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# GDR MoMaS

Quelques problèmes rencontrés en chimie numérique

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## Optimal solution methods for aqueous speciation problems

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# Speciation modelling

Speciation is the distribution of chemical elements

- **between appearances**

- e.g.  $Zn^{2+}$ ,  $ZnOH^+$ ,  $ZnCl_2(aq)$ , ...

- **between oxydation states**

- e.g.  $Pu(IV)$  ( $Pu^{4+}$ ),  $Pu(V)$  ( $PuO_2^+$ ),  $Pu(VI)$  ( $PuO_2^{2+}$ ), ...

- **between phases**

- e.g. *aqueous phaes*, *minerals*, *organic and inorganic colloids*, *gases*,...



# Speciation at equilibrium

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- Mole balance of  $\text{CO}_2(\text{aq})$  ( $= \text{CO}_2 \cdot \text{H}_2\text{O}$ ):



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- Reaction affinity (mass-action law):

$$[\text{CO}_2(\text{aq})] = K[\text{CO}_3^{2-}][\text{H}^+]^2$$

$$[S] = K[C_1]^{\alpha_1}[C_2]^{\alpha_2}$$

$$[S] = K \prod_i^{N_b} [C_i]^{\alpha_i}$$

# Speciation at equilibrium

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- Reaction affinity (mass-action law):



- Molal mass balance:



# Speciation at equilibrium

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Example of  $\text{FeCl}_3$  in water:

4 principle components:

- $\text{H}_2\text{O}$ ,  $\text{H}^+$ ,  $\text{Fe}^{3+}$ ,  $\text{Cl}^-$

Derived species:

- $\text{OH}^-$ ,  $\text{FeCl}^{2+}$ ,  $\text{Fe}(\text{Cl})_2^+$ ,  $\text{FeOH}^{2+}$ ,  $\text{Fe}(\text{OH})_2^+$ ,  $\text{Fe}(\text{OH})_3(\text{aq}), \dots$

# Speciation at equilibrium

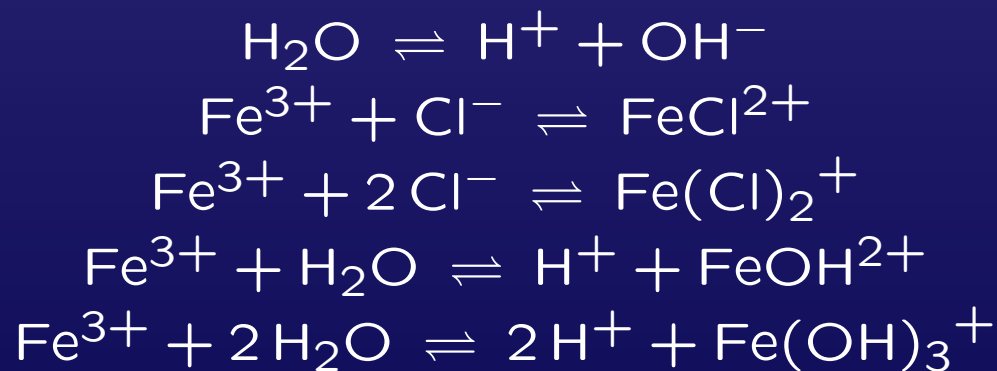
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...

# Generic solution methods

Generic (matrix) approach:

	H <sub>2</sub> O	H <sup>+</sup>	Fe <sup>3+</sup>	Cl <sup>-</sup>	<i>K</i>
H <sub>2</sub> O	1				
H <sup>+</sup>		1			
Fe <sup>3+</sup>			1		
Cl <sup>-</sup>				1	
OH <sup>-</sup>	1	-1			<i>K<sub>w</sub></i>
FeCl <sup>2+</sup>		1		1	<i>K<sub>1</sub></i>
Fe(Cl) <sub>2</sub> <sup>+</sup>		1		2	<i>K<sub>2</sub></i>
...					
	H <sub>2</sub> O <sub><i>T</i></sub>	(H) <sub><i>T</i></sub>	(Fe) <sub><i>T</i></sub>	(Cl) <sub><i>T</i></sub>	

Hor. = mole balances:  $\text{Fe}(\text{Cl})_2^+ = \text{Fe}^{3+} + 2 \text{Cl}^-$

laws of mass action:  $[\text{Fe}(\text{Cl})_2^+] = [\text{Fe}^{3+}][\text{Cl}^-]^2 K_2$

Ver. = molal mass balances:  $\text{Cl}_T = \text{Cl}^- + \text{FeCl}^{2+} + 2 \text{Fe}(\text{Cl})_2^+ \dots$

# Generic solution methods

Generic (matrix) approach:

	$C_1$	$C_2$	$\cdots$	$C_i$	$\cdots$	$C_{N_p}$	
$S_1$	$\alpha_{11}$	$\alpha_{12}$	$\cdots$	$\alpha_{1i}$	$\cdots$	$\alpha_{1N_p}$	$K_1$
$S_2$	$\alpha_{21}$	$\alpha_{22}$	$\cdots$	$\alpha_{2i}$	$\cdots$	$\alpha_{2N_p}$	$K_2$
$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$	$\ddots$	$\vdots$	$\vdots$
$S_j$	$\alpha_{j1}$	$\alpha_{j2}$	$\cdots$	$\alpha_{ji}$	$\cdots$	$\alpha_{jN_p}$	$K_j$
$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$	$\ddots$	$\vdots$	$\vdots$
$S_{N_s}$	$\alpha_{N_s 1}$	$\alpha_{N_s 2}$	$\cdots$	$\alpha_{N_s i}$	$\cdots$	$\alpha_{N_s N_p}$	$K_{N_s}$

Horizontally: laws of mass action:

$$S_j = K_j \prod_{i=1}^{N_p} C_i^{\alpha_{ji}}$$

Vertically: molal mass balances:

$$C_{i-TOT} = \sum_{j=1}^{N_s} \alpha_{ji} S_j$$

# Generic solution methods

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→ a multi-dimensional set of non-linear algebraic equations:

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or, simultaneously for all  $i$ :

$$\mathbf{C}_{-TOT} - \mathbf{P}(\mathbf{C}) = \mathbf{0}$$

approximative solution (based on an estimation of vector  $\mathbf{C}$ ) :

$$\mathbf{C}_{-TOT} - \mathbf{P}(\mathbf{C}) = \mathbf{E}(\mathbf{C})$$

**Minimization of vector  $\mathbf{E}(\mathbf{C})$  →→→ Newton-Raphson**

# Generic solution methods

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Newton-Raphson's root finding method:

$$C_{TOT} - P(C) = E(C^m)$$

→ Find vector  $C^{m+1}$  such that  $E(C^{m+1}) = 0$ :

$$E(C^m) + P(C^m) - P(C^m + dC) = 0$$

$$E(C^m) - dC P'(C^m) = 0$$

→ Solve for  $dC^{m+1}$ :

$$C^{m+1} = C^m + dC$$

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**Inconveniences:**

- poor global convergence
- Jacobian matrix ( $P'$ ) needs to be derived

# Generic solution methods

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Newton Raphson's method often fails for realistic chemical systems

Methods to improve the global convergence:

- **Bracketing based on physico-chemical constraints:**  
*concentrations are positive ( $C_i > 0 \forall i, i \in [0..Nb]$ )*  
*and  $C_i \leq C_{i-TOT} \forall \Omega, \Omega \subset [0..Nb]$*
- **relaxation methods, i.e. polishing**
- **combined zero'th and first order methods**  
*e.g. start with e.g. Continuous Fractions, then NR*

# Improving the solution method

## CHESSE' polishing factor

New estimates at iteration level  $m + 1$ :  $C^{m+1} = C^m + dC$

Polishing factor  $r(C, dC, a, b, c)$ :  $C^{m+1} = C^m + r \cdot dC$ ,  $0 < r < 1$

$$\alpha_i = \frac{|dC_i|}{C_i} \quad r_{\alpha > a} = \begin{cases} \frac{(b\alpha - a^2)C}{(b + \alpha - 2a)dC} & \text{if } dC > 0 \\ c \frac{(\alpha - a^2)C}{(1 + \alpha - 2a)dC} & \text{if } dC < 0 \end{cases}$$

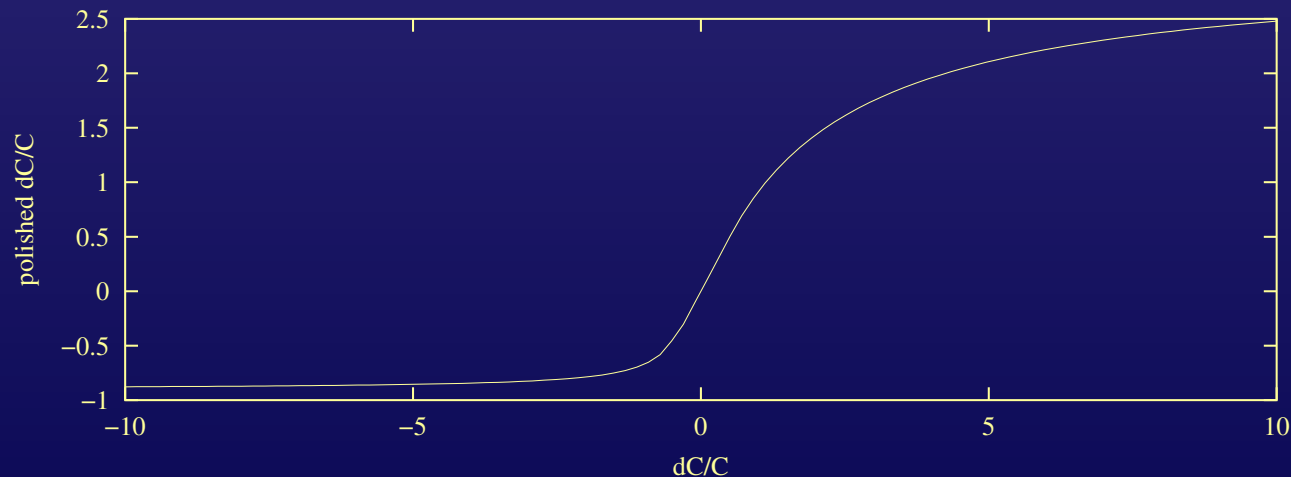
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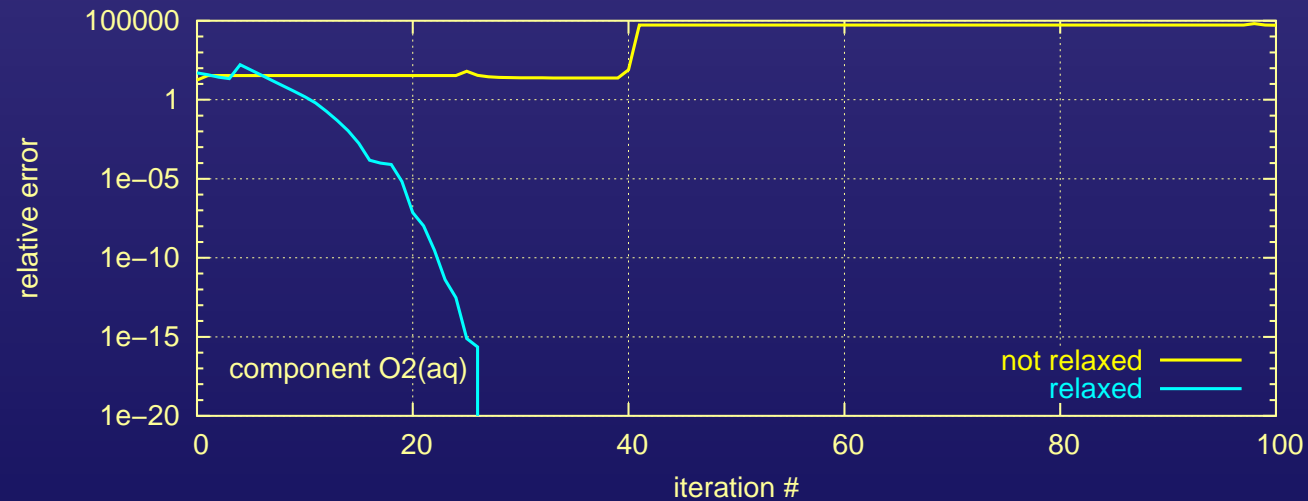
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## CHESS' polishing factor

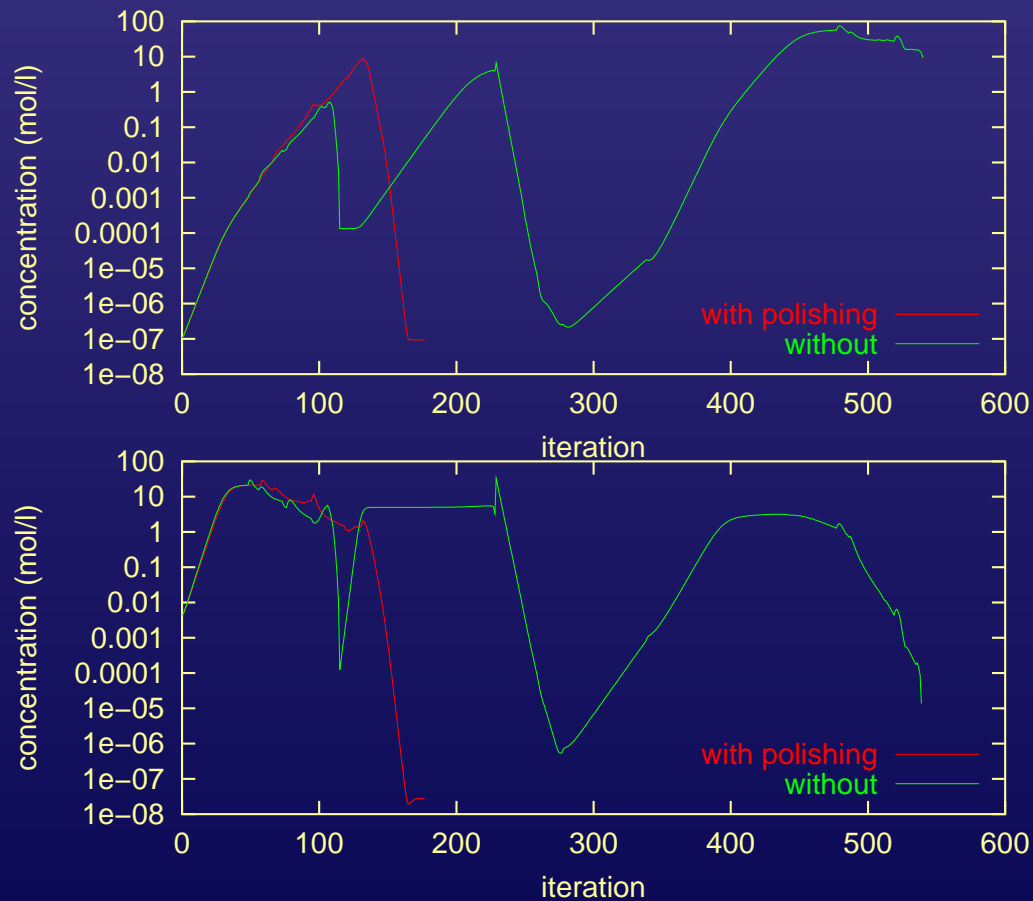
Test case: 10 g of metallic Fe in pure water:



# Improving the solution method

## CHESs' polishing factor

Test case: 1 g of mineral Pyrite in pure water



# Improving the solution method

## Zero'th order (Jacobianless) methods:

- Continuous Fractions method

$$C^{m+1} = R^m C^m$$
$$R^m = \frac{C_{i-TOT}}{C_{i-TOT} - E(C_i^m)}$$

such that for  $E(C_i^m) \rightarrow 0$ ,  $R \rightarrow 1$ .

With  $E(C_i^m) = C_{i-TOT} - P(C_i^m)$ , we readily find

$$R^m = \frac{C_{i-TOT}}{P(C_i^m)}$$

where, we recall,  $P(C_i)$  is defined as follows:

$$P(C_i) = \sum_{j=1}^{N_s} \alpha_{ji} S_j = \sum_{j=1}^{N_s} \alpha_{ji} K_j \prod_{i=1}^{N_p} C_i^{\alpha_{ji}}.$$

# Improving the solution method

## Zero'th order (Jacobianless) methods:

- **Positive Continuous Fractions method** (example for  $H^+$ )

$$P(H^+) = [H^+] - [H^+]^{-1}K_w - [Fe^{3+}][H^+]^{-1}K_wK_1^{-1} \\ - 2[Fe^{3+}][H^+]^{-2}K_w^2K_2^{-1} \dots$$

→ break the equation down to 2 absolutely positive parts:

$$P(H^+) = ([H^+] + \dots) - ([H^+]^{-1}K_w + [Fe^{3+}][H^+]^{-1}K_wK_1^{-1} + \dots) \\ = P^\oplus(H^+) - P^\ominus(H^+)$$

→ use to define  $R^m$ :

$$R_i^m = \begin{cases} (C_{i-TOT} + P_i^\ominus)/P_i^\oplus & \text{if } C_{i-TOT} \geq 0 \\ P_i^\ominus/(P_i^\oplus - C_{i-TOT}) & \text{otherwise} \end{cases}$$

such that  $R_i > 0 \forall i$ .

# Improving the solution method

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**Combined zero'th and first order methods (CHESS):**

1. Positive Continuous Fractions for 10 iterations...

# Improving the solution method

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## Combined zero'th and first order methods (CHESS):

1. Positive Continuous Fractions for 10 iterations...
2. ...then Newton-Raphson with polishing

# Improving the solution method

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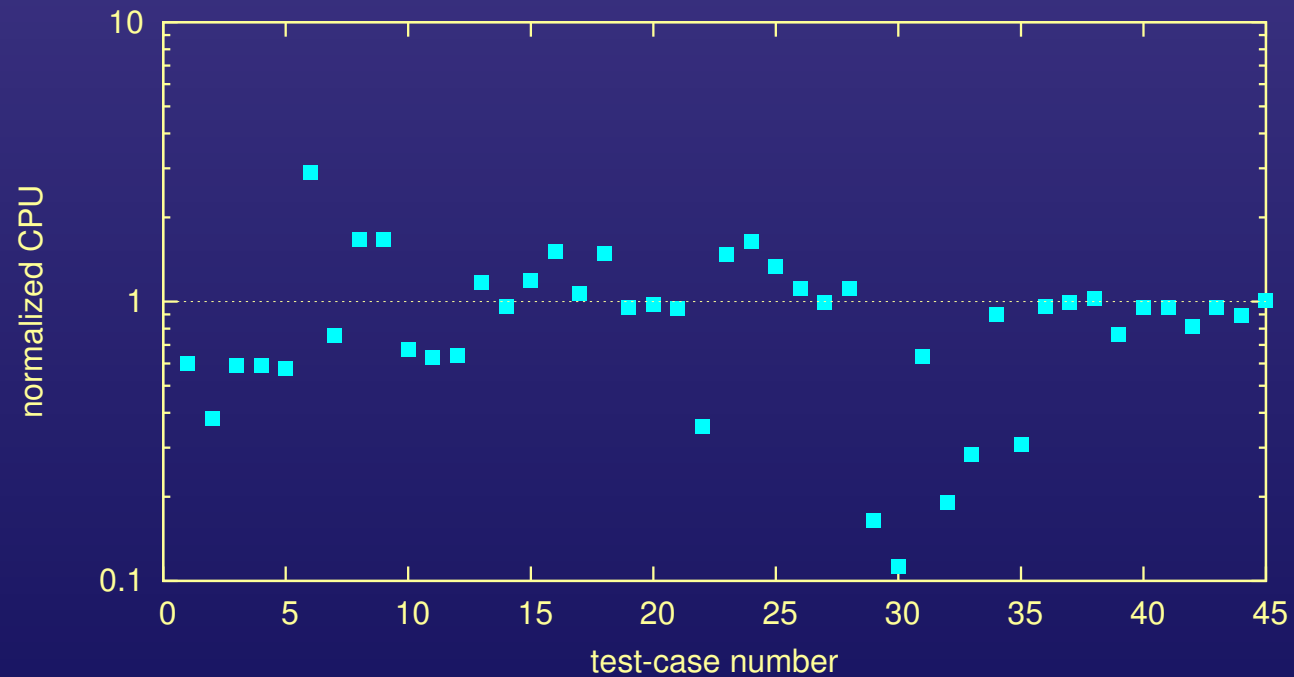
1. Positive Continuous Fractions for 10 iterations...
2. ...then Newton-Raphson with polishing

### Efficiency test

	iterations	CPU
polished NR only ( $V \leq 3.1$ )	3311	543542
combined approach ( $V \geq 3.2$ )	1606	148341
gain-factor since V3.2	2.06	3.66

# Improving the solution method

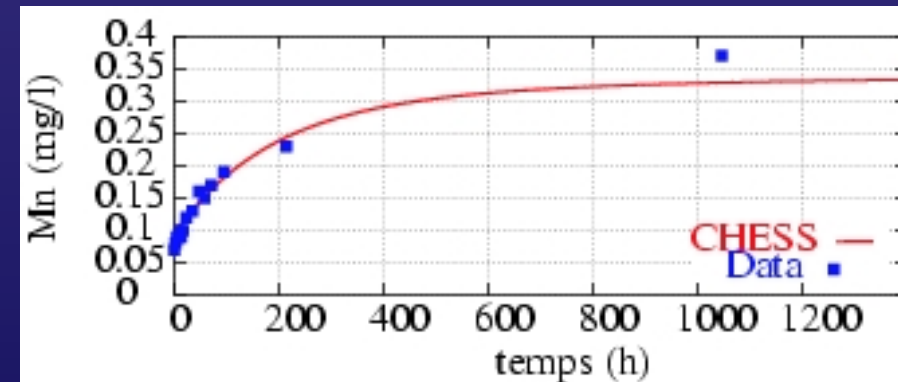
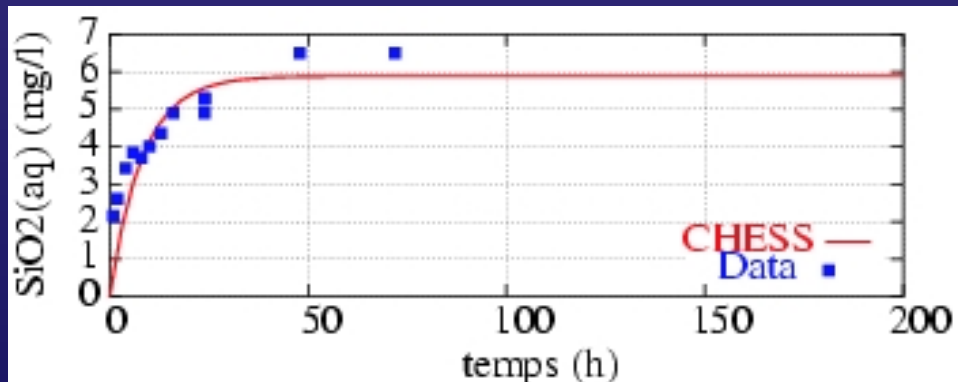
## Efficiency (gain CPU) for the combined approach



# Mixing equilibrium and kinetic reactions

Mixing of kinetic and equilibrium reactions is useful since:

- Most aqueous reactions in natural systems are fast (equilibrium approach justified)
- Many solids in natural systems are kinetically controlled



- We dispose of extensive thermodynamic databases for equilibrium systems, but kinetic parameters are scarce

# Mixing equilibrium and kinetic reactions

How do we include kinetics (Jacobian)?

equilibrium:

$$\begin{aligned}\frac{d(FeOH)}{d(H^+)} &= \frac{d(K[Fe^{3+}][H_2O][H^+]^{-1})}{d(H^+)} \\ &= [Fe^{3+}][H_2O][H^+]^{-2} \\ &= (FeOH)/(H^+)\end{aligned}$$

kinetic:

$$\begin{aligned}\frac{d(FeOH)}{d(H^+)} &= \frac{d\mathcal{F}(a, b, c, Fe^{3+}, H_2O, H^+, \dots)}{d(H^+)} \\ &= \dots\end{aligned}$$

**Solutions:**

- numerical solution of the Jacobian (generic solution)
- analytical solution (law-specific solutions)

# Mixing equilibrium and kinetic reactions

## Kinetic dissolution/precipitation of solids

Conditional formulation:

$$\frac{dS}{dt} = \begin{cases} A_v k_p W_p (\Omega^a - 1)^b & \text{if } \Omega^a \geq 1 \\ -A_v k_d W_d (1 - \Omega^c)^e & \text{if } \Omega^c < 1 \end{cases}$$

For example: formation of a zinc hydroxide:

$$\Omega = K_{\text{Zn(OH)}_2} [\text{Zn}^{2+}] [\text{H}_2\text{O}]^2 [\text{H}^+]^{-2}$$

A typical  $W$  factor:

$$W = [\text{H}^+]^m [\text{O}_2(\text{aq})]^n.$$

→ an *a priori* unknown relationship between  $A_v$  and  $S.x$

# Mixing equilibrium and kinetic reactions

## Kinetic dissolution/precipitation of solids

Sequential formulation:

$$\frac{dS}{dt} = \delta_p A_v k_p W_p (\Omega^a - 1)^b - \delta_d A_v k_d W_d (1 - \Omega^c)^e$$

with

$$\delta_p = \begin{cases} 1 & \text{if } \Omega^a \geq 1 \\ 0 & \text{if } \Omega^a < 1 \end{cases} = \delta_d \begin{cases} 0 & \text{if } \Omega^c \geq 1 \\ 1 & \text{if } \Omega^c < 1 \end{cases}$$

Numerical approach:

$$S(t + \tau) \simeq S(t) + \tau \delta_p A_v k_p W_p (\Omega^a - 1)^b - \tau \delta_d A_v k_d W_d (1 - \Omega^c)^e$$

# Mixing equilibrium and kinetic reactions

## Kinetic and the Jacobian

Each kinetic species is **replaced by 2 (4) specific terms** in the jacobian matrix:

$$\frac{dP(\text{H}_2\text{O})}{d(\text{H}_2\text{O})} = 1 + \frac{(\text{ZnOH})}{(\text{H}_2\text{O})} + 2\beta_p \frac{x_p W_p (\Omega^a - 1)^b}{(\text{H}_2\text{O})} + 2\alpha \frac{y_p W_p (\Omega^a - 1)^{b-1} \Omega^a}{(\text{H}_2\text{O})}$$

→ included as *kinetic virtual concentrations* in CHESS.

The generic approach:

$$\frac{dS_j}{dC_i} = \frac{1}{C_i} \sum_{k=0}^{N_{k'}} \beta_{ji} S_k.$$

remains valid (*efficiency*).

# Conclusions

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- **Chemical SOLVERS are best served by**
  - polished Newton-Raphson method
  - possibly combined with Positive Continuous Fraction
- **Mixed equilibrium-kinetics approach**
  - analytical resolution possible for accepted law-types
- **Optimization issues**
  - analytical resolution of the Jacobian is essential
  - creation of an efficient Jacobian helper matrix
  - still: 50-80% CPU spent on the evaluation of ...  
**logarithmic functions!**

# Conclusions

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- **Chemical MODELS are best served by**

- extended, trustworthy, thermodynamic databases

Common Thermodynamic Database Project

(<http://ctdp.ensmp.fr>)

- more knowledge on interface reactions

Surface complexation, cation exchange, electrostatic effects,

...

- organic, colloidal matter - metal interactions

reaction laws, databases,...

- **Natural systems are dynamic and open**

- Chemistry coupled with hydrodynamic models

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