

Multiphase Chemical Equilibrium: Formulation and Resolution

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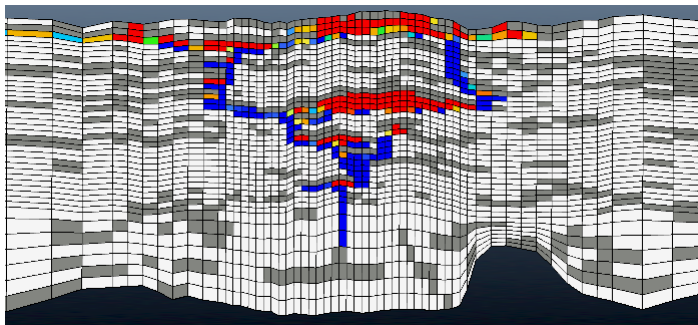
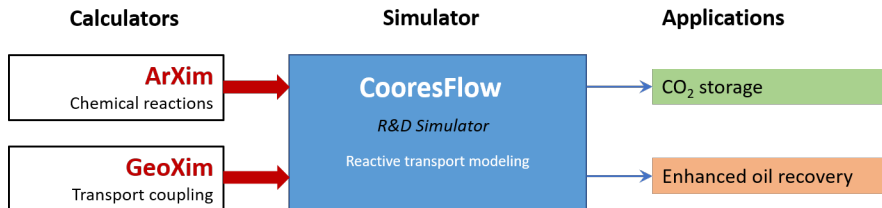
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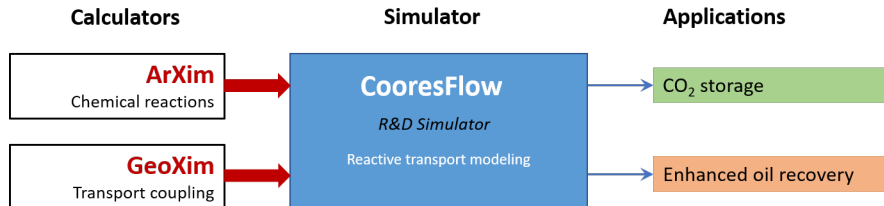
In collaboration with : C. Cancès, Q. H. Tran, T. Faney and I. Ben Gharbia



- 1 Context and motivation
- 2 Single-phase chemical equilibrium
 - Parametrization
 - Cartesian representation
 - Results
 - Conclusion
- 3 Multiphase chemical equilibrium
 - Complementary problem
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 - Conclusion

Software and applications





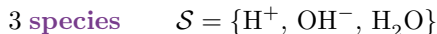
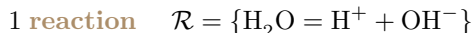
- ArXim issues:

- ▶ **robustness**
- ▶ **precision**
- ▶ **slowness**: up to 90% of CooresFlow's computational time !

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Chemical speciation example

- Water dissociation:



- Formula** and **stoichiometric** matrices:

$$\mathbf{A} = \begin{bmatrix} \text{H}^+ & \text{OH}^- & \text{H}_2\text{O} \\ 1 & 1 & 2 \\ 0 & 1 & 1 \end{bmatrix} \begin{matrix} \text{H} \\ \text{O} \end{matrix} \quad \mathbf{S} = \begin{bmatrix} 1 \\ 1 \\ -1 \end{bmatrix} \begin{matrix} \text{H}^+ \\ \text{OH}^- \\ \text{H}_2\text{O} \end{matrix} \quad \mathbf{AS} = \mathbf{0}$$

- Unknowns** and **constraints**:

$$\mathbf{n} = [n_{\text{H}^+}, n_{\text{OH}^-}, n_{\text{H}_2\text{O}}]^T \quad \mathbf{b} = [b_{\text{H}}, b_{\text{O}}]^T$$

- Elements conservation:

$$\mathbf{An} = \mathbf{b}$$

- Gibbs free energy:

$$G(\mathbf{n}) := \sum_{i \in \mathcal{S}} n_i \mu_i(\mathbf{n})$$

- Chemical potential:

$$\mu_i(\mathbf{n}) := \mu_i^\circ + \text{RT} \ln x_i(\mathbf{n})$$

- Mole fraction:

$$x_i(\mathbf{n}) := \frac{n_i}{\sum_{j=1}^{|\mathcal{S}|} n_j}$$

Chemical equilibrium problem

- **Gibbs energy minimization:**

$$\min_{\mathbf{A}\mathbf{n}=\mathbf{b}, \mathbf{n} \geq \mathbf{0}} G(\mathbf{n}) \Leftrightarrow \min_{\mathbf{A}\mathbf{n}=\mathbf{b}} G(\mathbf{n})$$

- **Euler-Lagrange equations:**

$$\begin{aligned} \mathbf{A}\mathbf{n} &= \mathbf{b} & \mathbf{A}\mathbf{n} &= \mathbf{b} \\ \boldsymbol{\mu}(\mathbf{n}) + \mathbf{A}^T \boldsymbol{\lambda} &= \mathbf{0} & \Leftrightarrow & \mathbf{S}^T \boldsymbol{\mu}(\mathbf{n}) = \mathbf{0} \end{aligned}$$

since $\mathbf{S}^T \mathbf{A}^T = \mathbf{0}$.

- Dimension: $|\mathcal{S}|$
- *Theorem*. There exists a unique solution. [*Shapiro & Shapley 1965*]

How to efficiently compute the solution ?

Chemical equilibrium problem

- **Gibbs energy minimization:**

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- Dimension: $|\mathcal{S}|$
- *Theorem*. There exists a unique solution. [*Shapiro & Shapley 1965*]

How to efficiently compute the solution ?

System transformation

- New unknown:

$$\omega = \frac{1}{\sum_{i=1}^{|\mathcal{S}|} n_i}$$

- Transformation:

$$\mathbf{x} = \omega \mathbf{n}$$

- Reformulated system:

$$\mathbf{1}^T \mathbf{x} - 1 = 0$$

$$\mathbf{A} \mathbf{x} - \omega \mathbf{b} = 0$$

$$\mathbf{S}^T [\boldsymbol{\mu}^\circ / (RT) + \ln \mathbf{x}] = 0$$

- Dimension: $|\mathcal{S}| + 1$

Classical resolution by Newton

- Residual:

$$\mathcal{F}(\mathbf{x}, \omega) = \begin{bmatrix} \mathbf{1}^T \mathbf{x} - 1 \\ \mathbf{A} \mathbf{x} - \omega \mathbf{b} \\ \mathbf{S}^T [\mu^\circ / (RT) + \ln \mathbf{x}] \end{bmatrix}$$

- Jacobian:

$$J(\mathbf{x}, \omega) = \begin{bmatrix} \mathbf{1}^T & 0 \\ \mathbf{A} & -\mathbf{b} \\ \mathbf{S}^T \text{diag} \left\{ \frac{1}{\mathbf{x}} \right\} & \mathbf{0} \end{bmatrix}$$

- Issues:

- ▶ $1/x_i$ **blows up** when $x_i \rightarrow 0$.
- ▶ **Does not preserve the positivity** of \mathbf{x} .
- ▶ **Orders of magnitude** of \mathbf{x} .

The log trick

- Modified residual:

$$\mathbf{y} = \ln \mathbf{x} \quad \Rightarrow \quad \mathcal{F}(\mathbf{y}, \omega) = \begin{bmatrix} \mathbf{1}^T \exp \mathbf{y} - 1 \\ \mathbf{A} \exp \mathbf{y} - \omega \mathbf{b} \\ \mathbf{S}^T [\boldsymbol{\mu}^\circ / (RT) + \mathbf{y}] \end{bmatrix}$$

- Jacobian:

$$J(\mathbf{y}, \omega) = \begin{bmatrix} \mathbf{1}^T \text{diag} \{ \exp \mathbf{y} \} & 0 \\ \mathbf{A} \text{diag} \{ \exp \mathbf{y} \} & -\mathbf{b} \\ \mathbf{S}^T & \mathbf{0} \end{bmatrix}$$

- Issue: $\exp y_i$ blows up when $y_i \rightarrow \infty$.

- Parametrization of the graph:

$$\mathbf{Y}(\boldsymbol{\tau}) = \ln \mathbf{X}(\boldsymbol{\tau})$$

- Residual:

$$\mathcal{F}(\boldsymbol{\tau}, \omega) = \begin{bmatrix} \mathbf{1}^T \mathbf{X}(\boldsymbol{\tau}) - 1 \\ \mathbf{A} \mathbf{X}(\boldsymbol{\tau}) - \omega \mathbf{b} \\ \mathbf{S}^T [\boldsymbol{\mu}^\circ / (\text{RT}) + \mathbf{Y}(\boldsymbol{\tau})] \end{bmatrix}$$

- Jacobian:

$$J(\boldsymbol{\tau}, \omega) = \begin{bmatrix} \mathbf{1}^T \text{diag} \{ \mathbf{X}'(\boldsymbol{\tau}) \} & 0 \\ \mathbf{A} \text{diag} \{ \mathbf{X}'(\boldsymbol{\tau}) \} & -\mathbf{b} \\ \mathbf{S}^T \text{diag} \{ \mathbf{Y}'(\boldsymbol{\tau}) \} & \mathbf{0} \end{bmatrix}$$

Choice of parametrization

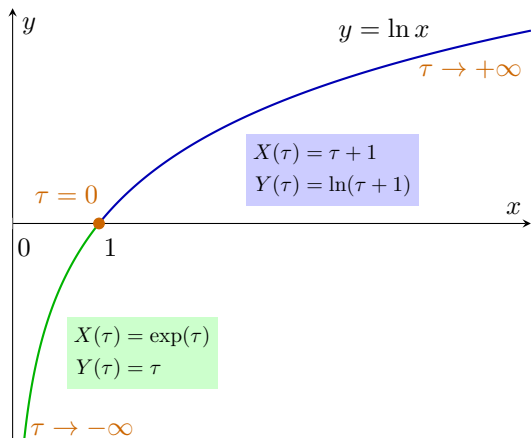
- Properties:

- ▶ $Y(\tau) = \ln(X(\tau))$
- ▶ X' and Y' are strictly monotonic bounded Lipschitz continuous
- ▶ $X'(\tau)$ and $Y'(\tau)$ do not vanish for the same value of τ

- Normalization condition:

$$\max(|X'(\tau)|, |Y'(\tau)|) = 1$$

The switch function [Brenner & Cancès 2017, Bassetto & al. 2021]



- Variable doubling and new function:

$$f(\mathbf{x}, \mathbf{y}) = 0 \Leftrightarrow \mathbf{y} = \ln \mathbf{x}$$

- Residual:

$$\mathcal{F}(\mathbf{x}, \mathbf{y}, \omega) = \begin{bmatrix} \mathbf{1}^T \cdot \mathbf{x} - 1 \\ \mathbf{A}\mathbf{x} - \omega\mathbf{b} \\ \mathbf{S}^T[\boldsymbol{\mu}^\circ / (RT) + \mathbf{y}] \\ f(\mathbf{x}, \mathbf{y}) \end{bmatrix}$$

- Jacobian:

$$J(\mathbf{x}, \mathbf{y}, \omega) = \begin{bmatrix} \mathbf{1}^T & \mathbf{0} & 0 \\ \mathbf{A} & \mathbf{0} & -\mathbf{b} \\ \mathbf{0} & \mathbf{S}^T & \mathbf{0} \\ J_{\mathbf{x}}f & J_{\mathbf{y}}f & 0 \end{bmatrix}$$

- Dimension: $2|\mathcal{S}| + 1$

Choice of Cartesian representation

- The discrepancy function f :

$$f(x, y) = V(y) - U(x), \quad \text{with } U = V \circ \ln$$

- Properties:

- ▶ $U(x) = V(y) \Leftrightarrow y = \ln(x)$
- ▶ U' and V' are strictly monotonic bounded Lipschitz continuous
- ▶ $U'(x)$ and $V'(y)$ do not vanish simultaneously

- Normalization condition:

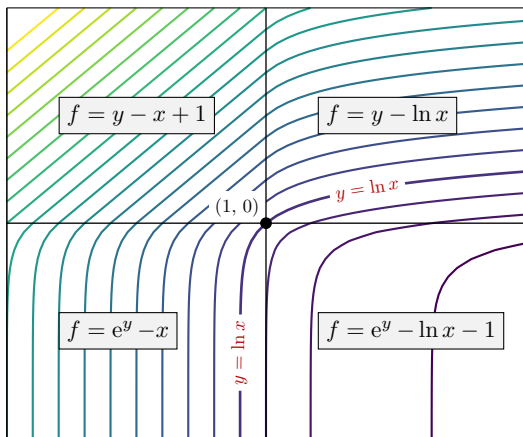
$$\max(|\partial_x f|, |\partial_y f|) = 1 \Leftrightarrow \max(|U'(x)|, |V'(y)|) = 1$$

The discrepancy function f

- $f(x, y) = V(y) - U(x)$ with:

$$V(y) = (\exp y - 1)\mathbf{1}_{y < 0} + y\mathbf{1}_{y > 0}$$

$$U(x) = (x - 1)\mathbf{1}_{x < 1} + (\ln x)\mathbf{1}_{x > 1}$$



- *Proposition*. The Jacobian matrices of the parametrization and Cartesian representation are **invertible at the solution point** of the associated system.
- *Theorem*. The Newton algorithm applied to the parametrization and the Cartesian representation techniques has a **local quadratic convergence**.

- log trick *vs.* ArXim *vs.* Switch *vs.* Discrepancy
- 3 test cases
- ArXim uses the log trick with a **line search** strategy:

$$\mathbf{x}^{(k+1)} = \mathbf{x}^{(k)} + \alpha^{(k)} \delta \mathbf{x}^{(k)}$$

- Tolerance for the Newton algorithm: $1e^{-7}$

- **Seawater:**

$$|\mathcal{S}| = 37, |\mathcal{E}| = 10, |\mathcal{R}| = 27$$

- **Water-Clay (Redox constraint):**

$$|\mathcal{S}| = 88, |\mathcal{E}| = 12, |\mathcal{R}| = 75$$

- **Water-Concrete (Redox constraint):**

$$|\mathcal{S}| = 88, |\mathcal{E}| = 12, |\mathcal{R}| = 75$$

Seawater test case

- $|\mathcal{S}| = 37$, $|\mathcal{E}| = 10$, $|\mathcal{R}| = 27$

Initialization (molar fraction)				
H ₂ O	1	1	1	1
Other species	$1e^{-2}$	$1e^{-4}$	ϵ_{32}	ϵ_{64}
Number of iterations				
log trick	18	×	×	×
ArXim	16	13	22	33
Switch	18	25	27	28
Discrepancy	23	23	23	23

Seawater test case

- $|\mathcal{S}| = 37$, $|\mathcal{E}| = 10$, $|\mathcal{R}| = 27$

Initialization (molar fraction)				
H ₂ O	1	1	1	1
Other species	$1e^{-2}$	$1e^{-4}$	ϵ_{32}	ϵ_{64}
Number of iterations				
log trick	18	×	×	×
ArXim	16	13	22	33
Switch	18	25	27	28
Discrepancy	23	23	23	23

Water-Clay test case

- $|\mathcal{S}| = 88$, $|\mathcal{E}| = 12$, $|\mathcal{R}| = 75$

Initialization				
H ₂ O	1	1	1	1
Other species	$1e^{-2}$	$1e^{-4}$	ϵ_{32}	ϵ_{64}
Number of iterations				
log trick	×	×	×	×
ArXim	28	25	28	×
Switch	31	29	×	×
Discrepancy	32	32	32	32

Water-Concrete test case

- $|\mathcal{S}| = 88$, $|\mathcal{E}| = 12$, $|\mathcal{R}| = 75$

Initialization (molar fraction)				
H ₂ O	1	1	1	1
Other species	$1e^{-2}$	$1e^{-4}$	ϵ_{32}	ϵ_{64}
Number of iterations				
log trick	×	×	×	×
ArXim	65	47	34	×
Switch	×	×	59	×
Discrepancy	52	52	52	52

- From the different test cases and initializations:

Discrepancy > Arxim > Switch > log trick

- The discrepancy function:
 - ▶ **is more robust**
 - ▶ **does not require ad-hoc strategies**, unlike ArXim

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Chemical equilibrium: the multiphase case

- N_{Sp} species in N_{Ph} phases:

$$\sigma : i \in \{1, \dots, N_{Sp}\} \mapsto \alpha \in \{1, \dots, N_{Ph}\}$$

- Gibbs free energy:

$$G(\mathbf{n}) := \sum_{\alpha=1}^{N_{Ph}} G_{\alpha}(\mathbf{n}^{\alpha}) \quad \text{where} \quad G_{\alpha}(\mathbf{n}^{\alpha}) = \sum_{i \in \sigma^{-1}(\alpha)} n_i \mu_i(\mathbf{n}^{\alpha})$$

- Chemical potential:

$$\mu_i(\mathbf{n}^{\alpha}) := \mu_i^{\circ} + RT \ln x_i(\mathbf{n}^{\alpha})$$

- Mole fraction:

$$x_i(\mathbf{n}^{\alpha}) := \frac{n_i}{\sum_{j \in \sigma^{-1}(\alpha)} n_j}$$

Chemical equilibrium problem

- Gibbs energy minimization:

$$\min_{\mathbf{A}\mathbf{n}=\mathbf{b}, \mathbf{n} \geq \mathbf{0}} G(\mathbf{n}) \Leftrightarrow \min_{\mathbf{A}\mathbf{n}=\mathbf{b}} \sum_{\alpha=1}^{N_{Ph}} \mathcal{G}_{\alpha}(\mathbf{n}^{\alpha})$$

$$\text{where } \mathcal{G}_{\alpha}(\mathbf{n}^{\alpha}) := \begin{cases} G_{\alpha}(\mathbf{n}^{\alpha}) & \text{if } \mathbf{n}^{\alpha} \geq \mathbf{0} \\ +\infty & \text{otherwise} \end{cases}$$

- Euler-Lagrange equations:

$$\begin{array}{l} \mathbf{A}\mathbf{n} - \mathbf{b} = \mathbf{0}, \\ \boldsymbol{\mu} + \mathbf{A}^T \boldsymbol{\Lambda} = \mathbf{0}, \\ \boldsymbol{\mu} = (\boldsymbol{\mu}^{\alpha})_{\alpha=1, \dots, N_{Ph}} \\ \boldsymbol{\mu}^{\alpha} \in \partial \mathcal{G}_{\alpha}(\mathbf{n}^{\alpha}) \end{array} \Leftrightarrow \begin{array}{l} \mathbf{A}\mathbf{n} - \mathbf{b} = \mathbf{0}, \\ \mathbf{S}^T \boldsymbol{\mu} = \mathbf{0}, \\ \boldsymbol{\mu} = (\boldsymbol{\mu}^{\alpha})_{\alpha=1, \dots, N_{Ph}} \\ \boldsymbol{\mu}^{\alpha} \in \partial \mathcal{G}_{\alpha}(\mathbf{n}^{\alpha}) \end{array}$$

where

$$\boldsymbol{\mu}^{\alpha} \in \partial \mathcal{G}_{\alpha}(\mathbf{n}^{\alpha}) \Leftrightarrow \mathcal{G}_{\alpha}(\mathbf{m}^{\alpha}) \geq \mathcal{G}_{\alpha}(\mathbf{n}^{\alpha}) + \langle \boldsymbol{\mu}^{\alpha}, \mathbf{m}^{\alpha} - \mathbf{n}^{\alpha} \rangle, \forall \mathbf{m}^{\alpha} \in \mathbb{R}^{\#\sigma^{-1}(\alpha)}$$

Chemical equilibrium problem

- *Proposition*: let $\mathbf{n}^\alpha \geq 0$, then $\boldsymbol{\mu}^\alpha \in \partial\mathcal{G}_\alpha(\mathbf{n}^\alpha)$ if and only if there exists \bar{n}_α , $\boldsymbol{\xi}^\alpha = (\xi_i)_{i \in \sigma^{-1}(\alpha)}$ such that:

$$\bar{n}_\alpha \geq 0, \boldsymbol{\xi}^\alpha > 0, \quad \sum_{i \in \sigma^{-1}(\alpha)} \xi_i \leq 1, \quad \bar{n}_\alpha \left(1 - \sum_{i \in \sigma^{-1}(\alpha)} \xi_i \right) = 0$$

and for all $i \in \sigma^{-1}(\alpha)$,

$$\mu_i = \mu_i^0 + RT \ln \xi_i, \quad n_i = \bar{n}_\alpha \xi_i.$$

- ξ_i are the extended mole fractions
- if $\bar{n}_\alpha > 0$, then $\bar{n}_\alpha = \sum_{i \in \sigma^{-1}(\alpha)} n_i$ and $\xi_i = x_i$

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Sketch of the proof

- \mathcal{G}_α is a continuous convex function, then:

$$\boldsymbol{\mu}_\alpha \in \partial \mathcal{G}_\alpha(\mathbf{n}^\alpha) \Leftrightarrow \mathbf{n}^\alpha \in \partial \mathcal{G}_\alpha^*(\boldsymbol{\mu}_\alpha),$$

where \mathcal{G}_α^* is the Legendre transform of \mathcal{G}_α :

$$\begin{aligned} \mathcal{G}_\alpha^*(\boldsymbol{\mu}^\alpha) &= \sup_{\mathbf{n}^\alpha \in \mathbb{R}^{\#\sigma^{-1}(\alpha)}} \sum_{i \in \sigma^{-1}(\alpha)} n_i \mu_i - \mathcal{G}_\alpha(\mathbf{n}^\alpha) \\ &= \sup_{\mathbf{n}^\alpha \in \mathbb{R}^{\#\sigma^{-1}(\alpha)}} \sum_{i \in \sigma^{-1}(\alpha)} n_i \mu_i - n_i (\mu_i^\circ + RT \ln x_i) \end{aligned}$$

- Using $n_i = x_i \bar{n}_\alpha$, we find:

$$\mathcal{G}_\alpha^*(\boldsymbol{\mu}^\alpha) = - \inf_{\bar{n}_\alpha \geq 0} \bar{n}_\alpha \min_{\mathbf{x}^\alpha \in X_\alpha} g_\alpha(\mathbf{x}^\alpha)$$

with

$$\begin{aligned} g_\alpha(\mathbf{x}^\alpha) &= \sum_{i \in \sigma^{-1}(\alpha)} x_i [\mu_i^\circ + RT \ln x_i - \mu_i] \\ X_\alpha &= \{\mathbf{x}^\alpha > 0 \mid \sum_{i \in \sigma^{-1}(\alpha)} x_i = 1\} \end{aligned}$$

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- Euler-Lagrange equations:

$$\begin{aligned} \mu_i^\circ + RT \ln x_i - \mu_i + RT - \lambda &= 0, \quad i \in \sigma^{-1}(\alpha), \\ \sum_{i \in \sigma^{-1}(\alpha)} x_i - 1 &= 0. \end{aligned}$$

- Therefore

$$\min_{\mathbf{x}^\alpha \in X_\alpha} g_\alpha(\mathbf{x}^\alpha) = \lambda - RT$$

- Let

$$\xi(\mu_i) := \exp\left(\frac{\mu_i - \mu_i^\circ}{RT}\right)$$

then

$$\xi(\mu_i) = x_i \exp\left(\frac{RT - \lambda}{RT}\right) \quad \text{and} \quad \sum_{i \in \sigma^{-1}(\alpha)} \xi(\mu_i) = \exp\left(\frac{RT - \lambda}{RT}\right)$$

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$$\sum_{i \in \sigma^{-1}(\alpha)} \xi(\mu_i) = \exp\left(\frac{RT - \lambda}{RT}\right)$$

- Therefore

$$\min_{\mathbf{x}^\alpha \in \bar{X}_\alpha} g_\alpha(\mathbf{x}^\alpha) = \lambda - RT = -RT \ln \sum_{i \in \sigma^{-1}(\alpha)} \xi(\mu_i)$$

- Back to the Legendre transform:

$$\begin{aligned} \mathcal{G}_\alpha^*(\mu^\alpha) &= - \inf_{\bar{n}_\alpha \geq 0} \bar{n}_\alpha \min_{\mathbf{x}^\alpha \in \bar{X}_\alpha} g_\alpha(\mathbf{x}^\alpha) \\ &= \sup_{\bar{n}_\alpha \geq 0} \bar{n}_\alpha RT \ln \sum_{i \in \sigma^{-1}(\alpha)} \xi(\mu_i) = \begin{cases} 0 & \text{if } \sum_i \xi(\mu_i) \leq 1 \\ +\infty & \text{otherwise} \end{cases} \end{aligned}$$

Sketch of the proof

- Let

$$\xi(\mu_i) := \exp\left(\frac{\mu_i - \mu_i^\circ}{RT}\right).$$

then

$$\sum_{i \in \sigma^{-1}(\alpha)} \xi(\mu_i) = \exp\left(\frac{RT - \lambda}{RT}\right)$$

- Therefore

$$\min_{\mathbf{x}^\alpha \in X_\alpha} g_\alpha(\mathbf{x}^\alpha) = \lambda - RT = -RT \ln \sum_{i \in \sigma^{-1}(\alpha)} \xi(\mu_i)$$

- Back to the Legendre transform:

$$\begin{aligned} \mathcal{G}_\alpha^\star(\boldsymbol{\mu}^\alpha) &= - \inf_{\bar{n}_\alpha \geq 0} \bar{n}_\alpha \min_{\mathbf{x}^\alpha \in X_\alpha} g_\alpha(\mathbf{x}^\alpha) \\ &= \sup_{\bar{n}_\alpha \geq 0} \bar{n}_\alpha RT \ln \sum_{i \in \sigma^{-1}(\alpha)} \xi(\mu_i) = \begin{cases} 0 & \text{if } \sum_i \xi(\mu_i) \leq 1 \\ +\infty & \text{otherwise} \end{cases} \end{aligned}$$

Sketch of the proof

- Back to the Legendre transform:

$$\mathcal{G}_\alpha^*(\boldsymbol{\mu}^\alpha) = \begin{cases} 0 & \text{if } \sum_i \xi(\mu_i) \leq 1 \\ +\infty & \text{otherwise} \end{cases}$$

- From the definition of the subdifferential:

$$\mathbf{n}^\alpha \in \partial \mathcal{G}_\alpha^*(\boldsymbol{\mu}^\alpha) \Leftrightarrow \underbrace{\mathcal{G}_\alpha^*(\boldsymbol{\eta}^\alpha)}_{=0} \geq \underbrace{\mathcal{G}_\alpha^*(\boldsymbol{\mu}^\alpha)}_{=0} + \langle \mathbf{n}^\alpha, \boldsymbol{\eta}^\alpha - \boldsymbol{\mu}^\alpha \rangle, \forall \boldsymbol{\eta}^\alpha \in \mathbb{R}^{\#\sigma^{-1}(\alpha)}$$

- The subdifferential of \mathcal{G}_α^* is:

$$\partial \mathcal{G}_\alpha^*(\boldsymbol{\mu}^\alpha) = \begin{cases} 0 & \text{if } \sum_{i \in \sigma^{-1}(\alpha)} \xi(\mu_i) < 1 \\ \gamma(\xi(\mu_i))_{i \in \sigma^{-1}(\alpha)}, \gamma \geq 0 & \text{if } \sum_{i \in \sigma^{-1}(\alpha)} \xi(\mu_i) = 1 \end{cases}$$

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$$\mathbf{n}^\alpha \in \partial \mathcal{G}_\alpha^*(\boldsymbol{\mu}^\alpha) \Leftrightarrow \begin{cases} n_i = \gamma \xi(\mu_i), \gamma \geq 0, \forall i \\ \sum_{i \in \sigma^{-1}(\alpha)} \xi(\mu_i) \leq 1 \end{cases} \Leftrightarrow \begin{cases} n_i = \bar{n}_\alpha \xi_i \\ \mu_i = \mu_i^\circ + RT \ln \xi_i \\ \sum_{i \in \sigma^{-1}(\alpha)} \xi_i \leq 1 \\ \bar{n}_\alpha (1 - \sum_i \xi_i) = 0 \end{cases}$$

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Sketch of the proof

- Back to the Legendre transform:

$$\mathcal{G}_\alpha^*(\boldsymbol{\mu}^\alpha) = \begin{cases} 0 & \text{if } \sum_i \xi(\mu_i) \leq 1 \\ +\infty & \text{otherwise} \end{cases}$$

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Chemical equilibrium problem

- Equations to solve:

$$\begin{aligned} \mathbf{A}\mathbf{n} - \mathbf{b} &= \mathbf{0}, \\ \mathbf{S}^T \boldsymbol{\mu} &= \mathbf{0}, \\ \boldsymbol{\mu} &= (\boldsymbol{\mu}^\alpha)_{\alpha=1, \dots, N_{Ph}} \\ \boldsymbol{\mu}^\alpha &\in \partial \mathcal{G}_\alpha(\mathbf{n}^\alpha) \end{aligned} \Leftrightarrow \begin{aligned} \sum_{\alpha=1}^{N_{Ph}} \bar{n}_\alpha \mathbf{A}^\alpha \boldsymbol{\xi}^\alpha - \mathbf{b} &= \mathbf{0}, \\ \mathbf{S}^T [\boldsymbol{\mu}^\circ / (RT) + \ln \boldsymbol{\xi}] &= \mathbf{0}, \\ \bar{n}_\alpha (1 - \sum_i \xi_i) &= 0, \quad (\forall \alpha), \\ \bar{n}_\alpha \geq 0, 1 - \sum_i \xi_i &\geq 0, \quad (\forall \alpha), \end{aligned}$$

- Transformation of the system:

$$\begin{aligned} \sum_{\alpha=1}^{N_{Ph}} \bar{n}_\alpha \mathbf{A}^\alpha \boldsymbol{\xi}^\alpha - \mathbf{b} &= \mathbf{0}, \\ r_\alpha = 1 - \sum_i \xi_i &\Rightarrow \mathbf{S}^T [\boldsymbol{\mu}^\circ / (RT) + \ln \boldsymbol{\xi}] = \mathbf{0}, \\ \sum_i \xi_i + r_\alpha - 1 &= 0, \quad (\forall \alpha), \\ \bar{n}_\alpha r_\alpha &= 0, \quad (\forall \alpha), \\ \bar{n}_\alpha \geq 0, r_\alpha &\geq 0, \quad (\forall \alpha), \end{aligned}$$

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- Two difficulties:

- ▶ The nonlinear terms:

$\ln \xi_i \rightarrow$ Parametrization and Cartesian representation

- ▶ The complementarity problem:

$$\begin{aligned} \bar{n}_\alpha r_\alpha &= 0, \\ \bar{n}_\alpha \geq 0, r_\alpha &\geq 0 \end{aligned}$$

- Residual for Param:

$$\mathcal{F}(\boldsymbol{\tau}, \bar{\mathbf{n}}, \mathbf{r}) = \begin{bmatrix} \sum_{\alpha} \bar{n}_{\alpha} \mathbf{A}^{\alpha} \mathbf{X}(\boldsymbol{\tau}^{\alpha}) - \mathbf{b} \\ \mathbf{S}^T [\boldsymbol{\mu}^{\circ} / (RT) + \mathbf{Y}(\boldsymbol{\tau})] \\ \mathbf{1}^T \mathbf{X}(\boldsymbol{\tau}^{\alpha}) + r_{\alpha} - 1 & (\forall \alpha) \\ \min(\bar{n}_{\alpha}, r_{\alpha}) & (\forall \alpha) \end{bmatrix}$$

- Residual for C.R.:

$$\mathcal{F}(\mathbf{x}, \mathbf{y}, \bar{\mathbf{n}}, \mathbf{r}) = \begin{bmatrix} \sum_{\alpha} \bar{n}_{\alpha} \mathbf{A}^{\alpha} \mathbf{x} - \mathbf{b} \\ \mathbf{S}^T [\boldsymbol{\mu}^{\circ} / (RT) + \mathbf{y}] \\ \mathbf{1}^T \mathbf{x} + r_{\alpha} - 1 & (\forall \alpha) \\ \min(\bar{n}_{\alpha}, r_{\alpha}) & (\forall \alpha) \\ f(\mathbf{x}, \mathbf{y}) \end{bmatrix}$$

- The complementarity is ensured:

$$\min(\bar{n}_{\alpha}, r_{\alpha}) = 0 \Leftrightarrow \bar{n}_{\alpha} r_{\alpha} = 0 \text{ and } \bar{n}_{\alpha} \geq 0, r_{\alpha} \geq 0$$

- New unknown ν
- Residual:

$$\mathcal{F}(\boldsymbol{\tau}, \bar{\mathbf{n}}, \mathbf{r}, \nu) = \begin{bmatrix} \sum_{\alpha} \bar{n}_{\alpha} \mathbf{A}^{\alpha} \mathbf{X}(\boldsymbol{\tau}^{\alpha}) - \mathbf{b} \\ \mathbf{S}^T [\boldsymbol{\mu}^{\circ} / (RT) + \mathbf{Y}(\boldsymbol{\tau})] \\ \mathbf{1}^T \mathbf{X}(\boldsymbol{\tau}^{\alpha}) + r_{\alpha} - 1 \\ \bar{n}_{\alpha} r_{\alpha} - \nu \\ \frac{1}{2N_{Ph}} (\langle \bar{\mathbf{n}}_{\alpha}, \mathbf{r}_{\alpha} \rangle^+)^2 + \frac{1}{2} \|\bar{\mathbf{n}}_{\alpha}^{-}\|^2 + \frac{1}{2} \|\mathbf{r}_{\alpha}^{-}\|^2 + 0.01\nu + \nu^2 \end{bmatrix}$$

- Update the iterates:

$$\begin{aligned} \boldsymbol{\tau}^{k+1} &= \boldsymbol{\tau}^k + \Delta \boldsymbol{\tau}^k \\ \bar{\mathbf{n}}^{k+1} &= \bar{\mathbf{n}}^k + \beta_{\mathbf{n}}^k \Delta \bar{\mathbf{n}}^k \\ \mathbf{r}^{k+1} &= \mathbf{r}^k + \beta_{\mathbf{r}}^k \Delta \mathbf{r}^k \\ \nu^{k+1} &= \nu^k + \Delta \nu^k \end{aligned}$$

such that $\bar{\mathbf{n}}^{k+1}, \mathbf{r}^{k+1} \geq 0$

Cartesian representation and NPIPМ

- Residual:

$$\mathcal{F}(\mathbf{x}, \mathbf{y}, \bar{\mathbf{n}}, \mathbf{r}, \nu) = \begin{bmatrix} \sum_{\alpha} \bar{n}_{\alpha} \mathbf{A}^{\alpha} \mathbf{x} - \mathbf{b} \\ \mathbf{S}^T [\boldsymbol{\mu}^{\circ} / (RT) + \mathbf{y}] \\ \mathbf{1}^T \mathbf{x} + r_{\alpha} - 1 \\ \bar{n}_{\alpha} r_{\alpha} - \nu \\ \frac{1}{2N_{Ph}} (\langle \bar{\mathbf{n}}_{\alpha}, \mathbf{r}_{\alpha} \rangle^+)^2 + \frac{1}{2} \|\bar{\mathbf{n}}_{\alpha}^{-}\|^2 + \frac{1}{2} \|\mathbf{r}_{\alpha}^{-}\|^2 + 0.01\nu + \nu^2 \\ f(\mathbf{x}, \mathbf{y}) \end{bmatrix}$$

- Update the iterates:

$$\begin{aligned} \mathbf{x}^{k+1} &= \mathbf{x}^k + \Delta \mathbf{x}^k \\ \mathbf{y}^{k+1} &= \mathbf{y}^k + \Delta \mathbf{y}^k \\ \bar{\mathbf{n}}^{k+1} &= \bar{\mathbf{n}}^k + \beta_{\mathbf{n}}^k \Delta \bar{\mathbf{n}}^k \\ \mathbf{r}^{k+1} &= \mathbf{r}^k + \beta_{\mathbf{r}}^k \Delta \mathbf{r}^k \\ \nu^{k+1} &= \nu^k + \Delta \nu^k \end{aligned}$$

such that $\bar{\mathbf{n}}^{k+1}, \mathbf{r}^{k+1} \geq 0$

Numerical results rules

- Reaktoro *vs.* Param. + min *vs.* Param. + NPIPМ *vs.* C.R. + min *vs.* C.R. + NPIPМ
- 5 test cases
- Tolerance for the Newton algorithm: $1e^{-7}$

Tests cases

- **TC1:**

$$|\mathcal{S}| = 5(4a, 1m), |\mathcal{E}| = 3, |\mathcal{R}| = 2$$

- **TC2:**

$$|\mathcal{S}| = 10(7a, 1m, 2g), |\mathcal{E}| = 4, |\mathcal{R}| = 6$$

- **TC3:**

$$|\mathcal{S}| = 11(8a, 2m, 1g), |\mathcal{E}| = 4, |\mathcal{R}| = 7$$

- **TC4:**

$$|\mathcal{S}| = 15(11a, 2m, 2g), |\mathcal{E}| = 5, |\mathcal{R}| = 10$$

- **TC5:**

$$|\mathcal{S}| = 72(50a, 20m, 2g), |\mathcal{E}| = 13, |\mathcal{R}| = 59$$

	TC 1	TC 2	TC 3	TC4	TC5
Reaktoro	35	36	46	50	140
Param + min	4	8	×	×	×
Param + NPIPМ	7	9	17	26	33
Cart + min	4	8	×	×	×
Cart + NPIPМ	7	9	81	×	×

Table: Number of iterations of Newton's method

- From the different test cases:

Param + NPIPМ > Reaktoro > others

- The Param + NPIPМ:
 - ▶ **is more robust**
 - ▶ **converges in a few iterations**

A first system reduction

- Conservation equations:

$$\begin{aligned}\mathbf{A}\mathbf{x} - \omega\mathbf{b} = 0 &\Leftrightarrow [\mathbf{A}_{Pr}, \mathbf{A}_{Sd}] \begin{bmatrix} \mathbf{x}_{Pr} \\ \mathbf{x}_{Sd} \end{bmatrix} - \omega\mathbf{b} = 0 \\ &\Leftrightarrow \mathcal{X}(\mathbf{x}_{Sd}, \omega) := \mathbf{x}_{Pr} = \mathbf{A}_{Pr}^{-1}(\omega\mathbf{b} - \mathbf{A}_{Sd}\mathbf{x}_{Sd})\end{aligned}$$

- Equilibrium equations:

$$\begin{aligned}\mathbf{S}^T \left(\frac{\boldsymbol{\mu}^\circ}{RT} + \mathbf{y} \right) = 0 &\Leftrightarrow [(\mathbf{A}_{Pr}^{-1}\mathbf{A}_{Sd})^T, -\mathbf{I}_{Sd}] \left(\frac{\boldsymbol{\mu}^\circ}{RT} + \begin{bmatrix} \mathbf{y}_{Pr} \\ \mathbf{y}_{Sd} \end{bmatrix} \right) = 0 \\ &\Leftrightarrow \mathcal{Y}(\mathbf{y}_{Pr}) := \mathbf{y}_{Sd} = \mathbf{S}^T \frac{\boldsymbol{\mu}^\circ}{RT} + (\mathbf{A}_{Pr}^{-1}\mathbf{A}_{Sd})^T \mathbf{y}_{Pr}\end{aligned}$$

A first system reduction

- Reduced system:

$$\mathbf{1}^T \cdot \begin{bmatrix} \mathcal{X}(\mathbf{x}_{Sd}, \omega) \\ \mathbf{x}_{Sd} \end{bmatrix} - 1 = 0$$
$$f \left(\begin{bmatrix} \mathcal{X}(\mathbf{x}_{Sd}, \omega) \\ \mathbf{x}_{Sd} \end{bmatrix}, \begin{bmatrix} \mathbf{y}_{Pr} \\ \mathcal{Y}(\mathbf{y}_{Pr}) \end{bmatrix} \right) = 0$$

- Dimension:

$|\mathcal{S}| + 1$ equations and $|\mathcal{S}| + 1$ unknowns

A second system reduction

- System:

$$\begin{bmatrix} \mathbf{1}^T & \mathbf{0} & 0 \\ \mathbf{A} & \mathbf{0} & -\mathbf{b} \\ \mathbf{0} & \mathbf{S}^T & \mathbf{0} \\ J_{\mathbf{x}}f & J_{\mathbf{y}}f & \mathbf{0} \end{bmatrix} \begin{bmatrix} \delta\mathbf{x} \\ \delta\mathbf{y} \\ \delta\omega \end{bmatrix} = \begin{bmatrix} -(\mathbf{1}^T \mathbf{x} - 1) \\ -(\mathbf{A}\mathbf{x} - \omega\mathbf{b}) \\ -\mathbf{S}^T(\boldsymbol{\mu}^\circ / (RT) + \mathbf{y}) \\ -f(\mathbf{x}, \mathbf{y}) \end{bmatrix}$$

- We multiply $J_{\mathbf{x}}f\delta\mathbf{x} + J_{\mathbf{y}}f\delta\mathbf{y} = -f(\mathbf{x}, \mathbf{y})$ by $(J_{\mathbf{x}}f)^{-1}(J_{\mathbf{y}}f)^{-1}$:

$$(J_{\mathbf{y}}f)^{-1}\delta\mathbf{x} + (J_{\mathbf{x}}f)^{-1}\delta\mathbf{y} = -(J_{\mathbf{x}}f)^{-1}(J_{\mathbf{y}}f)^{-1}f(\mathbf{x}, \mathbf{y})$$

- We define:

$$\begin{aligned} \delta\boldsymbol{\theta} &= -(J_{\mathbf{y}}f)^{-1}\delta\mathbf{x} - r(J_{\mathbf{x}}f)^{-1}(J_{\mathbf{y}}f)^{-1}f \\ &= (J_{\mathbf{x}}f)^{-1}\delta\mathbf{y} + (1 - r)(J_{\mathbf{x}}f)^{-1}(J_{\mathbf{y}}f)^{-1}f \end{aligned}$$

A second system reduction

- Then:

$$\delta \mathbf{x} = -J_{\mathbf{y}} f \delta \boldsymbol{\theta} - r(J_{\mathbf{x}} f)^{-1} f$$

$$\delta \mathbf{y} = J_{\mathbf{x}} f \delta \boldsymbol{\theta} - (1 - r)(J_{\mathbf{y}} f)^{-1} f$$

- Reduced system:

$$\begin{bmatrix} -\mathbf{1}^T J_{\mathbf{y}} f & 0 \\ -\mathbf{A} J_{\mathbf{y}} f & -\mathbf{b} \\ \mathbf{S}^T J_{\mathbf{x}} f & \mathbf{0} \end{bmatrix} \begin{bmatrix} \delta \boldsymbol{\theta} \\ \delta \omega \end{bmatrix} = \begin{bmatrix} r \mathbf{1}^T (J_{\mathbf{x}} f)^{-1} f - (\mathbf{1}^T \mathbf{x} - 1) \\ r \mathbf{A} (J_{\mathbf{x}} f)^{-1} f - (\mathbf{A} \mathbf{x} - \omega \mathbf{b}) \\ (1 - r) \mathbf{S}^T (J_{\mathbf{y}} f)^{-1} f - \mathbf{S}^T (\boldsymbol{\mu}^\circ / (RT) + \mathbf{y}) \end{bmatrix}$$

- Dimension:

$|\mathcal{S}| + 1$ equations and $|\mathcal{S}| + 1$ unknowns

- The jacobian matrix

$$\begin{bmatrix} \mathbf{1}^T & \mathbf{0} & 0 \\ \mathbf{A} & \mathbf{0} & -\mathbf{b} \\ \mathbf{0} & \mathbf{S}^T & \mathbf{0} \\ J_{\mathbf{x}}f & J_{\mathbf{y}}f & 0 \end{bmatrix}$$

is **sparse** because $J_{\mathbf{x}}f$ and $J_{\mathbf{y}}f$ are diagonals !

- The submatrix

$$\begin{bmatrix} \mathbf{1}^T & \mathbf{0} & 0 \\ \mathbf{A} & \mathbf{0} & -\mathbf{b} \\ \mathbf{0} & \mathbf{S}^T & \mathbf{0} \end{bmatrix}$$

does not change with iterations !

System based on molalities

- **Molality:**

$$\mu_i^\circ + RT \ln \frac{n_i}{\sum_{j=1}^N n_j} \approx \mu_i^\circ + RT \ln \frac{n_i}{n_{\text{H}_2\text{O}}} = \tilde{\mu}_i^\circ + RT \ln \frac{n_i}{n_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}}},$$

where $\tilde{\mu}_i^\circ := \mu_i^\circ + RT \ln M_{\text{H}_2\text{O}}$.

- **New system:**

$$\mathbf{A} \begin{bmatrix} 1 \\ \mathbf{x} \end{bmatrix} - \omega \mathbf{b} = \mathbf{0},$$
$$\mathbf{S}^T \begin{bmatrix} \mu_{\text{H}_2\text{O}}^\circ / (RT) + 0 \\ \boldsymbol{\mu}^\circ / (RT) + \mathbf{y}(\mathbf{x}) - \ln(M_{\text{H}_2\text{O}}) \end{bmatrix} = \mathbf{0}.$$

where $\omega = 1/n_{\text{H}_2\text{O}}$