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CHEMICAL EQUILIBRIUM AND KINETICS II

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Abstract. *A nonstoichiometric approach to the solution of the problem of the chemical equilibrium and kinetics consists in the functional minimization of the Gibbs free energy subject to linear, nonlinear and inequality constraints. Linear constraints represent a system of mass-balance equations with an electroneutrality equation added, if necessary. Nonlinear constraints arise from implicit discretization of kinetics (ordinary differential) equation. And finally inequality constraints correspond to physical considerations requiring quantities of components to be non-negative. Main modeling problems are caused by the strong non-linearity of activity coefficients. In some cases it even produces non-convexity of the Gibbs free energy. In this paper two approaches to activity coefficients are compared. Numerical examples are given.*

Keywords: chemical equilibrium, kinetics, optimization.

1 DEFINITION OF THE GIBBS FREE ENERGY

Assuming the solution contains 1 kilogram of water (it means 55.5 mol) and that the amount of water is basically constant during reaction. Then molality m_r and the amount of substance (the amount of mol) n_r numerically agrees and **the Gibbs free energy of k-component system is given by the formula**

$$G(m) = \sum_{r=1}^{k} \mu_r n_r = \sum_{r=1}^{k} \mu_r m_r,$$

where m denotes k-component vector of **molalities** m_r. To determine a function describing the Gibbs free energy it is necessary to establish chemical potentials of all present components (species). The complete expression for **the chemical potential** of the species i by using the standard state of unit mole fraction at infinite dilution is:

$$\mu_r = \mu_{x,r}^{\infty} + RT \ln x_r + RT \ln \gamma_r^{[x]}.$$

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In this expression, $\mu^{\infty}_{x,r}$ is the chemical potential (defined on the basis of mole fraction) of the pure species r in the same state of aggregation as the solution. Further $R = 8.314$ denotes universal gas constant, $T = 298.15$ temperature in K, x_r mole fraction of rth components, $\gamma_r^{[x]}$ **activity coefficient** defined on the basis of mole fraction. Since our input data will be in molality, we convert the above mentioned formula for the chemical potential on the standard state of unit molality. We use following two relations

$$\mu^{\infty}_{m,r} = \mu^{\infty}_{x,r} - RT \ln n, \qquad \gamma_r^{[m]} = \gamma_r^{[x]} x_n,$$

where $\gamma_r^{[m]}$ is activity coefficient and $\mu^{\infty}_{m,r}$ is chemical potential. Both of them are defined on the basis of unit molality. Further n is an amount of substance of solvent in 1 kilogram and x_n is a mole fraction of solvent. After conversion we obtain the chemical potential of dissolved substance by using standard state of unit molality at infinite dilution expressed by the relation

$$\mu_r = \mu^{\infty}_{m,r} + RT \ln m_r + RT \ln \gamma_r^{[m]}.$$

Now we have some possibilities how to choose coefficients of aqueous species. We employ here two approaches. Initially we define them with **the Extended Debye-Hückel Equation**

$$\ln\left(\gamma_r^{[m]}\right) = -z_r^2\, A \left(\frac{\sqrt{I}}{1 + B\sqrt{I}} + \frac{2}{B} \ln\left(1 + B\sqrt{I}\right)\right),$$

where A is a parameter dependent on temperature, pressure and on a solvent. For water at temperature 25° C is $A = 0.391475$ (kg/mol)$^{1/2}$. A parameter B is constant and is equal to 1.2 (kg/mol)$^{1/2}$.

The second approach consists in defining them with **the Davies Equation**

$$\ln\left(\gamma_r^{[m]}\right) = -z_r^2\, A \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - BI\right),$$

where A and B are parameters dependent on temperature, pressure and on a solvent. For this task we pick $A = 1.17$ and $B = 0.3$ both in $(kg/mol)^{1/2}$. I is **the ionic strength** of the aqueous solution defined by

$$I = \frac{1}{2} \sum_r m_r z_r^2.$$

The ionic strength is a function of the molality of all ions present in a solution. z_r is the integer charge of the ion (1 for H^+, 2 for Mg^{2+} etc.).

The chemical potential of the solvent (water in our case) is given by the following formula

$$\mu_r = \mu^o_{m,r} + RT \ln x_n,$$

where $\mu^o_{m,r}$ is the chemical potential by using standard state of the pure species r. The chemical potential of suspended solids is given by the following relation

$$\mu_r = \mu^o_{m,r}.$$

For further details see [1, 3, 4, 7, 8].

Constraining conditions:

- **Molality of all components have to be non-negative** - then $m \geq 0$ (the amount of any species can not be negative).
- **Equations of mass-balance** - represent an accounting of material entering and leaving a system. Fundamental to the balance is the conservation of mass principle, i.e. that matter can not disappear or be created. These conditions are described by a system of linear equations.
- **An electroneutrality equation** - ensures that a total charge remains constant during reactions. This condition is again described by a linear equation.
- **Kinetic reactions** - are described by ordinary differential equations. These equations are discretized ahead of minimization of the Gibbs free energy (differential equations are replaced by non-linear equations).

Our aim is to find a constrained minimum of the Gibbs free energy (satisfying all constraining conditions).

2 NUMERICAL METHODS

To discretize kinetic equation $y' = f(t, y)$ Crank-Nicholson method

$$y_{n+1} - y_n = h \, \frac{f(t+h, y_{n+1}) + f(t, y_n)}{2}$$

is used. It is the A-stable second order method. To minimize the Gibbs free energy two methods are employed. First we linearize kinetic constraining conditions and afterwards we use variable metric method (BFGS).

Minimization methods from this class are commonly used for either unconstrained or linearly constrained optimizations. In the second phase sequential quadratic programming method is employed. Initial values for the second method was set to obtained results from the first method. In case of minimization without kinetic equations both methods solve the same problem. In opposite case first method solves simplified problem. This approach was employed for reasons to increase reliability of obtained results. Both above mentioned methods were assumed from the optimization package UFO (see [5, 6]).

3 EXAMPLE OF NON-CONVEXITY OF THE GIBBS ENERGY

Now we will present here a very simple (real life) example of dissolution of $CaSO_4$, where the choice of the Extended Debye-Hückel Equation for activity coefficients causes non-convexity of the Gibbs free energy and it is non-physical. We assume, that we have three unknown molalities of species $m_3 = CaSO_4$, $m_2 = SO_4^{-2}$, $m_1 = Ca^{2+}$ and the constant amount of water equal to 55.5 mol. For the sake of simplicity we choose initial molalities of both dissolved substances equal to zero. Then from the mass-balance equations we obtain two linear constraints

$$m_1 = m_2, \qquad m_1 + m_3 = K$$

where K is the positive constant representing initial molality of $CaSO_4$.

The formula for the Gibbs free energy with the Davis Equation for activity coefficients is

$$\begin{aligned} G &= m_1\left(RT\ln\left(m_1\gamma^{[m]}\right) - 552790\right) + m_2\left(RT\ln\left(m_2\gamma^{[m]}\right) - 744540\right) \\ &\quad -1321830 m_3 + 55.5\left(-237130 + RT\ln\frac{55.5}{m_1 + m_2 + 55.5}\right), \end{aligned}$$

where

$$\ln\left(\gamma^{[m]}\right) = -z^2 A\left(\frac{\sqrt{I}}{1+\sqrt{I}} - BI\right),$$

$$\sqrt{I} = \sqrt{2m_1 + 2m_2}, \quad z = \pm 2,\ R = 8.314,\ T = 298.15,\ A = 1.17,\ B = 0.3.$$

And after simplification we obtain

$$\begin{aligned} G &= m_1\left(24500 + 2RT\ln\left(m_1\gamma^{[m]}\right)\right) - 1321830K \\ &\quad +55.5\left(-237130 + RT\ln\frac{55.5}{2m_1+55.5}\right). \end{aligned}$$

This is relatively simple function and we can find optimality condition. The solution of optimality condition matches the output of program. The Gibbs free energy of this system is in this case the convex function with only one solution. See Figure 1.

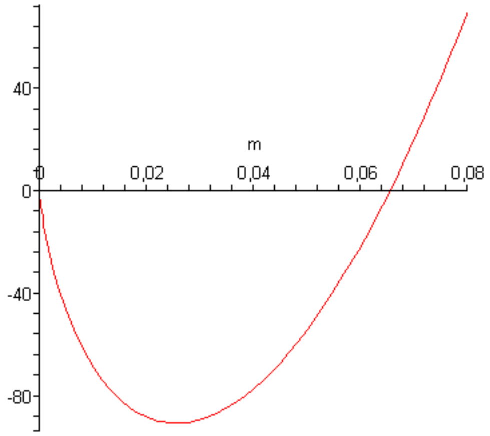

Figure 1: The Gibbs free energy of dissolution of $CaSO_4$ without constant terms (Davis).

Similarly we will proceed also in the case of the Extended Debye-Hückel Equation for activity coefficients. Now we obtain the following formula for the Gibbs free energy

$$\begin{aligned} G &= m_1\left(RT\ln\left(m_1\gamma^{[m]}\right) - 552790\right) + m_2\left(RT\ln\left(m_2\gamma^{[m]}\right) - 744540\right) \\ &\quad -1321830m_3 + 55.5\left(-237130 + RT\ln\frac{55.5}{m_1+m_2+55.5}\right), \end{aligned}$$

where

$$\ln\left(\gamma^{[m]}\right) = -4A\left(\frac{\sqrt{I}}{1+B\sqrt{I}} + \frac{2}{B}\ln\left(1+B\sqrt{I}\right)\right),$$

$$\sqrt{I} = \sqrt{2m_1+2m_2}, \quad R = 8.314,\ T = 298.15,\ A = 0.391475,\ B = 1.2.$$

After simplification we have

$$\begin{aligned} G = \quad & m_1\left(24500 + 2RT\ln\left(m_1\gamma^{[m]}\right)\right) - 1321830K \\ & +55.5\left(-237130 + RT\ln\frac{55.5}{2m_1+55.5}\right). \end{aligned}$$

However in this case the function of the Gibbs free energy is decreasing so that it has no relative minimum. It would mean that arbitrary the amount of $CaSO_4$ dissolve and this result does not correspond to reality. See Figure 2.

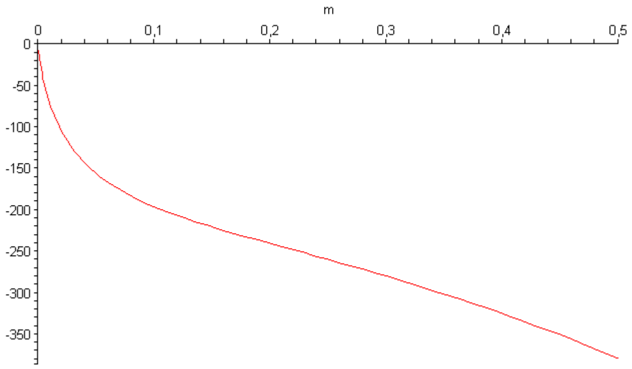

Figure 2: The Gibbs energy of dissolution of $CaSO_4$ without constant terms (Debye-Hückel).

4 ONE MORE COMPLICATED EXAMPLE

We will solve the same task as in [4] with two kinetic equations

$$\frac{dm_{C_2Cl_3H}}{dt} = -0.67\, m^-_{MnO_4}\, m_{C_2Cl_3H} \quad \text{and} \quad \frac{dm_{C_2Cl_4}}{dt} = -0.045\, m^-_{MnO_4}\, m_{C_2Cl_4}.$$

In the following two tables "Output 1" contains results of computation without kinetics, "Output 2" contains results of computation with kinetics in time $t = 1$s and finally "Output 3" contains results of computation with kinetics in time $t = 1000$s. The first table contains results of computations performed with the Extended Debye-Hückel activity coefficients and the second with the Davies activity coefficients. The computations accomplished with the Davies activity coefficients were approximately three times faster. At the end I would like to point out that results are strongly influenced by the choice of activity coefficients. Some mutually corresponding items in tables differ up to 30%.

Component	Input	Output 1	Output 2	Output 3
$CaCO_3$	10^{-1}	$0.11314D + 00$	$0.11314D + 00$	$0.11314D + 00$
$CaSO_4$	10^{-1}	$0.95250D - 01$	$0.95249D - 01$	$0.95249D - 01$
$MgCa(CO_3)_2$	10^{-1}	$0.91605D - 01$	$0.91607D - 01$	$0.91607D - 01$
$MnCO_3$	10^{-1}	$0.96789D - 01$	$0.96785D - 01$	$0.96785D - 01$
MnO_2	10^{-1}	$0.99999D - 01$	$0.10000D + 00$	$0.10000D + 00$
H_2O	55.5	55.5	55.5	55.5
${CO_3}^{2-}$	10^{-6}	$0.68589D - 02$	$0.68594D - 02$	$0.68594D - 02$
Ca^{2+}	10^{-6}	$0.53936D - 05$	$0.53924D - 05$	$0.53924D - 05$
${SO_4}^{2-}$	10^{-6}	$0.47514D - 02$	$0.47518D - 02$	$0.47518D - 02$
Mg^{2+}	10^{-6}	$0.83959D - 02$	$0.83939D - 02$	$0.83939D - 02$
Mn^{2+}	10^{-6}	$0.32143D - 02$	$0.32136D - 02$	$0.32136D - 02$
OH^-	10^{-6}	$0.34282D - 06$	$0.43141D - 06$	$0.43139D - 06$
H^+	10^{-6}	$0.54677D - 07$	$0.43430D - 07$	$0.43431D - 07$
CL^-	10^{-6}	$0.10000D - 04$	$0.30000D - 05$	$0.30011D - 05$
C_2Cl_3H	10^{-6}	$0.10000D - 11$	$0.10000D - 05$	$0.99967D - 06$
Cl_2	10^{-6}	$0.10000D - 11$	$0.10000D - 11$	$0.10000D - 11$
CO_2	10^{-6}	$0.66441D - 05$	$0.41940D - 05$	$0.41942D - 05$
${MnO_4}^-$	10^{-6}	$0.10000D - 11$	$0.10000D - 11$	$0.10000D - 11$
C_2Cl_4	10^{-6}	$0.10000D - 11$	$0.10000D - 05$	$0.99998D - 06$

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Component	Input	Output 1	Output 2	Output 3
$CaCO_3$	10^{-1}	$0.10976D+00$	$0.10976D+00$	$0.10976D+00$
$CaSO_4$	10^{-1}	$0.96474D-01$	$0.96473D-01$	$0.96473D-01$
$MgCa(CO_3)_2$	10^{-1}	$0.93767D-01$	$0.93768D-01$	$0.93768D-01$
$MnCO_3$	10^{-1}	$0.97617D-01$	$0.97612D-01$	$0.97612D-01$
MnO_2	10^{-1}	$0.99999D-01$	$0.10000D+00$	$0.10000D+00$
H_2O	55.5	55.5	55.5	55.5
${CO_3}^{2-}$	10^{-6}	$0.50921D-02$	$0.50929D-02$	$0.50929D-02$
Ca^{2+}	10^{-6}	$0.40049D-05$	$0.40039D-05$	$0.40039D-05$
${SO_4}^{2-}$	10^{-6}	$0.35275D-02$	$0.35280D-02$	$0.35280D-02$
Mg^{2+}	10^{-6}	$0.62341D-02$	$0.62326D-02$	$0.62326D-02$
Mn^{2+}	10^{-6}	$0.23867D-02$	$0.23861D-02$	$0.23861D-02$
OH^-	10^{-6}	$0.31843D-06$	$0.40116D-06$	$0.40115D-06$
H^+	10^{-6}	$0.50711D-07$	$0.40251D-07$	$0.40252D-07$
CL^-	10^{-6}	$0.10000D-04$	$0.30000D-05$	$0.30011D-05$
C_2Cl_3H	10^{-6}	$0.10000D-11$	$0.10000D-05$	$0.99967D-06$
Cl_2	10^{-6}	$0.10000D-11$	$0.10000D-11$	$0.10000D-11$
CO_2	10^{-6}	$0.66339D-05$	$0.41805D-05$	$0.41807D-05$
${MnO_4}^-$	10^{-6}	$0.10000D-11$	$0.10000D-11$	$0.10000D-11$
C_2Cl_4	10^{-6}	$0.10000D-11$	$0.10000D-05$	$0.99998D-06$