Chemical Equilibrium and Linear Programming

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Using a simple description based on mathematical programming, a new algorithm for the determination of the equilibrium composition of a complex mixture is proposed. The method, which is based on linear programming, leads to small and fast working computer programs even if the equilibrium composition involves simultaneously high and extremely low concentrations.

The problem of calculating equilibrium concentrations of chemical systems is of considerable interest in many situations. A chemical system is completely determined by the primary parameters: a number of equilibrium constants or formation energies and some linear functions of the concentrations relating these to the composition of the system, *i.e.* mass balance equations.

Traditionally the object of solving this equilibrium problem has been attacked by means of the mass action law with the intention of giving explicit expressions for the concentrations as functions of the primary parameters. Because of the mathematical difficulties, this will only succeed for very simple systems and it is usually necessary to apply approximations. This has led to a variety of formulas to be used in specific cases. A rather systematic treatment along this line has been given by Charlot and Gaugin.[1] The reactions are classified according to complexity and mass balance. A specific class of reactions is then subdivided according to the magnitude of the equilibrium constant into subclasses characterized as: reactions that are practically not taking place, practically quantitative reactions, and the "intermediate" case, which is the general case. The practically quantitative reactions are then treated according to the composition of the system, *i.e.* if the mass balance corresponds to equivalent amounts or not.

Now, this variety of formulas and cases was generated by the efforts for making explicit expressions. That the chemical equilibrium problem is implicit in nature is illustrated by the thermodynamic formulation of the equilibrium condition, namely that the free energy function shall attain a minimum.

Algorithms for solving the implicitly formulated problem has been proposed by several authors, Anthony and Himmelblau [2] and the references contained therein and Warga.[3] In spite of this further work has been done and it is believed that something has been gained in efficiency, speed and simplicity.

DESCRIPTION OF THE CHEMICAL EQUILIBRIUM MODEL

We will consider a chemical system containing m different species X_j, $j \in J = \{1,2,....,m\}$. Species of the same composition but appearing in different phases will be regarded as representing different species. Let these m species be described in terms of n fundamental building blocks which can be atomic elements or more complex structures. Let these fundamental species be taken as the first n species, *i.e.* X_i, $i \in I = \{1,2,....,n\} \subseteq J$; in other words, I is a subset of J including the possibility $I = J$. But, if $I = J$ no reactions take place in the system.

As an example let us consider an aqueous mixture of H^+, NH_3, PO_4^{3-}, and some non-reacting ions for the sake of electroneutrality. Neglecting solvolysis the following products can be included in the system, NH_4^+, HPO_4^{2-}, $H_2PO_4^-$, and H_3PO_4. Thus we have $n = 3$ and $m = 7$. The products are formed according to a number of "equations" such as

$$H_2PO_4^- \rightleftharpoons 2H^+ + PO_4^{3-}$$
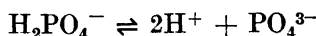
with a corresponding mass action expression

$$[H_2PO_4^-] = \beta[H^+]^2[PO_4^{3-}]$$

The number of moles and the concentration in moles per litre of X_j will be denoted x_j and c_j, respectively. For a reaction generally written as

$$X_j \rightleftharpoons \sum_{j \in I} a_{ij}X_i \quad j \in J \tag{1}$$

we can write

$$c_j = \beta_j \prod_{i \in I} (c_i)^{a_{ij}} \tag{2}$$

where the a_{ij}'s are stoichiometric coefficients and the β_j's are formation constants. Let d_i be the total number of moles of X_i in the system, *i.e.* the analytical amounts of the fundamental building blocks. Then the mass balance equations are

$$d_i = \sum_{j \in J} a_{ij} \times x_j \quad i \in I \tag{3}$$

In matrix notation

$$\mathbf{d} = \mathbf{A} \, \mathbf{x} \tag{3a}$$

Since $c_j = x_j/V$ we also have

$$\mathbf{d} = V \, \mathbf{A} \, \mathbf{c} \tag{3b}$$

V is the volume of the system, $\mathbf{A}$ is an $n \times m$ matrix with elements a_{ij}, $\mathbf{x}$, $\mathbf{c}$ and $\mathbf{d}$ are column vectors with elements x_j, c_j and d_i, respectively. For $j \leq n$ we have $\beta_j = 1$ and $a_{ij} = \delta_{ij}$ where δ_{ij} is the Kronecker delta.

In the above mentioned example one of the mass balance equations will be

$1 \cdot [H^+] + 0 \cdot [NH_3] + 0 \cdot [PO_4^{3-}] + 1 \cdot [NH_4^+] + 1 \cdot [HPO_4^{2-}] + 2 \cdot [H_2PO_4^-] + 3 \cdot [H_3PO_4] =$ the analytical amount of hydrogen ion.

The matrix $\mathbf{A}$ will then be as follows

$$\begin{Bmatrix} 1 & 0 & 0 & 1 & 1 & 2 & 3 \\ 0 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 1 & 1 \end{Bmatrix}$$

Now, a vector $\mathbf{c}'$ satisfying the mass balance equations will represent an equilibrium composition if it also satisfies the mass action laws (2) or minimizes the free energy function of the system.

In case of a system under constant pressure and temperature equilibrium is attained when the Gibbs free energy is minimum

$$\text{Min } \{G | \mathbf{Ax} = \mathbf{d}, \mathbf{x} \geq \mathbf{0}\} \qquad (4)$$

This formulation has been carefully investigated by Shapiro and Shapley [4] who proved that G is a convex function and that (4) under certain circumstances defines a unique solution that will satisfy (2) and (3).

Let the m-dimensional vector $\mathbf{c}$ be described in the real m-dimensional Euclidean space E^m and let this space be decomposed into two disjoint subspaces S_1 and S_2 so that S_1 is the n-dimensional space spanned by the row vectors of $\mathbf{A}$ and S_2 is the complement to S_1.

The decomposition of an arbitrary vector into components in S_1 and S_2 can be performed by means of the projection matrices $\mathbf{P}_1$ and $\mathbf{P}_2$.

For any vector satisfying (3a) we have

$$\mathbf{A\,P_1x} = \mathbf{d} \text{ and } \mathbf{A\,P_2x} = \mathbf{0}$$

Now, the only possibility for minimizing G without destroying mass balance lies in movements along directions that lie entirely in S_2.

Then another way of expressing the equilibrium conditions is

$$\mathbf{P_2}\mu = \mathbf{0}, \quad \mathbf{A\,x} = \mathbf{d}$$

where μ is the gradient vector of G. $\mathbf{P_2}\mu = \mathbf{0}$ is equivalent to the familar expression $\varDelta G = 0$.

$\mathbf{P_1}$ and $\mathbf{P_2}$ can be calculated [5] according to
$\mathbf{P_1} = \mathbf{A^T(AA^T)^{-1}A}$ and $\mathbf{P_2} = \mathbf{I} - \mathbf{P_1}$

where T denotes transposition and $\mathbf{I}$ is the m-dimensional unit matrix.

This implies that no concentration equals zero, in which case (3a) must also include suitable constraints in order to avoid negative concentrations. If the chemical system involves pure phases that might vanish, this can be the case, but, otherwise the infinite chemical potential for a zero concentration will force the solution to (4) to contain only non-zero concentrations.

THE ALGORITHM

The Gibbs free energy function of the system is given by

$$G = RT \sum_{j \in J} x_j \times \ln c_j + \sum_{j \in J} g_j x_j \qquad (5)$$

where g_j equals the energy of formation of species j.

So far the exposition is nearly identical to that of White, Johnson and Dantzig,[6] who solve the problem by minimizing (5) applying linear programming. The non-linear terms are substituted by a piecewise linear approximation. This method requires repeated calling of the linear programming procedure

and the linear constraints constitute an $(n + 2m) \times 4m$ matrix. Both features imply long computation times.

In the interval $0 \leq x_j \leq 1$ the contribution to the free energy from terms like $x_j \times \ln c_j$ will by far be exceeded by the contribution from the linear terms. An approximation to the free energy function will then be

$$G' = \sum_{j \in J} g_j x_j = \mathbf{g}^T \mathbf{x}$$

and the problem is reduced to linear programming

$$\text{Min } \{\mathbf{g}^T \mathbf{n} \,|\, \mathbf{Ax} = \mathbf{d}, \, \mathbf{x} \geq \mathbf{0}\} \tag{6}$$

This problem can generally be solved by library procedures.

Working out from the solution to (6) it turns out to be easy to reinclude the non-linear terms and obtain the solution to (5). This is so because emphasis is first given to species which are present in greater amounts.

The theory and application of linear programming is described by many authors, for example by Zoutendijk,[7] and we will only mention some important features here.

The matrix $\mathbf{A}$ is $n \times m$ with $n < m$ and a solution to (6) will contain (at most) n non-zero concentrations. The column vectors of $\mathbf{A}$ corresponding to these species constitute a square $n \times n$ matrix $\mathbf{B}$, called the basis and the corresponding set of indices is denoted L, $L \subset J$.

When using a simplex method for solving (6) one obtains besides the solution the inverse of the matrix $\mathbf{B}$. When writing the non-zero concentrations as an n-dimensional vector $\mathbf{x}_B$ the relation between this vector and $\mathbf{d}$ is simply

$$\mathbf{x}_B = \mathbf{B}^{-1}\mathbf{d} \tag{7}$$

By means of (2) and the relation $\ln \beta_k = -g_k/RT$ we can write

$$\ln c_l = -g_l/RT + \sum_{i \in I} b_{il} \ln c_i \quad l \in L \tag{8}$$

and since $\mathbf{B}^{-1}$ is known we can easily solve for $\ln c_i$, $i \in I$. Now all the zero concentrations of the solution to (6) can be adjusted to the values they must have for being in equilibrium with $\mathbf{c}_B$. This operation will destroy mass balance, but it turns out that in many cases the difference is small or even negligible. We have now calculated an exact solution, not that belonging to the original vector $\mathbf{d}$, but to an adjacent vector $\mathbf{d}^*$. If the difference is too great to be ignored we adjust $\mathbf{x}_B$ in the following way

$$\mathbf{x}_B' = \mathbf{x}_B - \mathbf{B}^{-1}(\mathbf{d}^* - \mathbf{d}) \tag{9}$$

for the purpose of "making room" for the difference. If the difference is small this will give the desired solution in one step.

DISCUSSION

The principles of iteration utilized in the algorithms cited can be divided into three classes:

1) mass balance satisfied all the time, while equilibrium is sought by iteration

2) equilibrium conditions fulfilled, while mass balance is sought by iteration.

3) both mass balance and equilibrium are sought by iteration.

The present method is particular in that it includes features from all three classes. Actually both mass balance and equilibrium are sought by iteration, but the steps in the iteration oscillate between states where either mass balance or equilibrium conditions are in focus.

The work with the algorithm was initiated by a need for simulating equilibria in aqueous solutions. Most of the algorithms cited were intended for the determination of gas equilibria and it was recognized that inclusion of extremely low concentrations had an adverse effect on convergence. Anthony and Himmelblau [2] experimented with an algorithm based on a search technique [8] and the third principle of iteration and found that when the ratio between the highest and the lowest concentration became of the order 10^4 to 10^5 numerical difficulties arose. They believed that this would be the case for any other procedure. It is believed that the success of the present method is due to two features, namely

1) the description on the basis of just n significant concentrations of the same order of magnitude.

2) the oscillation between the two complementary iteration principles.

The first point assures that the reported numerical difficulties don't come into operation and the second point is responsible for the fast convergence. No proof for convergence will be given here, since the ability of a numerical method necessarily must be demonstrated by experiment. But empirically the power of the method has been proved on several chemical systems with various dimensions of A and with various values of the formation energies. Its power is also demonstrated by the fact that the above mentioned "oscillation" often consists of just one step. Yet, if the first approximation is poor several cycles are needed.

The algorithm as described above has also some severe limitations, but as the iteration is the simplest possible there seems to be plenty of possibilities for incorporating more sophisticated strategies.

It has been implied that the solution to (6) was not degenerate, *i.e.* that it contained n non-zero concentrations. This is not always true and the degeneracy will leave one or more of the elements $\ln c_i$, $i \in I$ indeterminate and consequently one or more elements of d^* will be indeterminate. This can be met with in several ways, an obvious possibility is to perturb d in such a manner that the degeneracy is avoided and then by the subsequent iteration return to the initial vector d. Another possibility is to determine the lacking elements by a nesting procedure trying to minimize the distance between d^* and d.

This leads to the other observed inadequacy of the simple procedure. It can happen that the solution to (6) is a poor approximation to equilibrium composition. This can be the case if some of the equilibrium constants are of the same order of magnitude or when A contains negative elements. The last thing will occur if solvolysis is taking place in the system.

When the approximation is poor the distance between d^* and d becomes so great that the adjustment (9) is no improvement at all or even leads to

negative mass balance. Also here a nesting procedure using $\mathbf{d}-\mathbf{d}^*$ as the direction of iteration can prove useful.

But the simple procedure has proved quite adequate in a large number of cases.

The use of mole fractions or activities will imply additional iterations, but since both, like the free energy, are dependent on the large concentrations only, this will not offer any great difficulty.

The phosphate-ammonia system has been treated by a provisional ALGOL program on a GIER computer with an average execution time for an arithmetical operation of 0.2 milliseconds and approximate computing times of 1.5 sec per point were obtained. Solvolysis was neglected and consequently the matrix $\mathbf{A}$ contained no negative elements. If solvolysis is included the hydroxide ion is also taken in consideration. This case can be dealt with in two ways. The concentration of OH^- can be considered a negative hydrogen ion concentration. This seems to be most convenient if the water concentration can be taken as constant, but it leads to a negative element in $\mathbf{A}$, $n = 3$ and $m = 8$. Otherwise the concentration of water can be introduced, $n = 4$ and $m = 8$, but both procedures makes it possible that the first approximation supplied by the linear programming procedure is a poor approximation. The possibility for making an efficient procedure that will handle this case has not yet been investigated by the present author. In the above calculations activity factors were considered constant. If this is not feasible the variation of the ionic strength must be taken in account. One possibility is to calculate the ionic strength every time an approximate equilibrium composition has been estimated. Activity factors as functions of the ionic strength can then be included in the next step of iteration. Such a procedure has proved convergent in the phosphate-ammonia system with about ten times longer computing times. No efforts for optimizing the procedure has been made.

APPENDIX

As an example of the use of the method we can choose acetic acid. This will also demonstrate that even very simple systems can be treated with advantage by the algorithm. For the sake of simplicity we will only consider solutions in which we can ignore the concentration of OH^-. The system is then composed of H^+, Ac^-, and HAc. Then we have

$$\mathbf{A} = \begin{Bmatrix} 101 \\ 011 \end{Bmatrix}, \quad \mathbf{d} = \begin{Bmatrix} d_1 \\ d_2 \end{Bmatrix} = \begin{Bmatrix} [H^+]_{total} \\ [Ac^-]_{total} \end{Bmatrix}, \quad \mathbf{c} = \begin{Bmatrix} [H^+] \\ [Ac^-] \\ [HAc] \end{Bmatrix}, \quad \mathbf{g} = \begin{Bmatrix} 0 \\ 0 \\ -\ln \beta \end{Bmatrix}$$

Instead of formation energies negative logarithms to the formation constants are inserted in the $\mathbf{g}$ vector. This can be done since only the relative order of magnitudes of the elements of $\mathbf{g}$ are of importance to the linear programming procedure.

Traditionally this system can be treated as follows
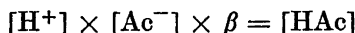
$$[H^+] \times [Ac^-] \times \beta = [HAc]$$

and introducing mass balance

$$(d_1-[\text{HAc}])(d_2-[\text{HAc}]) \times \beta = [\text{HAc}]$$

$$[\text{HAc}]^2-(d_1 + d_2 + \beta^{-1})[\text{HAc}] + d_1 d_2 = 0$$

Apart from the small perturbation, β^{-1}, the equation is seen to possess two positive roots, namely d_1 and d_2 and we are forced to choose between the two values and this is actually done by a process equivalent to linear programming.

Solving (6) linear programming will give us the first approximation. In this case the maximum amount of acetic acid will be formed. For $d_2 = 0.1$ M and $0.001 \le d_1 \le 0.09$ a maximum relative error in mass balance of 0.2 % was obtained when the zero concentrations of the initial solution were adjusted to equilibrium values. Applying the refining (9) once gave a solution well inside experimental uncertainties. For equivalent amounts of H^+ and Ac^- the above mentioned degeneracy became operative, i.e. the solution to (6) contained only one non-zero concentration.

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