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# Precipitation and dissolution of minerals in geochemistry

**Jocelyne Erhel and Tangi Migot**

**IRMAR, Rennes: INRIA and INSA**

**Workshop on reactive transport, Paris, February 2018**



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- 3 Optimization problem

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# One reaction with one salt

Chemical reactions



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  $\gamma(c) = K$

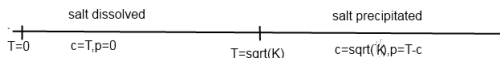
Mass conservation law:  $T = c + p$  thus  $T \geq 0$

# 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



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  $\gamma_i(c) = K_i, i = 1, 2$

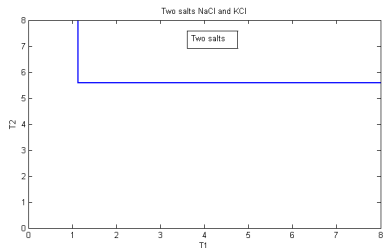
Mass conservation law:  $T_i = c_i + p_i, i = 1, 2$  thus  $T_i \geq 0$

# State with two salts precipitated

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

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

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

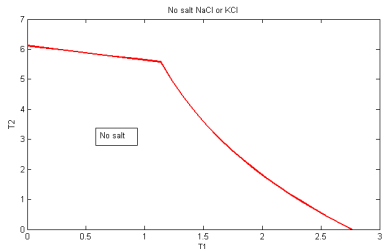


Two state boundaries

## 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:

$$p_1 = 0 \text{ and } p_2 = T_2 - c_2$$

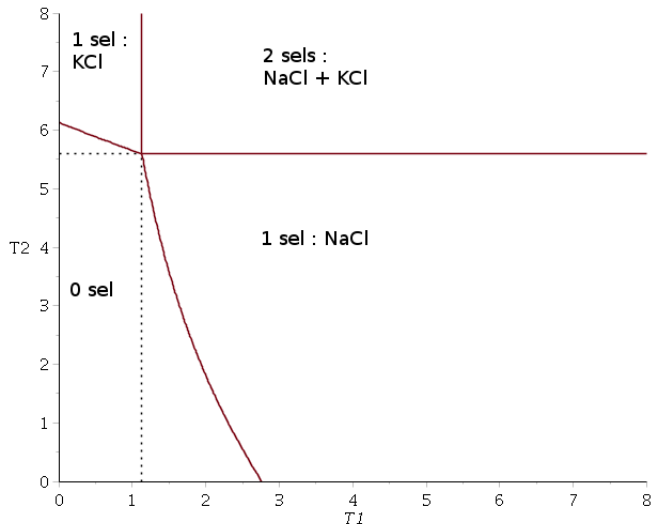
$$\left\{ \begin{array}{l} c_1 = T_1, \\ c_2(T_1 + c_2) = K_2, \\ T_2(T_1 + T_2) \geq K_2, \\ 0 \leq T_1 \leq \frac{K_1}{\sqrt{K_1 + K_2}} \end{array} \right.$$

Case of KCl dissolved:

$$p_1 = T_1 - c_1 \text{ and } p_2 = 0$$

$$\left\{ \begin{array}{l} c_2 = T_2, \\ c_1(c_1 + T_2) = K_1, \\ T_1(T_1 + T_2) \geq K_1, \\ 0 \leq T_2 \leq \frac{K_2}{\sqrt{K_1 + K_2}} \end{array} \right.$$

# Precipitation diagram with two salts



Présence de précipités. 2 sels : NaCl et KCl

# Geochemistry system

## Species involved

- $N_c$  primary aqueous species
- $N_\alpha$  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
- $\alpha$ : 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  $K_\alpha$  and  $K_p$  (reals)

	Matrix	Constant
$\alpha$	$S$	$K_\alpha$
$p$	$E$	$K_p$

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

$$\begin{cases} p \cdot (K_p - \gamma(c)) = 0, \\ p \geq 0, \\ \gamma(c) \leq K_p \end{cases}$$



# 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

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

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

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

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

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

KKT conditions of an optimization problem ?

# Optimization problem with constraints

Objective function

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

Gradient of  $f$

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

Hessian matrix of  $f$

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

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 multiplier  $p$ , 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 coefficients: calcite and gypsum

Three aqueous components

hydrogen ion  $H^+$ , calcium ion  $Ca^{2+}$ , sulfate ion  $SO_4^{2-}$

Mineral	Reaction	$K$
$CaCO_3$	$CaCO_3 + 2H^+ \rightleftharpoons Ca^{2+} + CO_2 + H_2O$	1
$CaSO_4$	$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$	$4 \cdot 10^{-5}$

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

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

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

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

# Computing mineral states

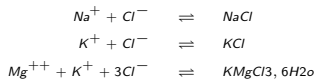
## Symbolic computations with a Computer Algebra System

- 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  $\gamma$  in function of  $T$

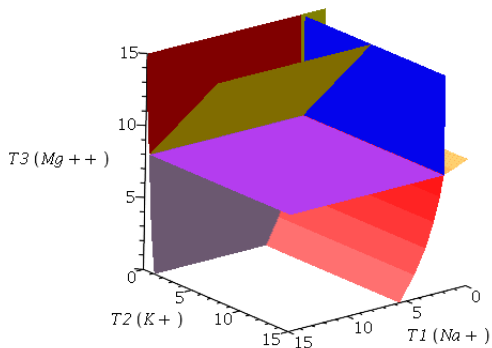
Implicit description of the boundaries

# Three salts

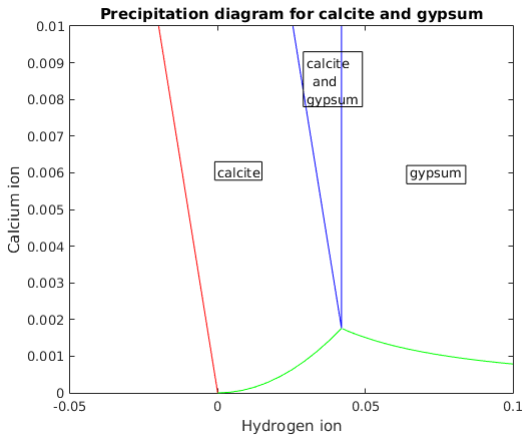
Chemical reactions:  $N_{\alpha} = 0$ ,  $N_p = 3$  and, using the electrical neutrality,  $N_c = 3$



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