftrightarrow Fe^{3+} + 3H_2O$	4.9
Quartz	$SiO_2\,(am) + 2H_2O \Leftrightarrow 3H_4SiO_4$	−2.7

Stoichiometric coefficients

$$\begin{pmatrix} E & c_1(H_4SiO_4) & c_2(H^+) & c_3(Fe^{3+}) & c_4(Al^{3+}) & c_5(Ca^{2+}) & c_6(SO_4^{2-}) & c_7(Fe^{2+}) & c_8(CO_3^{2-}) \\ p_6(Quartz) & 3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ p_3(Gibbsite) & 0 & -3 & 0 & 1 & 0 & 0 & 0 & 0 \\ p_5(Ferrihydrite) & 0 & -3 & 1 & 0 & 0 & 0 & 0 & 0 \\ p_1(Calcite) & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \\ p_2(Siderite) & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ p_4(Gypsum) & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 \end{pmatrix}$$

Using Maple, computations in 3 seconds with 50 MB of memory.

Coupling with transport

Example: sequential couplings
Space and time discretization for transport equation
At each timestep, a geochemistry system must be solved in each cell of the mesh

Embarrassingly parallel computations:
as many independent chemistry systems as cells

Current work

- Apply the method to systems with aqueous reactions
- Couple the method with transport equations
- Use a semi-smooth Newton method for the nonlinear complementary problem
- Use the state diagram to choose the initial guess