Simultaneous Chemical Equilibria

This is a set of notes on setting up the equations for determining the equilibrium concentrations of several simultaneous chemical equilibria.

We are given a chemical reaction with N species, $M_1, M_2, \ldots, M_N$. Each reaction, $r = 1, 2, \ldots, R$, is completely specified by its stoichiometric coefficients, $\nu_i^{(r)}$. E.g., for a reaction like

$$2M_5 + 1M_7 \rightleftharpoons 3M_3 + 4M_9 \tag{1}$$

one has

$$\nu_5 = -2; \nu_7 = -1; \nu_3 = 3; \nu_9 = 4 \tag{2}$$

and all other stoichiometric coefficients are zero. The equilibrium constant for the r^{th} reaction is

$$K^{(r)} = \prod_{i=1}^{N} \left(a_i\right)^{\nu_i^{(r)}} \tag{3}$$

where a_i is the activity of the reagent (which can be represented using the molality, partial pressure, number of molecules, molarity, etc. depending on the context).

The activity of each reagent is its initial activity plus the change. So

$$a_i = a_i^{(0)} + \sum_{r=1}^{R} \nu_i^{(r)} \xi^{(r)} \tag{4}$$

where $\xi^{(r)}$, the progress of reaction, is the "number of moles of the reaction that have occurred." It is understand that $\xi^{(r)} > 0$ for a reaction that goes in the forward direction and $\xi^{(r)} < 0$ for a reaction that goes in the reverse direction.

With this finished, one has a system of nonlinear equations to solve,

$$K^{(r)} = \prod_{i=1}^{N} \left(a_i^{(0)} + \sum_{r=1}^{R} \nu_i^{(r)} \xi^{(r)} \right)^{\nu_i^{(r)}} \qquad r = 1, 2, \ldots R \tag{5}$$

for the progress of reactions $\left\{\xi^{(1)}, \xi^{(2)}, \ldots, \xi^{(r)}\right\}$ and after this has been solved, the activity/molality of the species can be computed.

Because terms in the denominator are nasty, it may be better to write this system of equations in the following form,

$$K^{(r)} \prod_{\substack{i=1 \\ \nu_i^{(r)} < 0}}^{N} \left(a_i^{(0)} + \sum_{r=1}^{R} \nu_i^{(r)} \xi^{(r)} \right)^{-\nu_i^{(r)}} - \prod_{\substack{i=1 \\ \nu_i^{(r)} > 0}}^{N} \left(a_i^{(0)} + \sum_{r=1}^{R} \nu_i^{(r)} \xi^{(r)} \right)^{\nu_i^{(r)}} = 0 \qquad r = 1, 2, \ldots R \tag{6}$$

The Jacobian for this system of equations can be determined,

$$\begin{aligned} J_{rs} = K^{(r)} \sum_{\substack{i=1 \\ \nu_i^{(r)} < 0}}^{N} & \left[\left(\prod_{\substack{j=1 \\ j \neq i}}^{N} \left(a_i^{(0)} + \sum_{r=1}^{R} \nu_i^{(r)} \xi^{(r)} \right)^{-\nu_i^{(r)}} \right) \left(-\nu_i^{(r)} \left(a_i^{(0)} + \sum_{r=1}^{R} \nu_i^{(r)} \xi^{(r)} \right)^{-\nu_i^{(r)} - 1} \left(\nu_i^{(s)} \right) \right) \right] \\ - \sum_{\substack{i=1 \\ \nu_i^{(r)} > 0}}^{N} & \left[\left(\prod_{\substack{j=1 \\ j \neq i}}^{N} \left(a_i^{(0)} + \sum_{r=1}^{R} \nu_i^{(r)} \xi^{(r)} \right)^{\nu_i^{(r)}} \right) \left(\nu_i^{(r)} \left(a_i^{(0)} + \sum_{r=1}^{R} \nu_i^{(r)} \xi^{(r)} \right)^{\nu_i^{(r)} - 1} \left(\nu_i^{(s)} \right) \right) \right] \end{aligned} \tag{7}$$

(I did not double-check this).

The system of equations in Eq. (6) often requires a good initial guess to solve. So it can be solved with the good initial guess from kinetic Monte Carlo (like our net-event kinetic Monte Carlo method) or by using a "global" solver (e.g., treat it as a nonlinear least squares problem and use the CMA method

https://pypi.python.org/pypi/cma

or the paraopt package from Toon

https://github.com/tovrstra/paraopt

In either case, some final root-polishing using Newton's method with a good guess is likely to be useful.

Paul W. Ayers
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