Precipitation and dissolution of minerals in geochemistry

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1. Simple examples of geochemistry systems

One reaction with one salt

Chemical reactions

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

Electrical neutrality: $c_1 = c_2 = c$

Positivity 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 $\gamma(c) = K$

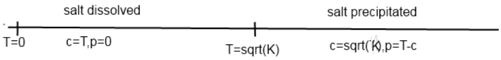
Mass conservation law: $T = c + p$ thus $T \geq 0$

Precipitation diagram with one salt

Three cases

- no solution $T < 0$
- salt dissolved $0 \leq T \leq \sqrt{K}, c = T, p = 0$
- salt precipitated $T \geq \sqrt{K}, c = \sqrt{K}, p = T - c$

Precipitation 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: $\gamma_i(c) = c_i c_3, i = 1, 2$
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 $\gamma_i(c) = K_i, i = 1, 2$

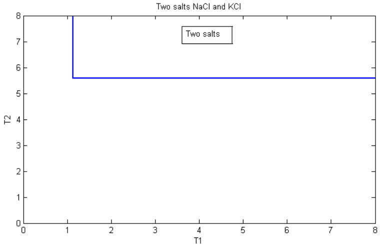
Mass conservation law: $T_i = c_i + p_i, i = 1, 2$ thus $T_i \geq 0$

State with two salts precipitated

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

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

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

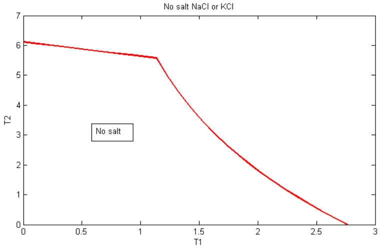


Two state boundaries

State with 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 state boundaries

States with one salt dissolved and one salt precipitated

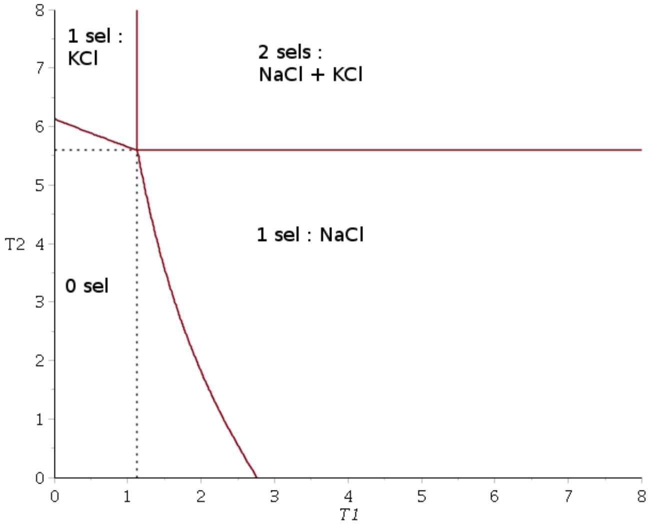
Case of NaCl dissolved:
$p_1 = 0$ and $p_2 = T_2 - c_2$

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

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

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

Precipitation diagram with two salts



Présence de précipités. 2 sels : NaCl et KCl

Geochemistry system

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: activity coefficients of aqueous species 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 S and E, with integer coefficients
Constants of reactions K_α and K_p (reals)

	Matrix	Constant
α	S	K_α
p	E	K_p

Mass action laws

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

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

Charge balance, with q electrical charges of ions

$$q^T T = q^T c$$

Electrical neutrality $q^T c = 0$

Chemistry model

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

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

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

Equivalent reduced model

If one coefficient for c_i is strictly negative, then $c_i > 0$.
If all coefficients for c_i are positive, then $T_i \geq 0$ and $T_i = 0 \Rightarrow c_i = 0$.

Equivalent model

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

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

Equivalent logarithmic model

Logarithmic variable $x = \log(c)$

Equivalent logarithmic model

$$\left\{ \begin{array}{l} \exp(x) + S^T \exp(\log(K_\alpha) + Sx) + E^T p - T = 0, \\ p^T (Ex - \log(K_p)) = 0, \\ p \geq 0, Ex \leq \log(K_p), \end{array} \right.$$

KKT conditions of an optimization problem ?

Optimization problem with constraints

Objective function

$$f(x) = e_{N_c}^T \exp(x) + e_{N_\alpha}^T \exp(\log(K_\alpha) + Sx) - T^T x, \ x \in \mathbb{R}^{N_c}$$

Gradient of f

$$\nabla f(x) = \exp(x) + S^T \exp(\log(K_\alpha) + Sx) - T$$

Hessian matrix of f

$$\nabla^2 f(x) = \mathcal{D}\left(\exp(x)\right) + S^T \mathcal{D}\left(\exp(\log(K_\alpha) + Sx)\right) S$$

Inequality constraints $g(x) \leq 0$ with

$$g(x) = Ex - \log(K_p)$$

Optimality conditions and uniqueness of solution

Convex optimization problem

$$\min_{g(x)\leq 0} f(x)$$

Assumption: E is of rank N_p.

minimization problem $\Leftrightarrow$ KKT conditions $\Leftrightarrow$ logarithmic model

If the minimization problem has a solution x with Lagrange muliplier p, they are unique.

Existence of solution

Assumption: E is of rank N_p.

if $T > 0$ the minimization problem has a unique solution.

if $S \geq 0$ and $E \geq 0$, the problem has a solution if and only if $T > 0$.

Example with negative coefficents: calcite and gypsum

Three aqueous components
hydrogen ion H^+, calcium ion Ca^{2+}, sulfate ion $SO4^{2-}$

Mineral	Reaction	κ
$CaCO_3$	$CaCO_3 + 2H^+ \rightleftarrows Ca^{2+} + CO_2 + H_20$	1
$CaSO_4$	$CaSO_4 \rightleftarrows Ca^{2+} + SO_4^{2-}$	$4\,10^{-5}$

Stoichiometric matrix E, of rank N_p

$$E = \begin{pmatrix} -2 & 1 & 0 \\ 0 & 1 & 1 \end{pmatrix}$$

The problem has a solution if and only if $T_2 > 0,\ T_3 > 0,\ T_1 + 2T_2 > 0$

Proof: Mass balance equation and positivity constraints imply these conditions, which imply that the function f is coercive.

Precipitation diagram

$\mathcal{T}$ is the set of T with a unique solution $(x(T), p(T))$

Precipitation diagram
Partition of $\mathcal{T}$ into at most 2^{N_p} non empty mineral states $\mathcal{M}_I$ corresponding to the subsets I of $\{1, 2, \dots, N_p\}$

Mineral state

$$\mathcal{M}_I = \{T \in \mathcal{T}, \forall i \in I : p_i(T) > 0 \text{ and } \forall i \in \bar{I} : p_i(T) = 0\}$$

I is the set of strongly active constraints

State boundaries
At most $N_p 2^{N_p - 1}$ algebraic curves interfacing the mineral states

Conservative variables

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 variables decoupled from minerals (such as charge balance)

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

Reduced model with c unknowns

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

Mineral state

One case among 2^{N_p} different cases

Set of precipitated minerals $I = \{i, 1 \leq i \leq N_p, \gamma_i(c) = K_{pi}, p_i(c) > 0\}$

Set of dissolved minerals $\bar{I} = \{i, 1 \leq i \leq N_p, \gamma_i(c) \leq K_{pi}, p_i(c) = 0\}$

$$\begin{cases} Q_2^T(c + S^T\alpha(c)) - Q_2^T T = 0, \\ \gamma_i(c) = K_{pi}, \forall i \in I, \\ p_i(c) = 0, \forall i \in \bar{I}, \\ c > 0, \\ p_i(c) > 0, \forall i \in I, \\ \gamma_i(c) \leq K_{pi}, \forall i \in \bar{I}, \end{cases}$$

Computing mineral states

Symbolic computations with a Computer Algebra System

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

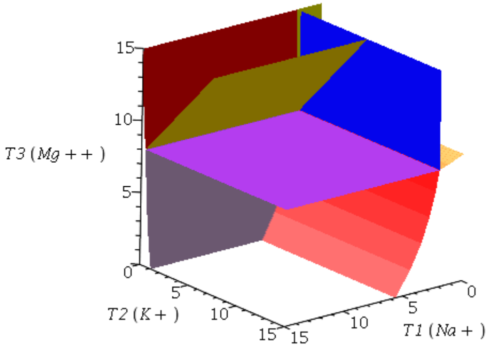
Implicit description of the boundaries

Three salts

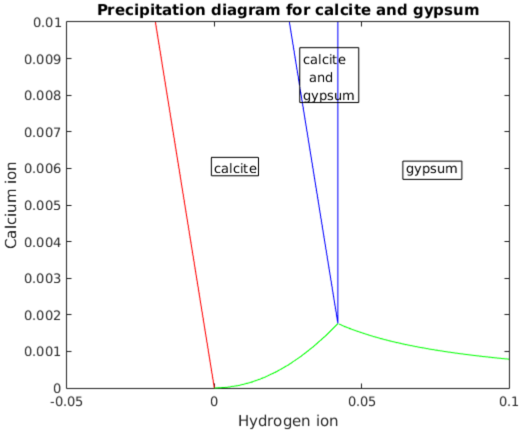
Chemical reactions: $N_\alpha = 0$, $N_p = 3$ and, using the electrical neutrality, $N_c = 3$

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

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



Calcite and gypsum



Future work

- Use interior point method for the nonlinear complementarity problem
- Use the precipitation diagram to choose the initial guess
- Couple the method with transport equations
- Compare with the Gibbs energy minimization
- Use a model with nonlinear activities