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Algorithms for activity correction on equilibrium chemistry computation.

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Modern reactive transport codes include activity correction models. We propose to compare the classical algorithm (inner fixed point) and two new approaches.

The equations describing the system are:

- Ionic strength (I) definition:

$$I = \frac{1}{2} \sum_{i=1}^{NcA} z_i^2 \left[C_i\right] \tag{1}$$

- Activity correction model, with γ_i the activity coefficient:

$$\ln\left(\gamma_i\right) = -A \cdot z_i^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - B \cdot I \right) \tag{2}$$

- Logarithm form of mass action laws, describe the formation of species C_i depending of the components activities ξ_j:

$$\ln\left[C_i\right] = \ln\left(K_i\right) + \sum_{j=1}^{Nx} a_{i,j} \xi_j - \ln\left(\gamma_i\right) \tag{3}$$

- Mass balances written as objective functions Y_j, with T_j the total concentration of the components.

$$Y_j = -T_j + \sum_{i=1}^{Nc} a_{i,j} \left[C_i\right] \tag{4}$$

Unknowns of the system are ξ_j (primary unknowns), $[C_i]$, I and γ_i. Algorithms for minimizing objective functions include Newton-like procedure that requires Jacobian matrix calculation.

$$Z_{j,k} = \frac{\partial Y_j}{\partial \xi_k} = \frac{\partial}{\partial \xi_k} \left\{ \sum_{i=1}^{Nc} a_{i,j} \cdot \exp\left(\ln\left(K_i\right) + \sum_{h=1}^{Nx} a_{i,h} \cdot \xi_h - \ln\left(\gamma_i\right) \right) \right\} \; \forall j,k = \left(1,...Nx\right)^2 \tag{5}$$

Inner fixed point

In this case, Jacobian matrix is computed according to relation.

$$Z_{j,k} = \sum_{i=1}^{Nc} a_{i,j} \cdot a_{i,k} \cdot \left[C_i\right] \; \forall j,k = \left(1,...Nx\right)^2 \tag{6}$$

Activity coefficients (**??**) are updated at each Newton loop. Equation (**??**) is then an approximation of (**??**).

Outer fixed point

In this case, ionic strength and activity coefficients are constant during all the minimization process. Equation (**??**) is the exact Jacobian matrix of the system. Once the convergence is reached, activity coefficients are updated and a new minimization process is running.

Full Newton

We fully explicit (**??**) with activity correction. Including the derivative of the activity coefficients in the Jacobian matrix is e complex because of the recursive form obtained. Equation (**??**) gives:

$$Z_{j,k}^{=} \sum_{i=1}^{Nc} b_{i,j} \cdot C_i^{:} \left(a_{i,k} - \frac{\partial \left[\ln \left(\gamma_i \right) \right]}{\partial \xi_k} \right) \forall j,k = (1, ...Nx)^2 \tag{7}$$

Using equations(**??**) to (**??**), leads to a recursive form:

$$\frac{\partial \left[\ln \left(\gamma_i \right) \right]}{\partial \xi_k} = -\frac{1}{2} A z_i^2 \left[\frac{1}{\sqrt{I}} \frac{1}{\left(1 + \sqrt{I} \right)^2} - B \right] \cdot \frac{1}{2} \sum_{p=1}^{NcA} z_p^2 \cdot \left[C_p \right] \cdot \left(a_{p,k} - \frac{\partial \left[\ln \left(\gamma_p \right) \right]}{\partial \xi_k} \right) \tag{8}$$

We tested theses algorithms and found that the full Newton algorithm does not improve the resolution. If the activity corrections are low, the number of Newton iteration is equivalent to this obtained with the inner fixed point, but the computing time is higher. In the case of high activity correction, only the outer fixed point algorithm ensures the convergence of the method.